13

EFFECT OF SOLVENT ON CHEMICAL REACTIONS AND REACTIVITY

13.1 SOLVENT EFFECTS ON CHEMICAL REACTIVITY

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13.1.1 INTRODUCTION

About a century ago, it was discovered that the solvent can dramatically change the rate of chemical reactions.[1] Since then, the generality and importance of solvent effects on chemical reactivity (rate constants or equilibrium constants) has been widely acknowledged. It can be said without much exaggeration that studying solvent effects is one of the most central topics of chemistry and remains ever-increasingly active. In the course of development, there are few topics in chemistry in which so many controversies and changes in interpretation have arisen as in the issue of characterizing solute-solvent interactions. In a historical context, two basic approaches to treating solvent effects may be distinguished: a phenomenological approach and a physical approach. The former may be subdivided further into the dielectric approach and the chemical approach.

- Phenomenological approach
  - Dielectric
  - Chemical
- Physical approach

That what follows is not intended just to give an overview of existing ideas, but instead to filter seminal conceptions and to take up more fundamental ideas. It should be mentioned that solvent relaxation phenomena, i.e., dynamic solvent effects, are omitted.

13.1.2 THE DIELECTRIC APPROACH

It has soon been found that solvent effects are particularly large for reactions in which charge is either developed or localized or vice versa, that is, disappearance of charge or spreading out of charge. In the framework of electrostatic considerations, which have been around since Berzelius, these observations led to the concept of solvation. Weak electrostatic interactions simply created a loose solvation shell around a solute molecule. It was in this climate of opinion that Hughes and Ingold[2] presented the first satisfactory qualitative account of solvent effects on reactivity by the concept of activated complex solvation.

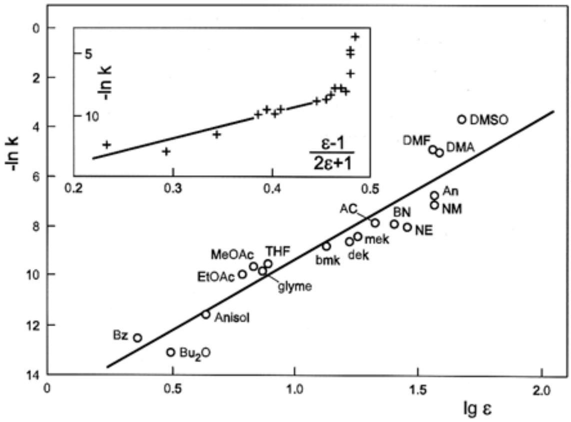


Figure 13.1.1. Relationship between second-order rate constants at 50°C of the reaction of p-nitrofluorobenzene and piperidine and the solvent dielectric properties [from ref. 21].

The first solvent property applied to correlate reactivity data was the static dielectric constant ε (also termed ε_s) in the form of dielectric functions as suggested from elementary electrostatic theories as those by Born (1/ε), Kirkwood (ε-1)/(2ε+1), Clausius-Mosotti (ε-1)/(ε+2), and (ε-1)/(ε+1). A successful correlation is shown in Figure 13.1.1 for the rate of the S_N2 reaction of p-nitrofluorobenzene with piperidine.[3] The classical dielectric functions predict that reactivity changes level out for dielectric constants say above 30. For instance, the Kirkwood function has an upper limiting value of 0.5, with the value of 0.47 reached at ε = 25. The insert in Figure 13.1.1 illustrates this point. Therefore, since it has no limiting value, the log ε function may be preferred. A theoretical justification can be given in the framework of the dielectric saturation model of Block and Walker.[4]

Picturing the solvent as a homogeneous dielectric continuum means in essence that the solvent molecules have zero size and that the molecules cannot move. The most adequate physical realization would be a lattice of permanent point dipoles that can rotate but cannot translate.

13.1.3 THE CHEMICAL APPROACH

Because of the often-observed inadequacies of the dielectric approach, that is, using the dielectric constant to order reactivity changes, the problem of correlating solvent effects was next tackled by the use of empirical solvent parameters measuring some solvent-sensitive physical property of a solute chosen as the model compound. Of these, spectral properties such as solvatochromic and NMR shifts have made a spectacular contribution. Other important scales are based on enthalpy data, with the best-known example being the donor number (DN) measuring solvent's Lewis basicity.

In the intervening years there is a proliferation of solvent scales that is really alarming. It was the merit particularly of Gutmann and his group to disentangle the great body of empirical parameters on the basis of the famous donor-acceptor concept or the coordination-chemical approach.[5] This concept has its roots in the ideas of Lewis going back to 1923, with the terms donor and acceptor introduced by Sidgwick.[6] In this framework, the two outstanding properties of a solvent are its donor (nucleophilic, basic, cation-solvating) and acceptor (electrophilic, acidic, anion-solvating) abilities, and solute-solvent interactions are considered as acid-base reactions in the Lewis' sense.

Actually, many empirical parameters can be lumped into two broad classes, as judged from the rough interrelationships found between various scales.[7] The one class is more concerned with cation (or positive dipole's end) solvation, with the most popular solvent basicity scales being the Gutmann DN, the Kamlet and Taft β, and the Koppel and Palm B. The other class is said to reflect anion (or negative dipole's end) solvation. This latter class includes the famous scales π*, α, $E_T(30)$, Z, and last but not least, the acceptor number AN. Summed up:

Cation (or positive dipole's end) solvation

• Gutmann	DN
• Kamlet and Taft	β
• Koppel and Palm	B (B*)

Anion (and negative dipole's end) solvation

• Gutmann	AN
• Dimroth and Reichardt	$E_T(30)$
• Kosower	Z
• Kamlet and Taft	α, π*

These two sets of scales agree in their general trend, but are often at variance when values for any two particular solvents are taken. Some intercorrelations have been presented by Taft et al., e.g., the parameters E_T, AN and Z can be written as linear functions of both α and π*.[8] Originally, the values of E_T and π* were conceived as microscopic polarity scales reflecting the "local" polarity of the solvent in the neighborhood of solutes ("effective" dielectric constant in contrast to the macroscopic one). In the framework of the donor-acceptor concept, however, they obtained an alternative meaning, based on the interrelationships found between various scales. Along these lines, the common solvents may be separated into six classes as follows.

1. nonpolar aliphatic solvents
2. protics or protogenetic solvents (at least one hydrogen atom is bonded to oxygen)
3. aromatic solvents
4. (poly)halogenated solvents
5. (perhaps) amines
6. select (or "normal" according to Abraham) solvents defined as non-protonic, non-chlorinated, aliphatic solvents with a single dominant bond dipole.

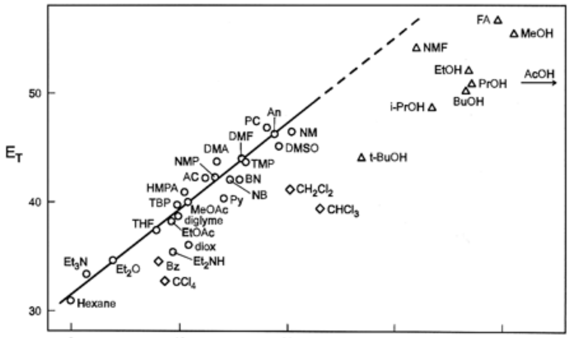


Figure 13.1.2. Relationship between the $E_T(30)$ values and the acceptor number [from ref. 21]. Triangles: protic solvents, squares: aromatic and chlorinated solvents.

A case study is the plot of AN versus E_T shown in Figure 13.1.2. While there is a quite good correspondence for the select solvents (and likely for the nonpolar aliphatic solvents), the other classes are considerably off-line.[9] This behavior may be interpreted in terms of the operation of different solvation mechanisms such as electronic polarizability, dipole density, and/or hydrogen-bonding (HB) ability. For instance, the main physical difference between π* and $E_T(30)$, in the absence of

HB interactions, is claimed to lie in different responses to solvent polarizability effects. Likewise, in the relationship between the π^* scale and the reaction field functions of the refractive index (whose square is called the optical dielectric constant e_∞) and the dielectric constant, the aromatic and the halogenated solvents were found to constitute special cases.[10] This feature is also reflected by the polarizability correction term in eq. [13.1.2] below. For the select solvents, the various "polarity" scales are more or less equivalent. A recent account of the various scales has been given by Marcus,[11] and in particular of π^* by Laurence et al.,[12] and of E_T by Reichardt.[13]

However, solvation is not the only mode of action taken by the solvent on chemical reactivity. Since chemical reactions typically are accompanied by changes in volume, even reactions with no alteration of charge distribution are sensitive to the solvent. The solvent dependence of a reaction where both reactants and products are neutral species ("neutral" pathway) is often treated in terms of either of two solvent properties. The one is the cohesive energy density ε_c or cohesive pressure measuring the total molecular cohesion per unit volume,

$$\varepsilon_c = \left(\Delta H_v - RT\right)/V \qquad [13.1.1]$$

where:

ΔH_v	molar enthalpy of vaporization
V	molar liquid volume

The square root of ε_c is termed the Hildebrand solubility parameter δ_H, which is the solvent property that measures the work necessary to separate the solvent molecules (disrupt and reorganize solvent/solvent interactions) to create a suitably sized cavity for the solute. The other quantity in use is the internal pressure P_i which is a measure of the change in internal energy U of the solvent during a small isothermal expansion, $P_i = (\partial U/\partial V)_T$. Interesting, and long-known, is the fact that for the highly dipolar and particular for the protic solvents, values of ε_c are far in excess of P_i.[14] This is interpreted to mean that a small expansion does not disrupt all of the intermolecular interactions associated with the liquid state. It has been suggested that P_i does not detect hydrogen bonding but only weaker interactions.

At first, solvent effects on reactivity were studied in terms of some particular solvent parameter. Later on, more sophisticated methods via multiparameter equations were applied such as[15]

$$XYZ = XYZ_0 + s\left(\pi^* + d\delta\right) + a\alpha + b\beta + h\delta_H \qquad [13.1.2]$$

where XYZ_0, s, a, b, and h are solvent-independent coefficients characteristic of the process and indicative of its sensitivity to the accompanying solvent properties. Further, δ is a polarizability correction term equal to 0.0 for nonchlorinated aliphatic solvents, 0.5 for polychlorinated aliphatics, and 1.0 for aromatic solvents. The other parameters have been given above, viz. π^*, α, β, and δ_H are indices of solvent dipolarity/polarizability, Lewis acidity, Lewis basicity, and cavity formation energy, respectively. For the latter, instead of δ_H, δ_H^2 should be preferred as suggested from regular solution theory.[16]

Let us just mention two applications of the linear solvation energy relationship (LSER). The one concerns the solvolysis of tertiary butyl-halides[17]

$$\log k(Bu^tCl) = -14.60 + 5.10\pi^* + 4.17\alpha + 0.73\beta + 0.0048\delta_H^2$$

$$n = 21,\ r = 0.9973,\ s = 0.242$$

and the other deals with the transfer of tetramethylammonium iodide through solvents with methanol as the reference solvent,[16]

$$\Delta G^0_{tr} = 10.9 - 15.6\pi* - 6.2\alpha + 0.022\delta_H$$

$$n = 18,\ r = 0.997,\ s = 0.3$$

where:

n	number of solvents
r	correlation coefficient
s	standard deviation

We will not finish this section without noting that there are also metal complexes available functioning as color indicators of the coordination properties of solvents.[18] Thus, Cu(tmen)(acac) ClO_4, where tmen = N,N,N',N'-tetramethylethylenediamine and acac = acetylacetonate, can be used as a Lewis-basicity indicator, and $Fe(phen)_2(CN)_2$, where phen = 1,10-phenanthroline, as a Lewis-acidity indicator. The physical origin of the underlying color changes is sketched in the Figures 13.1.3 and 13.1.4, as modified from ref. 18. These color indicators can be used as a quick method for assessing the coordination properties of solvents, solvent mixtures, and solutes not yet measured. This is very expedient since some classical parameters, particularly the donor numbers, are arduously amenable. The following equation

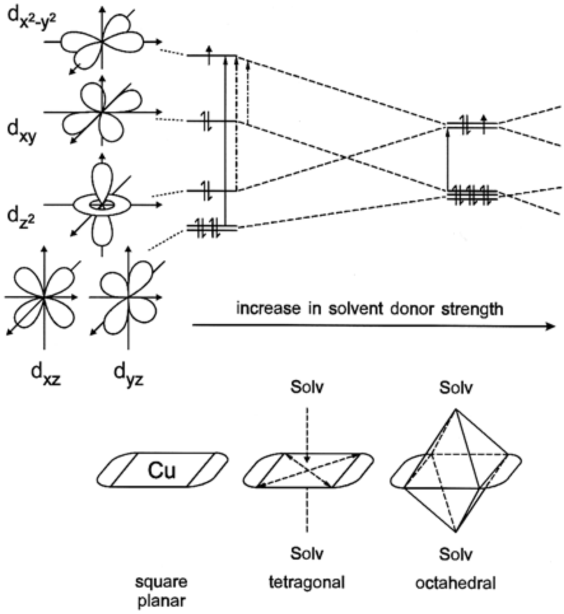


Figure 13.1.3. Relative orbital energy levels for Cu^{2+} in square planar, tetragonal, and octahedral environments [adapted from ref. 18].

$$DN = 195.5 - 0.0102\nu_0 \qquad [13.1.3]$$

$$n = 12,\ r = 0.990,\ s = 1.37$$

correlates the wave numbers ν_0 (in cm^{-1}) of the visible band of $Cu(tmen)(acac)^+$ and the solvent donor numbers. Similarly, the acceptor numbers are expressed as a function of the wave numbers of the long wavelength absorption of $Fe(phen)_2(CN)_2$,

$$AN = -133.8 - 0.00933\nu_0 \qquad [13.1.4]$$

$$n = 12,\ r = 0.980,\ s = 4.58$$

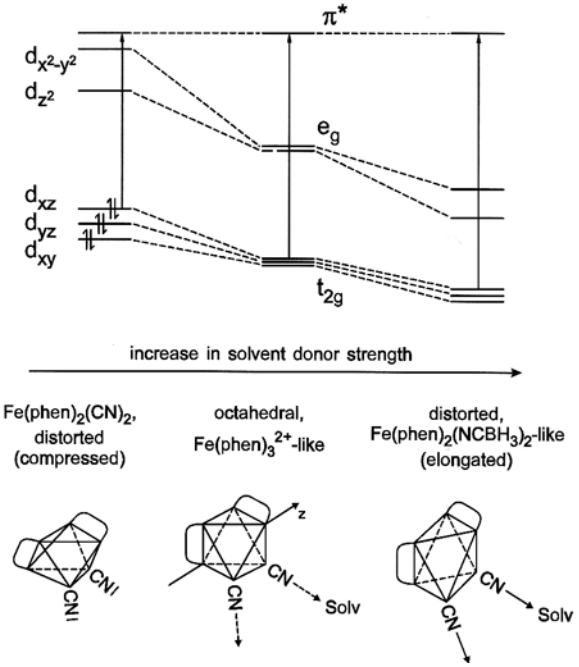
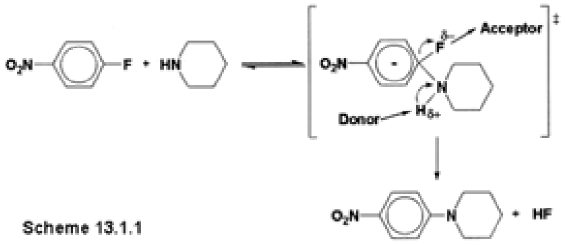


Figure 13.1.4. Simplified orbital scheme for the charge transfer transition in $Fe(phen)_2(CN)_2$ varying with solvation. The diagram, not drawn to scale, is adjusted so that π* is constant [adapted from ref. 18].



Scheme 13.1.1

13.1.4 DIELECTRIC VS. CHEMICAL APPROACH

Although the success of the empirical solvent parameters has tended to downgrade the usefulness of the dielectric approach, there are correlations that have succeeded as exemplified by Figure 13.1.1. It is commonly held that the empirical solvent parameters are superior to dielectric estimates because they are sensitive to short-range phenomena not captured in dielectric measurements. This statement may not be generalized, however, since it depends strongly on the chemical reaction investigated and the choice of solvents. For instance, the rate of the Menschutkin reaction between tripropylamine and methyl iodide in select solvents correlates better with the log ε function than with the solvent acceptor number.[19]

Thus the solution chemists were puzzled for a long time over the question about when and when not the dielectric approach is adequate. In the meantime, this issue has been unraveled, in that dielectric estimates have no relevance to the solvation of positive (partial) charge. Thus, there is no relationship between the free energies of transfer for cations and the dielectric constant.[7] Likewise, note the solvent-dependence of the solubilities of sodium chloride (Table 13.1.1) taken from Mayer's work.[19] For instance, the pairs of solvents H_2O/PC and DMF/MeCN have similar ε′s but vastly different abilities to dissolve NaCl. In similar terms, the inclusion of a donor number term improves somewhat the correlation in Figure 13.1.1, as may be seen in Figure 13.1.5. This would suggest that the hydrogen of piperidine in the activated complex becomes acidic and is attacked by the strong donor solvents DMF, DMA and DMSO (Scheme 13.1.1).

Table 13.1.1. Standard free energies of solution of sodium chloride in various solvents at 25°C. Data of ΔG^0_{solv} are from reference 19

Solvent	ΔG^0_{solv}, kJ mol^{-1}	ε_s	DN	AN
H_2O	-9.0	78.4	18	55
FA	-0.4	109	24	40
NMF	+3.8	182	27	32
MeOH	+14.1	32.6	19	41
DMSO	+14.9	46.7	30	19
DMF	+26.8	36.7	26	16
PC	+44.7	65	15	18
MeCN	+46.8	36	14	19

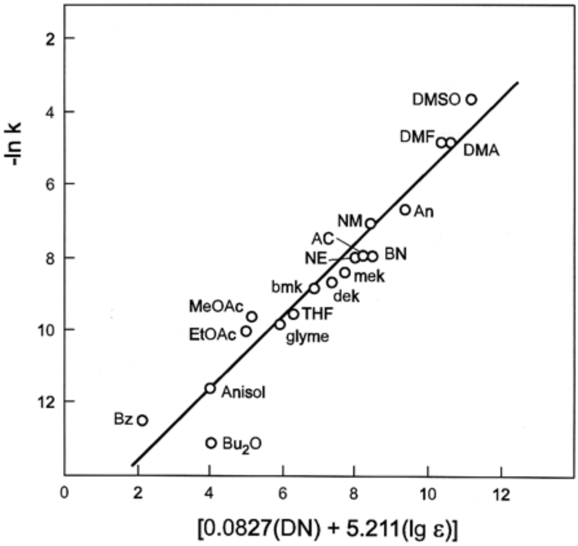


Figure 13.1.5. Correlation diagram for the same reaction as in Figure 13.1.1 [from ref. 21].

On the other hand, if negative charge is solvated in the absence of positive charge capable of solvation, the dielectric constant is often a pretty good guide to ranking changes in reactivity. As a consequence, the dielectric approach has still its place in organic chemistry while it is doomed to complete failure in inorganic reactions where typically cation solvation is involved. For select solvents, ultimately, the dielectric constant is related to the anion-solvating properties of solvents according to the regression equation[4]

$$\log \varepsilon = 0.32 + 0.073 (AN_E) \qquad [13.1.5]$$

$$n = 31, r = 0.950, s = 0.129$$

where:

AN_E E_T-based acceptor numbers, $AN_E = -40.52 + 1.29 E_T$

This equation works also quite well for the aromatics and the halogenated solvents, but it does not hold for the protic solvents. For these, the predicted values of the dielectric constants are orders of magnitude too large, revealing how poorly the associates are dissociated by the macroscopically attainable fields. A correlation similar to [13.1.5] has been proposed[20] between the gas phase dipole moment and π^*

$$\mu(D) = 4.3\pi^* - 0.1 \qquad [13.1.6]$$

$n = 28$, $r = 0.972$, $s = 0.3$

Along these lines the dielectric and the chemical approach are brought under one roof.[4,21] The statement, however, that the terms "good acceptor solvent" and "highly polar solvent" may be used synonymously would seem, though true, to be provocative.

13.1.5 CONCEPTUAL PROBLEMS WITH EMPIRICAL SOLVENT PARAMETERS

A highly suspect feature behind the concept of empirical solvent parameters lies in the interpretation of the results in that condensed phase matters are considered from the narrow viewpoint of the solute only with the solvent's viewpoint notoriously neglected. However, the solute is actually probing the overall action of the solvent, comprising two modes of interactions: solute-solvent (solvation) and solvent-solvent (restructuring) effects of unknown relative contribution. Traditionally, it is held that solvent structure only assumes importance when highly structured solvents, such as water, are involved.[22] But this view increasingly turns out to be erroneous. In fact, ignoring solvent-solvent effects, even in aprotic solvents, can lead to wrong conclusions as follows.

In the donor-acceptor approach, solutes and solvents are divided into donors and acceptors. Accordingly, correlations found between some property and the solvent donor (acceptor) ability are commonly thought to indicate that positive (negative) charge is involved. In the case of solvent donor effects this statement is actually valid. We are unaware, in fact, of any exception to the rule saying: "Increase in reaction rate with increasing solvent DN implies that positive charge is developed or localized and *vice versa*".[21] In contrast, correlations with the acceptor number or related scales do not simply point to anion solvation, though this view is commonly held. An example for such type of reasoning concerns the medium effect on the intervalence transition (IT) energy within a certain binuclear, mixed-valence, 5+ cation.[23] As the salt effect was found to vary with the solvent AN, anion, that is counterion, solvation in ion pairs was invoked to control the IT energy.

A conceptual problem becomes obvious by the at first glance astonishing result that the reduction entropies of essentially non-donor cationic redox couples such as $Ru(NH_3)_6^{3+/2+}$ are correlated with the solvent AN.[24] These authors interpreted this solvent dependence as reflecting changes in solvent-solvent rather than solvent-ligand interactions. That the acceptor number might be related to solvent structure is easy to understand since all solvents of high AN always are good donors (but not *vice versa*!) and therefore tend to be increasingly self-associated.[21] There is since growing evidence that the solvent's AN and related scales represent ambiguous solvent properties including solvent structural effects instead of measuring anion solvation in an isolated manner. Thus, correlations between Gibbs energies of cation transfer from water to organic solvents and the solvent DN are improved by the inclusion of a term in E_T (or a combination of α and π^*).[25] Consequently Marcus et al. rightly recognized that "E_T does not account exclusively for the electron pair acceptance capacity of solvents".[26] In more recent work[27] a direct relationship has been found between the solvent reorganizational energy accompanying the excitation of ruthenium(II) cyano complexes and the solvent acceptor number.

In the basicity scales, on the other hand, complications by solvent structure are not as obvious. If restriction is to aprotic solvents, as is usual, various scales though obtained under different conditions, are roughly equivalent.[21,4] There is for instance a remarkably good relationship between the DN scale (obtained in dilute dichloromethane solution, i.e., with medium effects largely excluded) and the B scale (derived from measurements performed with 0.4 M solutions of MeOD in the various solvents[4]). The relationship between β and B, on the other hand, separates out into families of solvents.[20] Donor measures for protic solvents eventually are hard to assess and often are at considerable variance from one scale to another.[28,29] To rationalize the discrepancies, the concept of "bulk donicity" was introduced[7] but with little success. Instead, the consideration of structure changes accompanying solvation might better help tackle the problem.

Another suspect feature of the common method of interpreting solvent-reactivity correlations is that it is notoriously done in enthalpic (electronic, bond-strength etc.) terms. This way of thinking goes back to the Hughes-Ingold theory. However, many reactions in solution are not controlled by enthalpy changes but instead by entropy. Famous examples are the class of Menschutkin reactions and the solvolysis of t-butyl halides. Both these reaction types are characterized by the development of halide ions in the transition state, which can be considered as ion-pair like. In view of this, rate acceleration observed in good acceptor (or, alternatively, highly polar) solvents seems readily explainable in terms of solvation of the developing halide ion with concomitant carbon-halogen bond weakening. If this is true, most positive activation entropies and highest activation enthalpies should be expected to occur for the poor acceptor solvents. However, a temperature dependence study of the t-butyl halide solvolysis revealed just the opposite.[17] This intriguing feature points to changes in solvent structure as a major determinant of the reaction rate with the ionic transition state acting as a structure maker in poor acceptor solvents, and as a structure maker in the protic solvents.

It is rather ironic that the expected increase in rate with increasing solvent acceptor strength is a result of the coincidence of two, from the traditional point of view, unorthodox facts: (i) The intrinsic solvation of the developing halide ion disfavors the reaction via the entropy term. However, (ii), the extent of that solvation is greater in the poorly coordinating solvents (providing they are polarizable such as the aromatic solvents and the polyhalogenated hydrocarbons). In keeping with this interpretation, the Menschutkin reaction between benzyl bromide and pyridine is characterized by more negative activation volumina (i.e., stronger contraction of the reacting system in going to the activated complex) in poor acceptor (but polarizable) solvents.[30] The importance is evident of studying temperature or pressure dependencies of solvent effects on rate in order to arrive at a physically meaningful interpretation of the correlations.

Another problem with the interpretation of multiparameter equations such as [13.1.2] arises since some of the parameters used are not fully independent of one another. As to this, the trend between π^* and α has already been mentioned. Similarly, the δ_H parameter displays some connection to the polarity indices.[31,32] Virtually, the various parameters feature just different blends of more fundamental intermolecular forces (see below). Because of this, the interpretations of empirical solvent-reactivity correlations are often based more on intuition or preconceived opinion than on physically defined interaction mechanisms. As it turns out, polar solvation has traditionally been overemphasized relative to nonpolar solvation (dispersion and induction), which is appreciable even in polar solvents.

The conceptual problems of the empirical solvent parameters summarized:

- The solvent acceptor number and other "polarity" scales include appreciable, perhaps predominant, contributions from solvent structure changes rather than merely measuring anion solvation.
- Care is urged in a rash interpretation of solvent-reactivity correlations in enthalpic terms, instead of entropic, before temperature-dependence data are available. Actually, free energy alone masks the underlying physics and fails to provide predictive power for more complex situations.
- Unfortunately, the parameters used in LSER's sometimes tend to be roughly related to one another, featuring just different blends of more fundamental intermolecular forces. Not seldom, fortuitous cancellations make molecular behavior in liquids seemingly simple (see below).

Further progress would be gained if the various interaction modes could be separated by means of molecular models. This scheme is in fact taking shape in current years giving rise to a new era of tackling solvent effects as follows.

13.1.6 THE PHYSICAL APPROACH

There was a saying that the nineteenth century was the era of the gaseous state, the twentieth century of the solid state, and that perhaps by the twenty-first century we may understand something about liquids.[33] Fortunately, this view is unduly pessimistic, since theories of the liquid state have actively been making breath-taking progress. In the meantime, not only equations of state of simple liquids, that is in the absence of specific solvent-solvent interactions,[34-36] but also calculations of simple forms of intermolecular interactions are becoming available. On this basis, a novel approach to treating solvent effects is emerging, which we may call the physical approach. This way of description is capable of significantly changing the traditionally accepted methods of research in chemistry and ultimately will lay the foundations of the understanding of chemical events from first principles.

A guiding principle of these theories is recognition of the importance of packing effects in liquids. It is now well-established that short-ranged repulsive forces implicit in the packing of hard objects, such as spheres or dumbbells, largely determine the structural and dynamic properties of liquids.[37] It may be noted in this context that the roots of the idea of repulsive forces reach back to Newton who argued that an elastic fluid must be constituted of small particles or atoms of matter, which repel each other by a force increasing in proportion as their distance diminishes. Since this idea stimulated Dalton, we can say that the very existence of liquids helped to pave the way for formulating modern atomic theory with Newton granting the position of its "grandfather".[38]

Since the venerable view of van der Waals, an intermolecular potential composed of repulsive and attractive contributions is a fundamental ingredient of modern theories of the liquid state. While the attractive interaction potential is not precisely known, the repulsive part, because of changing sharply with distance, is treatable by a common formalism in terms of the packing density η, that is the fraction of space occupied by the liquid molecules. The packing fraction is a key parameter in liquid state theories and is in turn related in a simple way to the hard sphere (HS) diameter σ in a spherical representation of the molecules comprising the fluid:

$$\eta = \pi\rho\sigma^3 / 6 = \rho V_{HS} \qquad [13.1.7]$$

where:

η	packing density
ρ	number density N/V= number of particles per unit volume
σ	HS diameter
V_{HS}	HS volume

For the determination of σ (and hence η), the most direct method is arguably that based on inert gas solubility data.[39,40] However, in view of the arduousness involved and the uncertainties in both the extrapolation procedure and the experimental solubilities, it is natural to look out for alternatives. From the various suggestions,[41,42] a convenient way is to adjust σ such that the computed value of some selected thermodynamic quantity, related to σ, is consistent with experiment. The hitherto likely best method[43] is the following: To diminish effects of attraction, the property chosen should probe primarily repulsive forces rather than attractions. Since the low compressibility of the condensed phase is due to short-range repulsive forces, the isothermal compressibility $\beta_T = -(1/V)(\partial V/\partial P)_T$ might be a suitable candidate, in the framework of the generalized van der Waals (vdW) equation of state

$$\beta_T (RT / V) Q_r = 1 \qquad [13.1.8]$$

where Qr is the density derivative of the compressibility factor of a suitable reference system. In the work referred to, the reference system adopted is that of polar-polarizable spheres in a mean field,

$$Q_r = \left[2\frac{5\eta^2 - 2\eta^3}{(1-\eta)^4} - 1 - 2Z_\mu \right] \qquad [13.1.9]$$

where Z_μ = compressibility factor due to dipole-dipole forces,[43] which is important only for a few solvents such as MeCN and $MeNO_2$. The HS diameters so determined are found to be in excellent agreement with those derived from inert gas solubilities. It may be noted that the method of Ben-Amotz and Willis,[44] also based on β_T, uses the nonpolar HS liquid as the reference and, therefore, is applicable only to liquids of weak dipole-dipole forces. Of course, as the reference potential approaches that of the real liquid, the HS diameter of the reference liquid should more closely approximate the actual hard-core length. Finally, because of its popularity, an older method should be mentioned that relies on the isobaric expansibility α_p as the probe, but this method is inadequate for polar liquids. It turns out that solvent expansibility is appreciably determined by attractions.

Some values of η and σ are shown in Table 13.1.2 including the two extreme cases. Actually, water and n-hexadecane have the lowest and highest packing density, respectively, of the common solvents. As is seen, there is an appreciable free volume, which may be expressed by the volume fraction $\eta - \eta_0$, where η_0 is the maximum value of η calculated for the face-centered cubic packing of HS molecules where all molecules are in contact with each other is $\eta_0 = \pi\sqrt{2} / 6 = 0.74$. Thus, 1 - η_0 corresponds to the minimum of unoccupied volume. Since η typically is around 0.5, about a quarter of the total liquid volume is empty enabling solvent molecules to change their coordinates and hence local density fluctuations to occur.

Packing density η

minimum		maximum
≈ 0	0.4 - 0.6	0.74
perfect gas	liquids	cubic close packed

Table 13.1.2. Packing densities in some liquids

Liquid	η	free volume, %
H_2O	0.41	59
n-C_6	0.50	50
Benzene	0.51	49
MeOH	0.41	59
Et_2O	0.47	53
n-C_{16}	0.62	38

These considerations ultimately offer the basis of a genuinely molecular theory of solvent effects, as compared to a mean-field theory. Thus, packing and repacking effects accompanying chemical reactions have to be taken into account for any realistic view of the solvent's role played in chemical reactions to be attained. The well-known cavity formation energy is the work done against intermolecular repulsions. At present, this energy is calculated for spherical cavities by the Boublik-Mansoori-Carnahan-Starling-Leland (BMCSL) mixed HS equation of state[45,46]

$$\frac{\Delta G_{rep}}{RT} = 2\frac{\eta d^3}{(1-\eta)^3} + 3\frac{\eta d^2}{(1-\eta)^2} + 3\frac{\eta d\left(-d^2 + d + 1\right)}{(1-\eta)} + \left(-2d^3 + 3d^2 - 1\right)\ln(1-\eta) \quad [13.1.10]$$

where $d = \sigma_0 / \sigma$ is the relative solute size (σ_0 is the solute HS diameter, and σ is the solvent diameter). Quite recently, a modification of this equation has been suggested for high liquid densities and large solute sizes.[47] Notice that under isochoric conditions the free energy of cavity formation is a totally entropic quantity. Ravi et al[48] have carried out an analysis of a model dissociation reaction ($Br_2 \rightarrow 2Br$) dissolved in a Lennard-Jones solvent (Ne, Ar, and Xe). That and the previous work[49] demonstrated that solvent structure contributes significantly to both chemical reaction volumes (which are defined as the pressure derivatives of reaction free energies) and free energies, even in systems containing no electrostatic or dispersion long-ranged solvent-solute interactions.

Let us now turn to the more difficult case of intermolecular attractive forces. These may be subdivided into:

Long-ranged or unspecific
- dispersion
- induction
- dipole-dipole
- higher multipole

Short-ranged or specific
- electron overlap (charge transfer)
- H-bonding

For the first three ones (dispersion, induction, dipole-dipole forces) adequate calculations are just around the corner. Let us give some definitions.

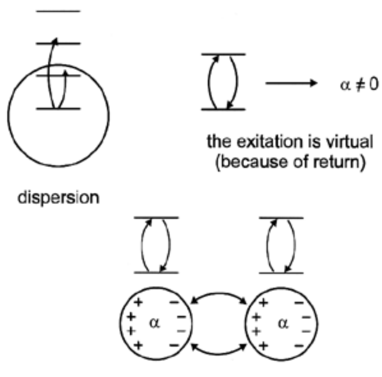


Figure 13.1.6

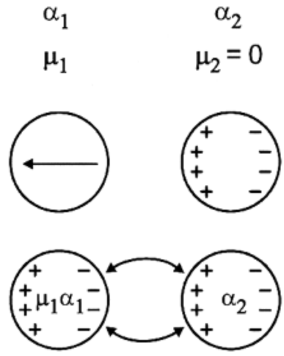


Figure 13.1.7

Dispersion forces are the result of the dipolar interactions between the virtually excited dipole moments of the solute and the solvent, resulting in a nonzero molecular polarizability. Although the average of every induced dipole is zero, the average of the product of two induced dipoles is nonzero (Figure 13.1.6).

Induction forces are caused by the interaction of the permanent solvent dipole with the solvent dipoles induced by the solute and solvent field (Figure 13.1.7).

Sometimes it is stated that dispersion is a quantum mechanical effect and induction is not. Thus, some clarifying comments are at place here. From the general viewpoint, all effects including polarizability are quantum mechanical in their origin because the polarizability of atoms and molecules is a quantum mechanical quantity and can be assessed only in the framework of quantum mechanics. However, once calculated, one can think of polarizability in classical terms representing a quantum molecular object as a classical oscillator with the mass equal to the polarizability, which is not specified in the classical framework. This is definitely wrong from a fundamental viewpoint, but, as it usually appears with harmonic models, a quantum mechanical calculation and such a primitive classical model give basically the same results about the induction matter. Now, if we implement this classical model, we would easily come up with the induction potential. However, the dispersion interaction will be absent. The point is that to get dispersions, one needs to switch back to the quantum mechanical description where both inductions and dispersions naturally appear. Thus the quantum oscillator may be used resulting in both types of potentials.[50] If in the same procedure one switches to the classical limit (which is equivalent to putting the Plank constant zero) one would get only inductions.

The calculation of the dispersive solvation energy is based on perturbation theories following the Chandler-Andersen-Weeks[51] or Barker-Henderson[52] formalisms, in which long-range attractive interactions are treated as perturbations to the properties of a hard body reference system. Essentially, perturbative theories of fluids are a modern version of van der Waals theory.[53] In the papers reviewed here, the Barker-Henderson approach was utilized with the following input parameters: Lennard-Jones (LJ) energies for the solvent, for which reliable values are now available, the HS diameters of solvent and solute, the solvent polarizability, and the ionization potentials of solute and solvent. A weak point is that in order to get the solute-solvent LJ parameters from the solute and solvent components, some combining rule has to be utilized. However, the commonly applied combining rules appear to be adequate only if solute and solvent molecules are similar in size. For the case of particles appreciably different both in LJ energy and size, the suggestion has been made to use an empirical scaling by introducing empirical coefficients so as to obtain agreement between calculated and experimental solvation energies for selected inert gases and nonpolar large solutes.[54]

In the paper referred to,[54] the relevance of the theoretical considerations has been tested on experimental solvation free energies of nitromethane as the solute in select solvents. The total solvation energy is a competition of the positive cavity formation energy and the negative solvation energy of dispersion and dipolar forces,

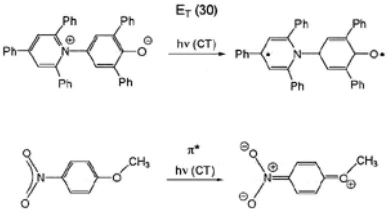
$$\Delta G = \Delta G_{cav} + \Delta G_{disp} + \Delta G_{dipolar} \qquad [13.1.11]$$

where the dipolar term includes permanent and induced dipole interactions. The nitromethane molecule is represented by the parameters of the HS diameter $\sigma = 4.36$ Å, the gas-phase dipole moment $\mu = 3.57$ D, the polarizability $\alpha = 4.95$ Å , and the LJ energy $\varepsilon_{LJ}/k = 391$K. Further, the solvent is modeled by spherical hard molecules of spherical polarizability, centered dipole moment, and central dispersion potential. To calculate the dipolar response, the Padé approximation was applied for the chemical potential of solvation in the dipolar liquid and then extended to a polarizable fluid according to the procedure of Wertheim. The basic idea of the Wertheim theory is to replace the polarizable liquid of coupled induced dipoles with a fictitious fluid with an effective dipole moment calculated in a self-consistent manner. Further, the Padé form is a simple analytical way to describe the dependence of the dipolar response on solvent polarity, solvent density, and solute/solvent size ratio. The theory/experiment agreement of the net solvation free energy is acceptable as seen in Table 13.1.3 where solvent ordering is according to the dielectric constant. Note that the contribution of dispersion forces is considerable even in strongly polar solvents.

Table 13.1.3. Thermodynamic potentials (kJ/mol) of dissolution of nitromethane at 25°C. Data are from reference 54

Solvent	ε_s	ΔG_{cav}	ΔG_{disp}	$\Delta G_{dipolar}$	ΔG(calc)	ΔG(exp)
n-C_6	1.9	23.0	-32.9	-2.2	-12.1	-12.1
c-C_6	2.0	28.1	-38.1	-2.8	-12.7	-12.0
Et_3N	2.4	24.2	-33.5	-2.9	-12.2	-15.2
Et_2O	4.2	22.6	-33.4	-5.8	-16.5	-17.5
EtOAc	6.0	28.0	-38.5	-9.7	-20.1	-21.2
THF	7.5	32.5	-41.5	-12.2	-21.1	-21.3
c-hexanone	15.5	35.1	-39.8	-17.9	-22.6	-21.8
2-butanone	17.9	28.3	-33.9	-18.9	-24.5	-21.9
Acetone	20.7	27.8	-31.2	-22.1	-25.5	-22.5
DMF	36.7	38.1	-32.1	-28.5	-22.5	-23.7
DMSO	46.7	41.9	-31.1	-31.0	-20.2	-23.6

With an adequate treating of simple forms of intermolecular attractions becoming available, there is currently great interest to making a connection between the empirical scales and solvation theory. Of course, the large, and reliable, experimental databases on



Scheme 13.1.2

empirical parameters are highly attractive for theoreticians for testing their computational models and improving their predictive power. At present, the solvatochromic scales are under considerable scrutiny. Thus, in a recent thermodynamic analysis, Matyushov et al.[55] analyzed the two very popular polarity scales, $E_T(30)$ and π^*, based on the solvent-induced shift of electronic absorption transitions (Scheme 13.1.2)

Table 13.1.4. Dye properties used in the calculations. Data are from reference 55

Molecular parameter	Betaine-30	4-Nitroanisole
Vacuum energy gap (eV)	1.62	4.49
R_0 (Å)	6.4	4.5
α_g (Å)	68	15
$\Delta\alpha$ (Å)	61	6
m_g (D)	14.8	4.7
m_e (D)	6.2	12.9
$\Delta\mu$ (D)	-8.6	+8.2

Solvatochromism has its origin in changes in both dipole moment and polarizability of the dye upon electronic excitation provoking differential solvation of the ground and excited states. The dipole moment, μ_e, of the excited state can be either smaller or larger than the ground state value μ_g. In the former case one speaks about a negatively solvatochromic dye such as betaine-30, whereas the π^* dye 4-nitroanisole is positively solvatochromic. Thus, polar solvent molecules produce a red shift (lower energy) in the former and a blue shift (higher energy) in the latter. On the other hand, polarizability arguably always increases upon excitation. Dispersion interactions, therefore, would produce a red shift proportional to $\Delta\alpha = \alpha_e - \alpha_g$ of the dye. In other words, the excited state is stabilized through strengthening of dispersive coupling. Finally, the relative contributions of dispersion and dipolar interactions will depend on the size of the dye molecules with dispersive forces becoming increasingly important the larger the solute. Along these lines, the dye properties entering the calculations are given in Table 13.1.4. The purpose of the analysis was to determine how well the description in terms of "trivial" dipolar and dispersion forces can reproduce the solvent dependence of the absorption energies (and thereby, by difference to experiment, expose the magnitude of specific forces),

$$\hbar\omega_{abs} = \Delta + \Delta E_{rep} + \Delta E_{disp} + \Delta E_{dipolar} + \Delta E_{ss} \qquad [13.1.12]$$

where

$\hbar\omega_{abs}$	absorption energy
Δ	vacuum energy gap
ΔE_{rep}	shift due to repulsion solute-solvent interactions (taken to be zero)
ΔE_{disp}	shift due to dispersion interactions
$\Delta E_{dipolar}$	shift due to dipolar forces of permanent and induced dipoles
ΔE_{ss}	solvent reorganization energy

For the detailed and arduous calculation procedure, the reader may consult the paper cited. Here, let us just make a few general comments. The solvent influence on intramolecular optical excitation is treated by implementing the perturbation expansion over the solute-solvent attractions. The reference system for the perturbation expansion is chosen to be the HS liquid with the imbedded hard core of the solute. It should be noted for clarity that ΔE_{disp} and $\Delta E_{dipolar}$ are additive due to different symmetries: dispersion force is non-directed (i.e., is a scalar quantity), and dipolar force is directed (i.e., is a vector). In other words, the attractive intermolecular potential can be split into a radial and an angle-dependent part. In modeling the solvent action on the optical excitation, the solute-solvent interactions have to be dissected into electronic (inertialess) (dispersion, induction, charge-transfer) and molecular (inertial) (molecular orientations, molecular packing) modes. The idea is that the inertial modes are frozen on the time scale of the electronic transition. This is the Franck-Condon principle with such types of transitions called vertical transitions.

Thus the excited solute is to be considered as a Frank-Condon state, which is equilibrated only to the electronic modes, whereas the inertial modes remain equilibrated to the ground state. According to the frozen solvent configuration, the dipolar contribution is represented as the sum of two terms corresponding to the two separate time scales of the solvent, (i) the variation in the solvation potential due to the fast electronic degrees of freedom, and (ii) the work needed to change the solute permanent dipole moment to the excited state value in a frozen solvent field. The latter is calculated for accommodating the solute ground state in the solvent given by orientations and local packing of the permanent solvent dipoles. Finally, the solvent reorganization energy, which is the difference of the average solvent-solvent interaction energy in going from the ground state to the excited state, is extracted by treating the variation with temperature of the absorption energy. Unfortunately, experimental thermochromic coefficients are available for a few solvents only.

The following results of the calculations are relevant. While the contributions of dispersions and inductions are comparable in the π^* scale, inductions are overshadowed in the $E_T(30)$ values. Both effects reinforce each other in π^*, producing the well-known red shift. For the $E_T(30)$ scale, the effects due to dispersion and dipolar solvation have opposite signs making the red shift for nonpolar solvents switch to the blue for polar solvents. Furthermore, there is overall reasonable agreement between theory and experiment for both dyes, as far as the nonpolar and select solvents are concerned, but there are also discrepant solvent classes pointing to other kinds of solute-solvent interactions not accounted for in the model. Thus, the predicted $E_T(30)$ values for protic solvents are uniformly too low, revealing a decrease in H-bonding interactions of the excited state with lowered dipole moment.

Another intriguing observation is that the calculated π^* values of the aromatic and chlorinated solvents are throughout too high (in contrast to the $E_T(30)$ case). Clearly, these deviations, reminiscent of the shape of the plots such as Figure 13.1.2, may not be explained in terms of polarizability as traditionally done (see above), since this solvent property has been adequately accommodated in the present model via the induction potential. Instead, the theory/experiment discord may be rationalized in either of two ways. One reason for the additional solvating force can be sought in terms of solute-solvent π overlap resulting in exciplex formation. Charge-transfer (CT) interactions are increased between the solvent and the more delocalized excited state.[55] The alternative, and arguably more reasonable, view considers the quadrupole moment which

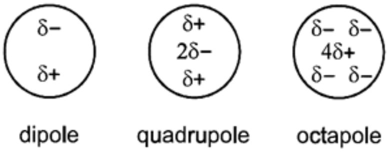


Figure 13.1.8

is substantial for both solvent classes.[56] Recently, this latter explanation in terms of dipole-quadrupole interactions is favored (Fig 13.1.8).

It is well-known that the interaction energy falls off more rapidly the higher the order of the multipole. Thus, for the interaction of an n-pole with an m-pole, the potential energy varies with distance as $E \propto 1/(r^{n+m+1})$. The reason for the faster decrease is that the array of charges seems to blend into neutrality more rapidly with distance the higher the number of individual charges contributing to the multipole. Consequently, quadrupolar forces die off faster than dipolar forces.

It has been calculated that small solute dipoles are even more effectively solvated by solvent quadrupoles than by solvent dipoles.[57] In these terms it is understandable that quadrupolar contributions are more important in the π^* than in the $E_T(30)$ scale. Similarly, triethylphosphine oxide, the probe solute of the acceptor number scale, is much smaller than betaine(30) and thus might be more sensitive to quadrupolar solvation. Thus, at long last, the shape of Figure 13.1.2 and similar ones seems rationalized. Note by the way that the quadrupole and CT mechanisms reflect, respectively, inertial and inertialess solvation pathways, and hence could be distinguished by a comparative analysis of absorption and fluorescence shifts (Stokes shift analysis). However, for 4-nitroanisole fluorescence data are not available.

Reverting once more to the thermodynamic analysis of the π^* and $E_T(30)$ scales referred to above, it should be mentioned that there are also other theoretical treatments of the solvatochromism of betaine(30). Actually, in a very recent computer simulation,[58] the large polarizability change $\Delta\alpha$ (nearly 2-fold, see Table 13.1.4) upon the excitation of betaine(30) has been (correctly) questioned. (According to a rule of thumb, the increase in polarizability upon excitation is proportional to the ground state polarizability, on the order $\Delta\alpha \approx 0.25\alpha_g$.[50]) Unfortunately, Matyushov et al.[55] derived this high value of $\Delta\alpha = 61$ Å^3 from an analysis of experimental absorption energies based on aromatic, instead of alkane, solvents as nonpolar reference solvents. A lower value of $\Delta\alpha$ would diminish the importance of dispersion interactions.

Further theoretical and computational studies of betaine(30) of the $E_T(30)$ scale are reviewed by Mente and Maroncelli.[58] Despite several differences in opinion obvious in these papers, an adequate treatment of at least the nonspecific components of solvatochromism would seem to be "just around the corner". Finally, a suggestion should be mentioned on using the calculated π^* values taken from ref. 55 as a descriptor of nonspecific solvent effects.[59] However, this is not meaningful since these values are just a particular blend of inductive, dispersive, and dipole-dipole forces.

13.1.7 SOME HIGHLIGHTS OF RECENT INVESTIGATIONS

The like dissolves like rule

The buzzword "polarity", derived from the dielectric approach, is certainly the most popular word dealing with solvent effects. It is the basis for the famous rule of thumb "similia similibus solvuntur" ("like dissolves like") applied for discussing solubility and miscibility. Unfortunately, this rule has many exceptions. For instance, methanol and toluene, with dielectric constants of 32.6 and 2.4, respectively, are miscible, as are water (78.4) and isopropanol (18.3). The problem lies in exactly what is meant by a "like" solvent. Originally, the term "polarity" was meant to be an abbreviation of "static dipolarity" and was thus associated with solely the dielectric properties of the solvent. Later on, with the advent of the empirical solvent parameters, it has assumed a broader meaning, sometimes even that of the overall solvating power.[13] With this definition, however, the term “polarity” is virtually superfluous.

Clearly, neither the dielectric constant nor the dipole moment is an adequate means to define polarity. The reason is that there are liquids whose constituent molecules have no net dipole moment, for symmetry reasons, but nevertheless have local polar bonds. This class of solvents, already mentioned above, comprises just the notorious troublemakers in solvent reactivity correlations, namely the aromatic and chlorinated solvents. These solvents, called “nondipolar” in the literature,[60] stabilize charge due to higher solvent multipoles (in addition to dispersive forces) like benzene (“quadrupolar”) and carbon tetrachloride (“octupolar”). Of this class, the quadrupolar solvents are of primary importance.

Thus, the gas-phase binding energy between of K^+ and benzene is even slightly greater than that of K^+-water. The interaction between the cation and the benzene molecule is primarily electrostatic in nature, with the ion-quadrupole interaction accounting for 60% of the binding energy.[61] This effect is size-dependent: Whereas at K^+ benzene will displace some water molecules from direct contact with the ion, Na^+_{aq} is resistant towards dehydration in an aromatic environment, giving rise to selectivity in some K^+ channel proteins.[62]

For the polarity of the C-H bonds, it should be remembered that electronegativity is not an intrinsic property of an atom, but instead varies with hybridization. Only the $C(sp^3)$-H bond can be considered as truly nonpolar, but not so the $C(sp^2)$-H bond.[63] Finally, ethine has hydrogen atoms that are definitely acidic. It should further be mentioned that higher moments or local polarities cannot produce a macroscopic polarization and thus be detected in infinite wavelength dielectric experiments yielding a static dielectric constant close to the squared refractive index. Because of their short range, quadrupolar interactions do not directly contribute to the dielectric constant, but are reflected only in the Kirkwood g_K factor that decreases due to breaking the angular dipole-dipole correlations with increasing quadrupolar strength.

In these terms it is strongly recommended to redefine the term polarity. Instead of meaning solely dipolarity, it should also include higher multipolar properties,

$$\textit{polarity} = \textit{dipolarity} + \textit{quadrupolarity} + \textit{octupolarity} \qquad [13.1.13]$$

This appears to be a better scheme than distinguishing between truly nonpolar and nondipolar solvents.[56] A polar molecule can be defined as having a strongly polar bond, but need not necessarily be a dipole. In this framework, the solvating power of the “nondipolar” solvents need no longer be viewed as anomalous or as essentially dependent on specific solvation effects.[10] Beyond this it should be emphasized that many liquids have both a dipole moment and a quadrupole moment, water for example. However, for dipolar solvents such as acetonitrile, acetone, and dimethyl sulfoxide, the dipolar solvation mechanism will be prevailing. For less dipolar solvents, like tetrahydrofuran, quadrupoles and dipoles might equally contribute to the solvation energetics.[57]

Notwithstanding this modified definition, the problem with polarity remains in that positive and negative charge solvation is not distinguished. As already pointed out above, there is no general relationship between polarity and the cation solvation tendency. For example, although nitromethane ($MeNO_2$) and DMF have the same dielectric constant, the extent of ion pairing in $MeNO_2$ is much greater than that in DMF. This observation is attributed to the weak basicity of $MeNO_2$ which poorly solvates cations. As a result, ion pairing is stronger in $MeNO_2$ in spite of the fact that long-range ion-ion interactions in the two solvents are equal.

Finally, a potential problem with polarity rests in the fact that this term is typically associated with enthalpy. But caution is urged in interpreting the like-dissolves-like rule in terms of enthalpy. It is often stated for example that nonpolar liquids such as octane and carbon tetrachloride are miscible because the molecules are held together by weak dispersion forces. However, spontaneous mixing of the two phases is driven not by enthalpy, but by entropy.

Water's anomalies

The outstanding properties and anomalies of water have fascinated and likewise intrigued physicists and physical chemists for a long time. During the past decades much effort has been devoted to finding phenomenological models that explain the (roughly ten) anomalous thermodynamic and kinetic properties, including the density maximum at 4°C, the expansion upon freezing, the isothermal compressibility minimum at 46°C, the high heat capacity, the decrease of viscosity with pressure, and the remarkable variety of crystalline structures. Furthermore, isotope effects on the densities and transport properties do not possess the ordinary mass or square-root-mass behavior.

Some of these properties are known from long ago, but their origin has been controversial. From the increasingly unmanageable number of papers that have been published on the topic, let us quote only a few that appear to be essential. Above all, it seems to be clear that the exceptional behavior of water is not simply due to hydrogen bonding, but instead due to additional "trivial" vdW forces as present in any liquid. A hydrogen bond occurs when a hydrogen atom is shared between generally two electronegative atoms; vdW attractions arise from interactions among fixed or induced dipoles. The superimposition and competition of both is satisfactorily accommodated in the framework of a "mixture model".

The mixture model for liquid water, promoted in an embryonic form by Röntgen[64] over a century ago, but later discredited by Kauzmann[65] and others,[66] is increasingly gaining ground. Accordingly there are supposed to be two major types of intermolecular bonding configurations, an open bonding form, with a low density, such as occurs in ice-Ih, plus a dense bonding form, such as occurs in the most thermodynamically stable dense forms of ice, e.g., ice-II, -III, -V, and -VI.[67] In these terms, water has many properties of the glassy states associated with multiple hydrogen-bond network structures.[68] Clearly, for fluid properties, discrete units, $(H_2O)_n$, which can move independently of each other are required. The clusters could well be octamers dissociating into tetramers, or decamers dissociating into pentamers.[69,70] (Note by the way that the unit cell of ice contains eight water molecules.) However, this mixture is not conceived to be a mixture of ices, but rather is a dynamic (rapidly fluctuating) mixture of intermolecular bonding types found in the polymorphs of ice. A theoretical study of the dynamics of liquid water has shown that there exist local collective motions of water molecules and fluctuation associated with hydrogen bond rearrangement dynamics.[68] The half-life of a single H bond estimated from transition theory is about $2x10^{-10}$ s at 300K.[71] In view of this tiny lifetime it seems more relevant to identify the two mixtures not in terms of different cluster sizes, but rather in terms of two different bonding modes. Thus, there is a competition between dispersion interactions that favor random dense states and hydrogen bonding that favors ordered open states. Experimental verification of the two types of bonding has been reviewed by Cho et al.[72]

From X-ray and neutron scattering, the open structure is characterized by an inner tetrahedral cage of four water molecules surrounding a central molecule, with the nearest-neighbor O···O distance of about 2.8 Å. This distance, as well as the nearest-neighbor count of four, remains essentially intact in both in all crystalline ice polymorphs and in the liquid water up to near the boiling point. In this open tetrahedral network the second-neighbor O···O distance is found at 4.5 Å. However, and most intriguing, another peak in the O···O radial distribution function (RDF), derived from a nonstandard structural approach (ITD), is found near 3.4 Å,[73] signaling a more compact packing than in an ordinary H-bonding structure. This dense bonding form is affected through dispersive O···O interactions supplanting H-bonding. Note, however, that in this array the H bonds may not be envisaged as being really broken but instead as being only bent. This claim is substantiated by a sophisticated analysis of vibrational Raman spectra[74] and mid-IR spectra[70] pointing to the existence of essentially two types of H bonds differing in strength, with bent H bonds being weaker than normal (i.e., linear) H bonds. It should be mentioned that the 3.4 Å feature is hidden by the ordinary minimum of open tetrahedral contributions to the RDF. Because of this, the ordinary integration procedure yields coordination numbers greater than four,[75] which confuses the actual situation. Instead, it is the outer structure that is changing whereas the inner coordination sphere remains largely invariant. Even liquid water has much of the tetrahedral H-bonding network of ice I.

As temperature, or pressure, is raised, the open tetrahedral hydrogen bonding structure becomes relatively less stable and begins to break down, creating more of the dense structure. Actually all the anomalous properties of water can be rationalized on the basis of this open → dense transformation. An extremum occurs if two opposing effects are superimposed. The density maximum, for instance, arises from the increase in density due to the thermal open → dense transformation and the decrease in density due to a normal thermal expansion.[72] As early as 1978 Benson postulated that the abnormal heat capacity of water is due to an isomerization reaction.[76] A clear explanation of the density anomaly is given by Silverstein et al.[77]: "The relatively low density of ice is due to the fact that H-bonding is stronger than the vdW interactions. Optimal H-bonding is incommensurate with the tighter packing that would be favored by vdW interactions. Ice melts when the thermal energy is sufficient to disrupt and disorder the H-bonds, broadening the distribution of H-bond angles and lengths. Now among this broadened H-bond distribution, the vdW interactions favor those conformations of the system that have higher density. Hence liquid water is denser than ice. Heating liquid water continues to further deform hydrogen bonds and increase the density up to the density anomaly temperature. Further increase of temperature beyond the density anomaly weakens both H bonds and vdW bonds, thus reducing the density, as in simpler liquids."

The same authors commented on the high heat capacity of water as follows: "Since the heat capacity is defined as $C_P = (\partial H/\partial T)_P$ the heat capacity describes the extent to which some kind of bonds are broken (increasing enthalpy) with increasing temperature. Breaking bonds is an energy storage mechanism. The heat capacity is low in the ice phase because thermal energy at those temperatures is too small to disrupt the H bonds. The heat capacity peaks at the melting temperature where the solid-like H bonds of ice are weakened to become the liquid-like H bonds of liquid water. The reason liquid water has a higher heat capacity than vdW liquids have is because water has an additional energy storage mechanism, namely the H bonds, that can also be disrupted by thermal energies."

Summed up, it appears that any concept to be used in a realistic study of water should have as a fundamental ingredient the competition between expanded, less dense structures, and compressed, more dense ones. Thus, the outer structure in the total potential of water should be characterized by a double minimum: open tetrahedral structure with a second-neighbor O···O distance of 4.5 Å and a bent H-bond structure with an O···O non-H-bonded distance of about 3.4 Å. Actually, according to a quite recent theoretical study, all of the anomalous properties of water are qualitatively explainable by the existence of two competing equilibrium values for the interparticle distance.[78] Along these lines the traditional point of view as to the structure of water is dramatically upset. Beyond that, also the classical description of the hydrogen bond needs revision. In contrast to a purely electrostatic bonding, quite recent Compton X-ray scattering studies have demonstrated that the hydrogen bonds in ice have substantial covalent character,[79] as already suggested by Pauling in the 1930s.[80] In overall terms, a hydrogen bond is comprised of electrostatic, dispersion, charge-transfer, and steric repulsion interactions. Similarly, there are charge-transfer interactions between biological complexes and water[81] that could have a significant impact on the understanding of biomolecules in aqueous solution.

Finally, we return to the physical meaning of the large difference, for the protic solvents, between the cohesive energy density ε_c and the internal pressure P_i, quoted in section 13.1.3. For water this difference is highest with the factor ε_c/P_i equal to 15.3. At first glance this would seem explainable in the framework of the mixture model if H bonding is insensitive to a small volume expansion. However, one should have in mind the whole pattern of the relationship between the two quantities. Thus, $\varepsilon_c - P_i$ is negative for nonpolar liquids, relatively small (positive or negative) for polar non-associated liquids, and strongly positive for H-bonded liquids. A more rigorous treatment[41] using the relations, $P_i = (\partial U/\partial V)_T = T(\partial P/\partial T)_V - P$ and the thermodynamic identity $(\partial S/\partial V)_T = (\partial P/\partial T)_V$ reveals that the relationship is not as simple and may be represented by the following equation with dispersion detached from the other types of association,

$$\varepsilon_c - P_i = P - \frac{RT}{V}\left[Z_0 + \frac{U_{disp}}{RT}\right] - \rho U_{ass} + \rho^2 T(\partial S_{ass}/\partial \rho)_T \qquad [13.1.14]$$

where:

P	external pressure
V	liquid volume
Z_0	compressibility factor due to intermolecular repulsion
U_{disp}	potential of dispersion
U_{ass}	potential of association excluding dispersion
ρ	liquid number density
S_{ass}	entropy of association excluding dispersion

With the aid of this equation we readily understand the different ranges of $\varepsilon_c - P_i$ found for the different solvent classes. Thus, for the nonpolar liquids, the last two terms are negligible, and for the usual values, $Z_o \approx 10$, $-U_{disp}/RT \approx 8$, and $V \approx 150\ cm^3$, we obtain the typical order of $\varepsilon_c - P_i \approx -(300 - 400)$ atm (equal to -(30 - 40) J cm^{-3}, since 1 J $cm^{-3} \equiv 9.875$ atm). For moderately polar liquids, only the last term remains small, while the internal energy of dipolar forces is already appreciable $-\rho U_{polar} \approx (200-500)$ atm giving the usual magnitude of $\varepsilon_c - P_i$. For H-bonded liquids, ultimately, the last term turns out to dominate reflecting the large increase in entropy of a net of H-bonds upon a small decrease in liquid density.

Table 13.1.5. Solution thermodynamics of methane in water and carbon tetrachloride at 25°C. [Data from T. Lazaridis and M. E. Paulaitis, *J. Phys. Chem.*, 96, 3847 (1992) and ref. 108]

	Water	CCl_4
ΔS*, J/mol K	- 64.4	- 7.1
300ΔS*, kJ/mol	- 19.3	- 2.1
ΔH°, kJ/mol	- 10.9	- 1.2
ΔG*, kJ/mol	+ 8.4	+ 0.9
ΔC_p, J/mol K	217.5	0 to 42

The hydrophobic effect

In some respects the hydrophobic effect may be considered as the converse of the like-dissolves-like rule. The term hydrophobic effect refers to the unusual behavior of water towards nonpolar solutes. Unlike simple organic solvents, the insertion of nonpolar solutes into water is (1) strongly unfavorable though slightly favored by enthalpy, but (2) strongly opposed by a large, negative change in entropy at room temperature, and (3) accompanied by a large positive heat capacity. An example is given in Table 13.1.5 for the thermodynamic properties of methane dissolved in water and in carbon tetrachloride. In dealing with the entropy (and free energy) of hydration, a brief remark on the choice of standard states is in order. The standard molar entropy of dissolution, $\Delta_{solv}S°$ pertains to the transfer from a 1 atm gas state to a 1 mol L^{-1} solution and hence includes compression of the gas phase from 1 mol contained in 24.61 L (at 300 K) to 1 mol present in 1 L. Since theoretical calculations disregard volume contributions, it is proper to exclude the entropy of compression equal to -Rln24.61 = -26.63 J K^{-1} mol^{-1}, and instead to deal with $\Delta_{solv}S^*$.[82] Thus,

$$\Delta_{solv}S^* = \Delta_{solv}S^o + 26.63 JK^{-1}mol^{-1} \qquad [13.1.15]$$

and

$$\Delta_{solv}G^*_{300} = \Delta_{solv}H^o - 300\Delta_{solv}S^* \qquad [13.1.16]$$

Hydrophobicity forms the basis for many important chemical phenomena including the cleaning action of soaps and detergents, the influence of surfactants on surface tension, the immiscibility of nonpolar substances in water,[83] the formation of biological membranes and micelles,[84,85] the folding of biological macromolecules in water,[86] clathrate hydrate formation,[87] and the binding of a drug to its receptor.[88] Of these, particularly intriguing is the stabilization of protein structure due to the hydrophobicity of nonpolar groups. Hydrophobic interactions are considerably involved in self-assembly, leading to the aggregation of nonpolar solutes, or equivalently, to the tendency of nonpolar oligomers to adopt chain conformations in water relative to a nonpolar solvent.[89]

Ever-increasing theoretical work within the last years is being lifting the veil of secrecy about the molecular details of the hydrophobic effect, a subject of vigorous debate. Specifically, the scientific community would eagerly like to decide whether the loss in entropy stems from the water-water or the water-solute correlations. There are two concepts. The older one is the clathrate cage model reaching back to the "iceberg" hypothesis of Frank and Evans,[90] and the other, newer one, is the cavity-based model. It should be stressed here that the vast literature on the topic is virtually impossible to survey comprehensively. In the following we will cite only a few papers (and references therein) that paved the way to the present state of the art.

The clathrate cage model states that the structure of water is strengthened around a hydrophobic solute, thus causing a large unfavorable entropic effect. The surrounding water molecules adopt only a few orientations (low entropy) to avoid "wasting" hydrogen bonds, with all water configurations fully H-bonded (low energy). There is experimental evidence of structure strengthening, such as NMR and FT-IR studies,[91] NMR relaxation,[92] dielectric relaxation,[93] and HPLC.[94] A very common conclusion is that the small solubility of nonpolar solutes in water is due to this structuring process.

In the cavity-based model the hard core of water molecules is more important to the hydrophobic effect than H-bonding of water. The process of solvation is dissected into two components, the formation of a cavity in the water to accommodate the solute and the interaction of the solute with the water molecules. The creation of a cavity reduces the volume of the translational motion of the solvent particles. This causes an unfavorable entropic effect. The total entropy of cavity formation at constant pressure[54]

$$\Delta S_{cav,P} = \rho\alpha_p \left(\partial \Delta G_{cav} / \partial \rho\right)_T - \Delta G_{cav} / T \qquad [13.1.17]$$

where

$\Delta S_{cav,P}$ cavity formation entropy at constant pressure
ρ liquid number density
ΔG_{cav} free energy of cavity formation

is the result of the opposing nature of the (positive) liquid expansibility term and the (negative) chemical potential summand. Along these lines the large and negative entropy of cavity formation in water is traced to two particular properties of water: the small molecular size (σ = 2.87 Å) and the low expansibility ($\alpha_p = 0.26\mathrm{x}10^{-3}\ \mathrm{K}^{-1}$), with the latter having the greater impact. It is interesting to note that in both aspects water is extraordinary. Water's low expansibility reflects the fact that chemical bonds cannot be stretched by temperature. There is also a recent perturbation approach showing that it is more costly to accommodate a cavity of molecular size in water than in hexane as example.[95] Considering the high fractional free volume for water (Table 13.1.2), it is concluded that the holes in water are distributed in smaller packets.[96] Compared to a H-bonding network, a hard-sphere liquid finds more ways to configure its free volume in order to make a cavity.

In the cavity-based model, large perturbations in water structure are not required to explain hydrophobic behavior. This conclusion arose out of the surprising success of the scaled particle theory (SPT),[39] which is a hard-sphere fluid theory, to account for the free energy of hydrophobic transfers. Since the theory only uses the molecular size, density, and pressure of water as inputs and does not explicitly include any special features of H-bonding of water, the structure of water is arguably not directly implicated in the hydration thermodynamics. (However, the effect of H-bonds of water is implicitly taken into account through the size and density of water.) The proponents of this hypothesis argue that the entropic and enthalpic contributions arising from the structuring of water molecules largely compensate each other. In fact, there is thermodynamic evidence of enthalpy-entropy compensation of solvent reorganization.[97-100] Furthermore, recent simulations[101,102] and neutron scattering data[103-105] suggest that solvent structuring might be of much lower extent than previously believed. Also a recent MD study report[106] stated that the structure of water is preserved, rather than enhanced, around hydrophobic groups.

Finally, the contribution of solute-water correlations to the hydrophobic effect may be displayed, for example, in the framework of the equation

$$\Delta G_{sol} = \Delta G_{cav} + \Delta G_{att} \qquad [13.1.18]$$

where:

ΔG_{sol}	free energy of dissolution
ΔG_{cav}	free energy of cavity formation
ΔG_{att}	free energy of attractive interactions

This equation has been used by de Souza and Ben-Amotz[107] to calculate values of ΔG_{att} from the difference between experimental solubilities of rare gases, corresponding to ΔG_{sol}, and ΔG_{cav} assessed from eqn. [13.1.10], i.e., using a hard-sphere fluid (HF) model. The values of ΔG_{att} so obtained have been found to correlate with the solute polarizabilities suggesting a dispersive mechanism for attractive solvation. It is interesting to note that, in water, the solubility of the noble gases increases with increasing size, in contrast to the aliphatic hydrocarbons whose solubility decreases with size. This differential behavior is straightforwardly explained in terms of the high polarizability of the heavy noble gases having a large number of weakly bound electrons, which strengthens the vdW interactions with water. It can be shown that for noble gases, on increasing their size, the vdW interactions increase more rapidly than the work of cavity creation, enhancing solubility. On the contrary, for the hydrocarbons, on increasing the size, the vdW interactions increase less rapidly than the work of cavity creation, lowering the solubility.[108]

We have seen that there is evidence of either model, the clathrate cage model and the cavity-based model. Hence the importance of water structure enhancement in the hydrophobic effect is equivocal. The reason for this may be twofold. First, theoretical models have many adjustable parameters, so their physical bases are not always clear. Second, the free energy alone masks the underlying physics in the absence of a temperature dependence study, because of, amongst other things, the entropy-enthalpy compensation noted above. In place of the free energy, other thermodynamic derivatives are more revealing. Of these, the study of heat capacity changes arguably provides a better insight into the role of changes in water structure upon hydration than analysis of entropy or enthalpy changes alone. Note that heat capacity is the most complex of the four principal thermodynamic parameters describing solvation (ΔG, ΔH, ΔS, ΔC_p), with the following connections,

$$\Delta C_p = \frac{\partial \Delta H}{\partial T} = T\frac{\partial \Delta S}{\partial T} = -T^2 \frac{\partial^2 \Delta G}{\partial T^2} \qquad [13.1.19]$$

It should be stressed that the negative entropy of hydration is virtually not the main characteristic feature of hydrophobicity, since the hydration of any solute, polar, nonpolar, or ionic, is accompanied by a decrease in entropy.[109] The qualitative similarity in hydration entropy behavior of polar and nonpolar groups contrasts sharply with the opposite sign of the heat capacity change in polar and nonpolar group hydration. Nonpolar solutes have a large positive heat capacity of hydration, while polar groups have a smaller, negative one. Thus, the large heat capacity increase might be what truly distinguishes the hydrophobic effect from other solvation effects.[110]

Recently, this behavioral difference of nonpolar and polar solutes could be reproduced by heat capacity calculations using a combination of Monte Carlo simulations and the random network model (RNM) of water.[110-112] It was found that the hydrogen bonds between the water molecules in the first hydration shell of a nonpolar solute are shorter and less bent (i.e., are more ice-like) compared to those in pure water. The opposite effect occurs around polar solutes (the waters become less ice-like). The increase in H-bond length and angle has been found to decrease the water heat capacity contribution, while decreases in length and angle have been found to cause the opposite effect.

Note further that a large heat capacity implies that the enthalpy and entropy are strong functions of temperature, and the free energy vs. temperature is a curved function, increasing at low temperatures and decreasing at higher temperatures. Hence there will be a temperature at which the solubility of nonpolar in water is a minimum. The low solubility of nonpolar species in water at higher temperatures is caused by unfavorable enthalpic interactions, not unfavorable entropy changes. Some light on these features has been shed by using a "simple" statistical mechanical MB model of water in which the water molecules are represented as Lennard-Jones disks with hydrogen bonding arms.[113] (the MB model is called this because of the resemblance of each model water to the Mercedes-Benz logo.) As an important result, the insertion of a nonpolar solute into cold water causes ordering and strengthening of the H bonds in the first shell, but the reverse applies in hot water. This provides a physical interpretation for the crossover temperatures T_H and T_S, where the enthalpy and entropy of transfer equal zero. T_H is the temperature at which H-bond reorganizations are balanced by solute-solvent interactions. On the other hand, T_S is the temperature at which the relative H-bonding strengths and numbers of shell and bulk molecules reverse roles.

Although the large positive free energy of mixing of hydrocarbons with water is dominated by entropy at 25°C, it is dominated by enthalpy at higher temperatures (112°C from Baldwin's extrapolation for hydrocarbons, or 150°C from the measurements of Crovetto for argon)[113] where the disaffinity of oil for water is maximal. Ironically so, where hydrophobicity is strongest, entropy plays no role. For this reason, models and simulations of solutes that focus on cold water, around or below 25°C, miss much of the thermodynamics of the oil/water solvation process. Also, a clathrate-like solvation shell emerged from a recent computer simulation study of the temperature dependence of the structural and dynamical properties of dilute O_2 aqueous solutions.[114] In the first hydration shell around O_2, water-water interactions are stronger and water diffusional and rotational dynamics slower than in the bulk. This calls to one's mind an older paper by Hildebrand[115] showing that at 25°C, methane's diffusion coefficient in water is 40% less than it is in carbon tetrachloride ($D(H_2O) = 1.42\text{x}10^{-5}$ cm^2/s vs $D(CCl_4) = 2.89\text{x}10^{-5}$ cm^2/s). Presumably the loose clathrate water cages serve to inhibit free diffusion of the nonpolar solute. From these data it seems that both the nonpolar solute and the aqueous solvent experience a decrease in entropy upon dissolving in water. It should also be mentioned in this context that pressure increases the solubility. The effect of pressure on the entropy was examined and it was found that increase in the pressure causes a reduction of orientational correlations, in agreement with the idea of pressure as a "structure breaker" in water.[116] Actually, frozen clathrate hydrates trapped beneath oceans and arctic permafrost may contain more than 50% of the world's organic carbon reserves.[117,118] Likewise, the solubility of aromatics is increased at high pressure and temperature, with π bond interactions involved.[119]

Only at first glance, the two approaches, the clathrate cage model and the cavity-based model, looked very different, the former based on the hydrogen bonding of water, and the later on the hard core of water. But taken all results together it would appear that both are just different perspectives on the same physics with different diagnostics reporting consequences of the same shifted balance between H bonds and vdW interactions. Actually, in a very recent paper, a unified physical picture of hydrophobicity based on both the hydrogen bonding of water and the hard-core effect has been put forward.[120] Hydrophobicity features an interplay of several factors.

The structure of liquids

A topic of abiding interest is the issue of characterizing the order in liquids which may be defined as the entropy deficit due to preferential orientations of molecular multipoles relative to random orientations (orientational order) and nonuniformly directed intermolecular forces (positional order). Phenomenologically, two criteria are often claimed to be relevant for deciding whether or not a liquid is to be viewed as ordered: the Trouton entropy of vaporization or Trouton quotient and the Kirkwood correlation factor g_K.[121] Strictly speaking, however, both are of limited relevance to the issue.

The Trouton quotient is related to structure of the liquids only at their respective boiling points, of course, which may markedly differ from their structures at room temperature. This should be realized especially for the high-boiling liquids. As these include the highly dipolar liquids such as HMPA, DMSO, and PC, the effect of dipole orientation to produce order in the neat liquids remains obscure. All that can be gleaned from the approximate constancy of the Trouton quotient for all sorts of aprotic solvents is that at the boiling point the entropy of attractions becomes unimportant relative to the entropy of unpacking liquid molecules, that is repulsions.[122] In terms of the general concept of separating the interaction potential into additive contributions of repulsion and attraction, the vaporization entropy can be expressed by

$$\Delta_v H / T_b = \Delta_v S = \Delta S_o - S_{att} \qquad [13.1.20]$$

where:

$\Delta_v H$ vaporization enthalpy at the boiling point T_b
ΔS_o entropy of depacking hard spheres = entropy of repulsion
S_{att} entropy of attraction

ΔS_o can be separated into the entropy $f_o(\eta)$ of depacking hard spheres to an ideal gas at the liquid volume V, and the entropy of volume expansion to $V_g = RT/P$,

$$\Delta S_o / R = f_o(\eta) + \ln(V_g / V) \qquad [13.1.21]$$

Further, $f_o(\eta)$ can be derived from the famous Charnahan-Starling equation as[43]

$$f_o(\eta) = (4\eta - 3\eta^2) / (1-\eta)^2 \qquad [13.1.22]$$

It can in fact be shown that, for the nonpolar liquids, $\Delta_v S/R$ is approximately equal to $f_o(\eta)$.[122] Along these lines, Trouton's rule is traced to two facts: (i) The entropy of depacking is essentially constant, a typical value being $\Delta S_o/R \approx 9.65$, due to the small range of packing densities encompassed. In addition, the entropies of HS depacking and of volume change vary in a roughly compensatory manner. (ii) The entropy of attraction is insignificant for all the aprotics. Only for the protics the contributions of S_{att} may not be neglected. Actually the differences between $\Delta_v S$ and ΔS_o reflect largely the entropy of hydrogen bonding. However, the application of the eqns [13.1.20] to [13.1.22] to room temperature data reveals, in contrast to boiling point conditions, not unimportant contributions of S_{att} even for some aprotic liquids (see below).

On the other hand, the g_K factor is, loosely speaking, a measure of the deviation of the relative dielectric constant of the solvent with the same dipole moment and polarizability would have if its dipoles were not correlated by its structure. However, the g_K factor is only the average cosine of the angles between the dipole moments of neighboring molecules. There may thus be orientational order in the vicinity of a molecule despite a g_K of unity if there are equal head-to-tail and antiparallel alignments. Furthermore, the g_K factor is not related to positional order.

The better starting point for assessing order would be experimental room temperature entropies of vaporization upon applying the same method as described above for the boiling point conditions. (Note however, that the packing density, and hence the molecular HS diameter, varies with temperature. Therefore, in the paper[122] the packing densities have been calculated for near boiling point conditions.) Thus we choose the simplest fluid as the reference system. This is a liquid composed of spherical, nonpolar molecules, approximated to a HS gas moving in a uniform background or mean field potential provided by the attractive forces.[43] Since the mean field potential affects neither structure nor entropy, the excess entropy S_{ex}

$$S_{ex} / R = \ln\left(V_g / V\right) + f_o(\eta) - \Delta_v H / RT \qquad [13.1.23]$$

may be viewed as an index of orientational and positional order in liquids. It represents the entropy of attractions plus the contributions arising from molecular nonsphericity. This latter effect can be estimated by comparing the entropy deficits for spherical and hard convex body repulsions in the reference system. Computations available for three n-alkanes suggest that only ≈ 20% of S_{ex} are due to nonsphericity effects.

Table 13.1.6. Some liquid properties concerning structure. Data are from ref. 55 and 128 (g_K)

Solvent	$\Delta_v H/RT$	$\Delta_v S_o/R$	$-S_{ex}/R$	g_K
c-C_6	18.21	17.89	0.32	
THF	12.83	12.48	0.35	
CCl_4	13.08	12.72	0.36	
n-C_5	10.65	10.21	0.44	
$CHCl_3$	12.62	12.16	0.46	
CH_2Cl_2	11.62	11.14	0.48	
Ph-H	13.65	13.08	0.57	
Ph-Me	15.32	14.62	0.70	
n-C_6	12.70	11.89	0.81	
Et_2O	10.96	10.13	0.83	
c-hexanone	18.20	17.30	0.90	

Solvent	$\Delta_v H/RT$	$\Delta_v S_o/R$	$-S_{ex}/R$	g_K
Py	16.20	15.22	0.98	
MeCN	13.40	12.37	1.03	1.18
Me_2CO	12.50	11.40	1.10	1.49
MeOAc	13.03	11.79	1.24	
EtCN	14.53	13.25	1.28	1.15
$PhNO_2$	22.19	20.89	1.30	1.56
$MeNO_2$	15.58	14.10	1.48	1.38
NMP	21.77	20.25	1.52	1.52
EtOAc	14.36	12.76	1.60	
DMSO	21.33	19.30	2.03	1.67
DMF	19.19	17.04	2.15	1.60
DMA	20.26	18.04	2.22	1.89
HMPA	24.65	22.16	2.49	1.44
PhCN	21.97	19.41	2.56	
NMF	22.69	19.75	2.94	4.52
$n\text{-}C_{11}$	22.76	19.66	3.10	
FA	24.43	21.26	3.17	2.04
H_2O	17.71	14.49	3.22	2.79
MeOH	15.10	11.72	3.38	2.99
$n\text{-}C_{13}$	26.72	22.51	4.21	
EtOH	17.07	12.85	4.22	3.08
PC	26.33	22.06	4.27	1.86
n-PrOH	19.14	14.29	4.85	3.23
n-BuOH	21.12	15.90	5.22	3.26

The calculations for some common liquids are given in Table 13.1.6 ordered according to decreasing S_{ex}. An important result is the appreciable order produced by the hydrocarbon chain relative to polar groups and hydrogen-bonding effects. For instance, S_{ex} would project for water the same degree of order as for undecane. In like terms, ethanol is comparable to tridecane. However, the same magnitude of the excess entropy does by no means imply that ordering is similar. Much of the orientational ordering in liquids composed of elongated molecules is a consequence of efficient packing such as the intertwining of chains. In contrast, the structure of water is largely determined by strong electrostatic interactions leading to sharply-defined directional correlations characteristic of H-bonding. Although contrary to chemical tradition, there are other indications that the longer-chain hydrocarbon liquids are to be classified as highly structured as judged from thermodynamic[123,124] and depolarized Rayleigh scattering data,[125,126] and vibrational spectra.[127]

For nonprotic fluids, as Table 13.1.6 further shows, the vaporization entropy is strongly dominated by the entropy of HS depacking. This is an at least qualitative representation of the longstanding claim that repulsions play the major role in the structure of dense fluids.[37] This circumstance is ultimately responsible for the striking success of the description of neutral reactions in the framework of a purely HS liquid, as discussed in Section 13.1.6.

Also included in the Table are values of g_K as determined in the framework of a generic mean spherical approximation.[128] Since these values differ from those from other sources,[129,121] because of differences in theory, we refrain from including the latter. It is seen that the g_K parameter is unsuited to scale order, since positional order is not accounted for. On the other hand, values of g_K exceed unity for the highly dipolar liquids and thus both S_{ex} and g_K attest to some degree of order present in them.

Solvent reorganization energy in ET

Electron transfer (ET) reactions in condensed matter continue to be of considerable interest to a wide range of scientists. The reasons are twofold. Firstly, ET plays a fundamental role in a broad class of biological and chemical processes. Secondly, ET is rather simple and very suitable to be used as a model for studying solvent effects and to relate the kinetics of ET reactions to thermodynamics. Two circumstances make ET reactions particularly appealing to theoreticians:

- Outer-sphere reactions and ET within rigid complexes of well-defined geometry proceed without changes in the chemical structure, since bonds are neither formed nor broken.
- The long-ranged character of interactions of the transferred electron with the solvent's permanent dipoles.

As a consequence of the second condition, a qualitative (and even quantitative) description can be achieved upon disregarding (or reducing through averaging) the local liquid structure changes arising on the length of molecular diameter dimensions relative to the charge-dipole interaction length. Because of this, it becomes feasible to use for outer-sphere reactions in strongly polar solvents the formalism first developed in the theory of polarons in dielectric crystals.[130] In the treatment, the polar liquid is considered as a dielectric continuum characterized by the high-frequency ε_∞ and static ε_s dielectric constants, in which the reactants occupy spherical cavities of radii R_a and R_d, respectively. Electron transitions in this model are supposed to be activated by inertial polarization of the medium attributed to the reorientation of permanent dipoles. Along these lines Marcus[131] obtained his well-known expression for the free energy ΔF of ET activation

$$\Delta F = \frac{(\Delta F_o + E_r)^2}{4E_r} \qquad [13.1.24]$$

where ΔF_o is the equilibrium free energy gap between products and reactants and E_r is the reorganization energy equal to the work applied to reorganize inertial degrees of freedom changing in going from the initial to the final charge distribution and can be dissected into inner-sphere and solvent contributions:

$$E_r = E_i + E_s \qquad [13.1.25]$$

where:

E_i inner-sphere reorganization energy
E_s solvent reorganization energy

For outer-sphere ET the solvent component E_s of the reorganization energy

$$E_s = e^2 c_o g \qquad [13.1.26]$$

is the product of the medium-dependent Pekar factor $c_o = 1/\varepsilon_\infty - 1/\varepsilon_s$ and a reactant-dependent (but solvent independent) geometrical factor

$$g = 1/2R_a + 1/2R_d - 1/R \qquad [13.1.27]$$

where:

R the donor-acceptor separation
e the electron charge

Further advancements included calculations of the rate constant preexponent for nonadiabatic ET,[132] an account of inner-sphere[133] and quantum intramolecular[134-136] vibrations of reactants and quantum solvent modes.[137,138] The main results were the formulation of the dependencies of the activation energy on the solvent dielectric properties and reactant sizes, as well as the bell-shaped relationship between ΔF and ΔF_o. The predicted activation energy dependence on both the solvent dielectric properties[139,140] and the donor-acceptor distance[141] has, at least qualitatively, been supported by experiment. A bell-shaped plot of ΔF vs ΔF_o was obtained for ET in exciplexes,[142] ion pairs,[143] intramolecular[144] and outer-sphere[145] charge shift reactions. However, the symmetric dependence predicted by eq. [13.1.24] has not yet been detected experimentally. Instead, always asymmetric plots of ΔF against ΔF_o are obtained or else, in the inverted region ($\Delta F_o < -E_r$), ΔF was found to be nearly invariant with ΔF_o.[146] A couple of explanations for the asymmetric behavior are circulating in the literature (see, e.g., the review by Suppan[147]). The first one[148,149] considered vibrational excitations of high-frequency quantum vibrational modes of the donor and acceptor centers. Another suggestion[150] was that the frequencies of the solvent orientational mode are significantly different around the charged and the neutral reactants. This difference was supposed to be brought about by dielectric saturation of the polar solvent. This model is rightly questioned[151] since dielectric saturation cannot affect curvatures of the energy surface at the equilibrium point. Instead, dielectric saturation displays itself in a nonlinear deviation of the free energy surface from the parabolic form far from equilibrium. Hence, other sources of this behavior should be sought. Nevertheless, both concepts tend to go beyond the structureless description advocating a molecular nature of either the donor-acceptor complex or the solvent.

Nowadays, theories of ET are intimately related to the theories of optical transitions. While formerly both issues have developed largely independently, there is now growing desire to get a rigorous description in terms of intermolecular forces shifting the research of ET reactions toward model systems amendable to spectroscopic methods. It is the combination of steady state and transient optical spectroscopy that becomes a powerful method of studying elementary mechanisms of ET and testing theoretical concepts. The classical treatments of ET and optical transition have been facing a serious problem when extended to weakly polar and eventually nonpolar solvents. Values of E_{op} (equal to E_r in eq [13.1.25]) as extracted from band-shape analyses of absorption spectra were found to fall in the range 0.2 - 0.4 eV. Upon partitioning these values into internal vibrations and solvent degrees of freedom, although this matter is still ambiguous, the contribution of the solvent could well be on the order of 0.2 - 0.3 eV.[152-154] Unfortunately, all continuum theories predict zero solvent reorganization energies for ET in nonpolar liquids.

It is evident that some new mechanisms of ET, alternatively to permanent dipoles' reorientation, are to be sought. It should be emphasized that the problem cannot be resolved by treatments of fixed positions of the liquid molecules, as their electronic polarization follows adiabatically the transferred electron and thus cannot induce electronic transitions. On the other hand, the displacement of molecules with induced dipoles are capable of activating ET. In real liquids, as we have stated above, the appreciable free volume enables the solvent molecules to change their coordinates. As a result, variations in charge distribution in the reactants concomitantly alter the packing of liquid molecules. This point is corroborated by computer simulations.[155] Charging a solute in a Stockmayer fluid alters the inner coordination number from 11.8 for the neutral entity to 9.5 for the positively charged state, with the process accompanied by a compression of the solvation shell. It is therefore apparent that solvent reorganization involves reorganization of liquid density, in addition to the reorientational contribution. This concept has been introduced by Matyushov,[156] who dissected the overall solvent reorganization energy E_s into a dipole reorganization component E_p and a density reorganization component E_d,

$$E_s = E_p + E_d \qquad [13.1.28]$$

It should be mentioned that the two contributions can be completely separated because they have different symmetries, i.e., there are no density/orientation cross terms in the perturbation expansion involved in the calculations. The density component comprises three mechanisms of ET activation: (i) translations of permanent dipoles, (ii) translations of dipoles induced by the electric field of the donor-acceptor complex (or the chromophore), and (iii) dispersion solute-solvent forces. On the other hand, it appears that in the orientational part only the permanent dipoles (without inductions) are involved.

With this novel molecular treatment of ET in liquids the corundum of the temperature dependence of the solvent reorganization energy is straightforwardly resolved. Dielectric continuum theories predict an increase of E_s with temperature paralleling the decrease in the dielectric constants. In contrast, experimental results becoming available quite recently show that E_s decreases with temperature. Also curved Arrhenius plots eventually featuring a maximum are being reported, in weakly polar[157] and nonpolar[158] solvents. The bell-shaped temperature dependence in endergonic and moderately exergonic regions found for ET quenching reactions in acetonitrile[159] was attributed to a complex reaction mechanism. Analogously, the maximum in the Arrhenius coordinates, peculiar to the fluorescence of exciplexes formed in the intramolecular[160] and bimolecular[161] pathways, is commonly attributed to a temperature dependent competition of exciplex formation and deactivation rates. A more reasonable explanation can be given in terms of the new theory as follows.

A maximum in the Arrhenius coordinates follows from the fact that the two terms in eq. [13.1.28] depend differently on temperature. Density fluctuation around the reacting pair is determined mainly by the entropy of repacking hard spheres representing the repulsive part of the intermolecular interaction. Mathematically, the entropy of activation arises from the explicit inverse temperature dependence $E_d \propto 1/T$. Since the liquid is less packed at higher temperature, less energy is needed for reorganization. Repacking of the solvent should lead to larger entropy changes than those of dipoles' reorientation that is enthalpic in nature due to the long-range character of dipole-dipole forces. The orientational component increases with temperature essentially as predicted by continuum theories. In these ways the two solvent modes play complementary roles in the solvent's total response. This feature would lead to curved Arrhenius plots of ET rates with slight curvatures in the normal region of ET ($-\Delta F_o < E_r$), but even a maximum in the inverted region ($-\Delta F_o > E_r$).[162,163] The maximum may however be suppressed by intramolecular reorganization and should therefore be discovered particularly for rigid donor-acceptor pairs.

Photoinduced ET in binuclear complexes with localized electronic states provides at the moment the best test of theory predictions for the solvent dependent ET barrier. This type of reaction is also called metal-metal charge-transfer (MMCT) or intervalence transfer (IT). The application of the theory to IT energies for valence localized biruthenium complexes and the acetylene-bridged biferricenium monocation[164] revealed its superiority to continuum theories. The plots of E_s vs. E_{op} are less scattered, and the slopes of the best-fit lines are closer to unity. As a major merit, the anomalous behavior of some solvents in the continuum description - in particular HMPA and occasionally water - becomes resolved in terms of the extreme sizes, as they appear at the opposite ends of the solvent diameter scale.

Recently, it became feasible for the first time, to measure experimentally for a single chemical system, viz. a rigid, triply linked mixed-valence binuclear iron polypyridyl complex, $[Fe(440)_3Fe]^{5+}$, the temperature dependencies of both the rate of thermal ET and the optical IT energy (in acetonitrile-d_3).[165] The net E_r associated with the intramolecular electron exchange in this complex is governed exclusively by low frequency solvent modes, providing an unprecedented opportunity to compare the parameters of the theories of thermal and optical ET in the absence of the usual complications and ambiguities. Acceptable agreement was obtained only if solvent density fluctuations around the reacting system were taken into account. In these ways the idea of density fluctuations is achieving experimental support. The two latest reports on negative temperature coefficients of the solvent reorganization energy (decrease in E_s with temperature) should also be mentioned.[166,167]

Thus, two physically important properties of molecular liquids are absent in the continuum picture: the finite size of the solvent molecules and thermal translational modes resulting in density fluctuations. Although the limitations of the continuum model are long known, the necessity for a molecular description of the solvent, curiously, was first recognized in connection with solvent dynamic effects in ET. Solvent dynamics, however, affects the preexponent of the ET rate constant and, therefore, influences the reaction rate much less than does the activation energy. From this viewpoint it is suspicious that the ET activation energy has so long been treated in the framework of continuum theories. The reason of this affection is the otherwise relative success of the latter, traceable to two main features. First, the solvents usually used are similar in molecular size. Second, there is a compensation because altering the size affects the orientational and translational parts of the solvent barrier in opposite directions.

The solution ionic radius

The solution ionic radius is arguably one of the most important microscopic parameters. Although detailed atomic models are needed for a full understanding of solvation, simpler phenomenological models are useful to interpret the results for more complex systems. The most famous model in this respect is that of Born, originally proposed in 1920,[168] representing the simplest continuum theory of ionic solvation. For a spherical ion, the Born excess free energy ΔG_B of solvation was derived by considering the free energy change resulting from the transfer of an ion from vacuum to solvent. The equation has a very simple dependence on the ionic charge z, the radius r_B, and the solvent dielectric constant ε (for the prime see eq. [13.1.16]):

$$\Delta G_B^* = \frac{-e^2 z^2}{2r_B}\left(1 - \frac{1}{\varepsilon}\right) \qquad [13.1.29]$$

While Born assumes that the dielectric response of the solvent is linear, nonlinear effects such as dielectric saturation and electrostriction should occur due to the high electric field near the ion.[169] Dielectric saturation is the effect that the dipoles are completely aligned in the direction of the field so that any further increase in the field cannot change the degree of alignment. Electrostriction, on the other hand, is defined as the volume change or compression of the solvent caused by an electric field, which tends to concentrate dipoles in the first solvation shell of an ion. Dielectric saturation is calculated to occur at field intensities exceeding 10^4 V/cm while the actual fields around monovalent ions are on the order of 10^8 V/cm.[170]

In the following we concentrate on ionic hydration that is generally the focus of attention. Unaware of nonlinear effects, Latimer et al.[171] showed that the experimental hydration free energies of alkali cations and halide anions were consistent with the simple Born equation when using the Pauling crystal radii r_P increased by an empirical constant Δ equal to 0.85 Å for the cations and 0.1 Å to the anions. In fact three years earlier a similar relationship was described by Voet.[172] The distance $r_P + \Delta$ was interpreted as the radius of the cavity formed by the water dipoles around the ion. For cations, it is the ion-oxygen distance while for anions it is the ion-hydrogen distance of the neighboring water molecules. From those days onwards, the microscopic interpretation of the parameters of the Born equation has continued to be a corundum because of the ambiguity of using either an effective radius (that is a modification of the crystal radii) or an effective dielectric constant.

Indeed, the number of modifications of the Born equation is hardly countable. Rashin and Honig,[173] as example, used the covalent radii for cations and the crystal radii for anions as the cavity radii, on the basis of electron density distributions in ionic crystals. On the other hand, Stokes[174] put forward that the ion's radius in the gas-phase might be appreciably larger than that in solution (or in a crystal lattice of the salt of the ion). Therefore, the loss in self-energy of the ion in the gas-phase should be the dominant contributor. He could show indeed that the Born equation works well if the vdW radius of the ion is used, as calculated by a quantum mechanical scaling principle applied to an isoelectronic series centering around the crystal radii of the noble gases. More recent accounts of the subject are available.[175,176]

Irrespective of these ambiguities, the desired scheme of relating the Born radius with some other radius is facing an awkward situation: Any ionic radius depends on arbitrary divisions of the lattice spacings into anion and cation components, on the one hand, and on the other, the properties of individual ions in condensed matter are derived by means of some extra-thermodynamic principle. In other words, both properties, values of r and ΔG^*, to be compared with one another, involve uncertain apportionments of observed quantities. Consequently, there are so many different sets of ionic radii and hydration free energies available that it is very difficult to decide which to prefer.

In a most recent paper,[82] a new table of absolute single-ion thermodynamic quantities of hydration at 298 K has been presented, based on conventional enthalpies and entropies upon implication of the thermodynamics of water dissociation. From the values of $\Delta_{hyd}G^*$ the Born radii were calculated from

$$r_B\,(\text{Å}) = -695\, z^2/\Delta_{hyd}G^*(kJ) \qquad [13.1.30]$$

as given in Table 13.1.7. This is at first a formal definition whose significance may be tested in the framework of the position of the first maximum of the radial distribution function (RDF) measured by solution X-ray and neutron diffraction.[177] However, the procedure is not unambiguous as is already reflected by the names given to this quantity, viz. (for the case of a cation) ion-water[178] or ion-oxygen distance. The ambiguity of the underlying interpretation resides in the circumstance that the same value of 1.40 Å is assigned in the literature to the radius of the oxide anion, the water molecule and the vdW radius of the oxygen atom.

Table 13.1.7. Some radii (Å). Data are from ref. 82

Atom	r_B[a]	r_{aq}[b]	r_{metal}
Li	1.46	1.50	1.52
Na	1.87	1.87	1.86
K	2.33	2.32	2.27
Rb	2.52		2.48
Cs	2.75	2.58	2.65
Be	1.18	1.06	1.12
Mg	1.53	1.52	1.60
Ca	1.86	1.86	1.97
Sr	2.03	2.02	2.15
Ba	2.24	2.27	2.17
F	1.39	1.29	
Cl	1.86	1.85	
Br	2.00	2.00	
I	2.23	2.30	

[a]From eqn. [13.1.30], [b]eqns. [13.1.31] and [13.1.32].

It seems that many workers would tend to equate the distance (d) corresponding to the first RDF peak with the average distance between the center of the ion and the centers of the nearest water molecules, $d = r_{ion} + r_{water}$. Actually, Marcus[179,180] presented a nice relationship between d, averaged over diffraction and simulation data, and the Pauling crystal radius in the form $d = 1.38 + 1.102\, r_p$. Notwithstanding this success, it is preferable to implicate not the water radius but instead the oxygen radius. This follows from the close correspondence between d and the metal-oxygen bond lengths in crystalline metal hydrates.[82]

The gross coincidence of the solid and solution state distances is strong evidence that the value of d measures the distance between the nuclei of the cation ad the oxygen rather than the center of the electron cloud of the whole ligand molecule. Actually, first RDF peaks for ion solvation in water and in nonaqueous oxygen donor solvents are very similar despite the different ligand sizes. Examples include methanol, formamide and dimethyl sulfoxide.[180]

Nevertheless, the division of d into ion and ligand components is still not unequivocal. Since the traditional ionic radius is often considered as a literal measure of size, it is usual to interpret crystallographic metal-oxygen distances in terms of the sum of the vdW radius of oxygen and the ionic radius of the metal. It should b emphasized, however, that the division of bond lengths into "cation" and "anion" components is entirely arbitrary. If the ionic radius is retained, the task remains to seek a connection to the Born radius, an issue that has a long-standing history beginning with the work of Voet.[172] Of course, any addition to the ionic radius necessary to obtain good results from the Born equation needs a physical explanation. This is typically done in terms of the water radius, in addition to other correction terms such as a dipolar correlation length in the MSA (mean spherical approximation).[181-183] In this case, however, proceeding from the first RDF peak, the size of the water moiety is implicated twice.

It has been shown[82] that the puzzle is unraveled if the covalent (atomic) radius of oxygen is subtracted from the experimental first peak position of the cation-oxygen radial distribution curve (strictly, the upper limits instead of the averages). The values of r_{aq} so obtained are very close to the Born radius,

$$d(cation\text{-}O) - r_{cov}(O) = r_{aq} \approx r_B \tag{13.1.31}$$

Similarly, for the case of the anions, the water radius, taken as 1.40 Å, is implicated,

$$d(anion\text{-}O) - r(water) = r_{aq} \approx r_B \tag{13.1.32}$$

Furthermore, also the metallic radii (Table 13.1.7) are similar to values of r_{aq}. This correspondence suggests that the positive ion core dimension in a metal tends to coincide with that of the corresponding rare gas cation. The (minor) differences between r_{aq} and r_{metal} for the alkaline earth metals may be attributed, among other things, to the different coordination numbers (CN) in the metallic state and the solution state. The involvement of the CN is apparent in the similarity of the metallic radii of strontium and barium which is obviously a result of cancellation of the increase in the intrinsic size in going from Sr to Ba and the decrease in CN from 12 to 8.

Along these lines a variety of radii are brought under one umbrella, noting however a wide discrepancy to the traditional ionic radii. Cation radii larger than the traditional ionic radii would imply smaller anion radii so as to meet the (approximate) additivity rule. In fact, the large anion radii of the traditional sets give rise to at least two severe inconsistencies: (i) The dramatic differences on the order of 1 Å between the covalent radii and the anion radii are hardly conceivable in view of the otherwise complete parallelism displayed between ionic and covalent bonds.[184] (ii) It is implausible that non-bonded radii[185] should be smaller than ionic radii. For example, the ionic radius of oxygen of 1.40 Å implies that oxygen ions should not approach each other closer than 2.80 Å. However, non-bonding oxygen-oxygen distances as short as 2.15 Å have been observed in a variety of crystalline environments. "(Traditional) ionic radii most likely do not correspond to any physical reality," Baur notes.[186] It should be remarked that the scheme of reducing the size of the anion at the expense of that of the cation has been initiated by Gourary and Adrian, based on the electron density contours in crystals.[187]

The close correspondence seen between r_B and r_{aq} supports the idea that the Born radius (in aqueous solution) is predominantly a distance parameter without containing dielectric, i.e., solvent structure, contributions. This result could well be the outcome of a cancellation of dielectric saturation and electrostriction effects as suggested recently from simulations.[188-191] It should be emphasized, however, that the present discussion might be confined to water as the solvent. Recent theoretical treatments advise the cavity radius not to be considered as an intrinsic property of the solute, but instead to vary with solvent polarity, with orientational saturation prevailing at low polarity and electrostriction at high polarity.[191,192] It would appear that the whole area of nonaqueous ion solvation deserves more methodical attention. It should in addition be emphasized that the cavity radius is sensitive to temperature. Combining eq. [13.1.29] with

$$\Delta H^o = \Delta G^* + T\left(\frac{\partial \Delta G^*}{\partial T}\right) \qquad [13.1.33]$$

one obtains[177]

$$\Delta H^o = \Delta G^*\left[1 + \frac{T}{(\varepsilon - 1)\varepsilon}\left(\frac{\partial \varepsilon}{\partial T}\right)_P - \frac{T}{r}\left(\frac{\partial r}{\partial T}\right)_P\right] \qquad [13.1.34]$$

The derivation of $(\partial r/\partial T)_P$ from reliable values of ΔH° and ΔG* is interesting, in that nominally the dielectric effect (-0.018 for water) is smaller than the size effect (-0.069 for chloride), a result that has not given previously the attention due to it. Consequently, as Roux et al.[177] stated, unless a precise procedure for evaluating the dependence of the radius on the temperature is available, the Born model should be restricted to the free energy of solvation. Notwithstanding this, beginning with Voet,[172] the Born model has usually been tested by considering the enthalpies of hydration.[193] The reason for the relative success lies in the fact that ion hydration is strongly enthalpy controlled, i.e., ΔH° ~ ΔG*.

The discussion of radii given here should have implications to all calculations involving aqueous ionic radii, for instance the solvent reorganization energy in connection with eq. [13.1.26]. Thus, treatments using the crystal radii as an input parameter[194-197] may be revisited.

13.1.8 THE FUTURE OF THE PHENOMENOLOGICAL APPROACH

Originally, the empirical solvent parameters have been introduced to provide guidelines for the comparison of different solvent qualities and for an orientation in the search for an understanding of the complex phenomena in solution chemistry. Indeed, the choice of the right solvent for a particular application is an everyday decision for the chemist: which solvent should be the best to dissolve certain products, and what solvent should lead to increased reaction yields and/or rates of a reaction?

In the course of time, however, a rather sophisticated scheme has developed of quantitative treatments of solute-solvent interactions in the framework of LSERs.[198] The individual parameters employed were imagined to correspond to a particular solute-solvent interaction mechanism. Unfortunately, as it turned out, the various empirical polarity scales feature just different blends of fundamental intermolecular forces. As a consequence, we note at the door to the twenty-first century, alas with melancholy, that the era of combining empirical solvent parameters in multiparameter equations, in a scientific context, is beginning to fade away. As a matter of fact, solution chemistry research is increasingly being occupied by theoretical physics in terms of molecular dynamics (MD) and Monte Carlo (MC) simulations, the integral equation approach, etc.

In the author's opinion, it seems that further usage of the empirical parameters should more return to the originally intended purpose, emphasizing more the qualitative aspects rather than to devote too much effort to multilinear regression analyses based on parameters quoted to two decimal places. Admittedly, such a scheme may nevertheless still be used to get some insight concerning the nature of some individual solvent effect as in the recent case of an unprecedented positive wavelength shift in the solvatochromism of an aminobenzodifuranone.[199]

The physical approach, though still in its infancy, has been helping us to see the success of the phenomenological approach in a new light. Accordingly, the reason for this well documented and appreciated success can be traced back to the following features

- The molecular structure and the molecular size of many common solvents are relatively similar. The majority belongs to the so-called select solvents having a single dominant bond dipole, which, in addition, is typically hard, viz. an O- or N-donor. For example, if also soft donors (e.g., sulfur) had been employed to a larger extent, no general donor strength scale could have been devised. Likewise, we have seen that solvents other than the select ones complicate the issue.
- As it runs like a thread through the present treatment, various cancellations and competitions (enthalpy/entropy, repulsion/attraction, etc.) appear to be conspiring to make molecular behavior in complex fluids seemingly simple.

Notwithstanding this, the phenomenological approach will remain a venerable cornerstone in the development of unraveling solvent effects. Only time will tell whether a new generation of solvent indices will arise from the physical approach.

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13.2 SOLVENT EFFECTS ON FREE RADICAL POLYMERIZATION

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13.2.1 INTRODUCTION

Free radical polymerization is one of the most useful and lucrative fields of chemistry ever discovered - recent years have seen a tremendous increase in research into this area once considered a mature technological field. Free radical synthetic polymer chemistry is tolerant of diverse functionality and can be performed in a wide range of media. Emulsion and suspension polymerizations have been established as important industrial processes for many years. More recently, the ‘green’ synthesis of polymers has diversified from aqueous media to supercritical fluids and the fluorous biphase. An enduring feature of the research literature on free radical polymerization has been studies into specific solvent effects. In many cases the influence of solvent is small, however, it is becoming increasingly evident that solvent effects can be used to assist in controlling the polymerization reaction, both at the macroscopic and at the molecular levels. The purpose of this chapter is to give a brief introduction to the types of specific solvent effect that can be achieved in both free radical homo- and co-polymerizations.

13.2.2 HOMOPOLYMERIZATION

Free radical polymerization can be conveniently codified according to the classical chain reaction steps of initiation, propagation, transfer and termination. In cases where a significant solvent effect is operative then the effect is normally exerted in all of these steps. However, for the purpose of facilitating discussion this chapter is broken down into these specific reaction steps.

13.2.2.1 Initiation

Solvent effects on the initiation reaction are primarily on the rate of decomposition of initiator molecules into radicals and in the efficiency factor, f, for polymerization. However, in some instances the solvent plays a significant role in the initiation process, for example, in initiation reactions with t-butoxy radical where the primary radical rarely initiates a chain but instead abstracts a hydrogen atom from the solvent medium, which subsequently initiates the chain.[1] The consequence of this is that the polymer chains contain fragments of solvent. As the stability of the chains to thermal and photochemical degradation is governed, in part, by the nature of the chain ends then the solvent moieties within the chain can have a substantial impact on the material performance of the polymer. The efficiency factor, f, decreases as the viscosity of the reaction medium increases.[2] This is caused by an increase in the radical lifetime within the solvent cage, leading to an increased possibility of radical-radical termination. In this regard the diffusion rates of the small radicals becomes an important consideration and Terazima and co-workers[3,4] have published results indicating that many small radicals diffuse slower than expected. They have attributed this to specific interactions between radical and solvent molecules.

13.2.2.2 Propagation

The ability of solvents to affect the homopropagation rate of many common monomers has been widely documented. For example, Bamford and Brumby[5] showed that the propagation rate (k_p) of methyl methacrylate (MMA) at 25°C was sensitive to a range of aromatic solvents. Burnett et al.[6] found that the k_p of styrene (STY) was depressed by increasing concentrations of benzonitrile, bromobenzene, diethyl phthalate, dinonyl phthalate and diethyl malonate, while in other studies[7,8] they found that the k_p for MMA was enhanced by halobenzenes and naphthalene. More recent work by Zammit et al.[9] has shown that solvents capable of hydrogen-bonding, such as, benzyl alcohol and N-methyl pyrrolidone have a small influence on both the activation energy (E_a) and pre-exponential factor (A) in STY and MMA homopropagation reactions. These are but a few of the many instances of solvent effects in the homopolymerization reactions of two typical monomers, STY and MMA. For these monomers, solvent effects are relatively small, and this is indicative of the majority of homopropagation reactions. However, in some instances much larger effects are observed, especially in cases where specific interactions such as H-bonding or ionization occur. Examples of this type include the polymerization of N-vinyl-2-pyrrolidone (where water has been found to dramatically increase k_p)[10] and the polymerization of acrylamide (where pH plays a strong role).[11] There is only limited data on the Arrhenius parameters for homopropagation reactions in different solvents and this indicates that both the activation energy and pre-exponential factor are affected.[9,12] In some cases the solvent effect is not on the elementary rate constant k_p but on the local monomer concentration (sometimes referred to as the ‘Bootstrap" effect). This effect can originate in the preferential solvation of either the monomer (which is always present as a solvent) or the added solvent. It has also been suggested that in some instances the growing polymer coil can ‘shield’ the radical chain-end resulting in a low monomer concentration. This shielding effect would be expected to be greatest in poor solvents (hence a tighter coil).[13] For methyl methacrylate and styrene the largest solvent effects on propagation seem to be in the order of a 40% change in k_p.[14,15] In some solvents there seems to be reasonably strong evidence that the solvent does cause changes to the geometry of the transition state (e.g., dimethyl formamide and acetonitrile in styrene polymerization)[14] and in liquid carbon dioxide it appears that the 40% change in k_p for methyl methacrylate can be ascribed to the poor solvent medium.[16] Recent work has found that some fluoro-alcohols[17] can influence the tacticity of free radical polymerization lending further credence to the concept of solvent-induced changes to the transition state of the radical addition reaction. The largest solvent effects observed on k_p for homopropagations have been for vinyl acetate[18] and for α-(hydroxymethyl) ethyl acrylate.[12] In the former case the radical is highly unstable and some form of π-complexation between the vinyl acetate radical and aromatic solvents seems plausible. However, the large solvent effect cannot be explained by a simple radical stabilization argument (because of the early transition state for free radical propagation reactions)[19] and again the evidence points towards a change in the geometry of the transition state. The solvent effects on α-(hydroxymethyl) ethyl acrylate are in the order of 300% on k_p and there are large changes in both the Arrhenius parameters as the solvent medium is changed.[12] In monomers exhibiting a strong solvent effect on propagation it is plausible that some control of the stereochemistry of the chains is possible by manipulating the solvent and possibly utilizing Lewis acids as additives. This approach is already being successfully applied to the control of radical reactions in conventional organic chemistry.[20]

13.2.2.3 Transfer

Solvent effects on transfer reactions have not received too much attention. It would be expected (owing to the similarities between the transition states for radical addition and abstraction reactions) that these solvent effects should emulate those found in propagation reactions. However, there is potential for significant polar interactions in transfer reactions. Odian[21] has suggested that polar interactions play a significant role in the transfer reactions between styrene and carbon tetrachloride. More recent work supports this idea.[22] Significant solvent effects have been observed in catalytic chain transfer reactions using cobaloximes where the transfer reaction appears (in some cases at least) to be diffusion controlled and therefore the speed of the reaction is governed, in part, by the viscosity of the polymerizing medium.[23] In transfer reactions involving organometallic reagents then solvent effects may become important where ligand displacement may occur. This is thought to happen in catalytic chain transfer when pyridine is utilized as a solvent.[24]

13.2.2.4 Termination

The solvent effects on the termination reaction have been extensively studied. In early work, it was established that the radical-radical termination reaction is diffusion controlled and the efficacy of termination was found to have a strong relationship with the solvent viscosity.[25] Subsequently, more complex models have been developed accounting for the quality of the solvent (hence the size of the polymer coil).[26] The current debate centers on the relative roles played by segmental and translational diffusion at different stages of conversion for a variety monomers. Clearly in both cases the nature of the solvent becomes important. Solvent effects are known to play a significant role in determining the strength and onset conversion of the gel effect. This work originated in the classical paper by Norrish and Smith[27] who reported that poor solvents cause an earlier gel effect in methyl methacrylate polymerization. Recent careful studies of the gel effect by Torkelson and co-workers[28] have reinforced observations made by Cameron and Cameron[29] over two decades ago concluding that termination is hindered in poor solvents due to formation of more tightly coiled polymer radicals.

13.2.3 COPOLYMERIZATION

When solvent effects on the propagation step occur in free-radical copolymerization reactions, they result not only in deviations from the expected overall propagation rate, but also in deviations from the expected copolymer composition and microstructure. This may be true even in bulk copolymerization, if either of the monomers exerts a direct effect or if strong cosolvency behavior causes preferential solvation. A number of models have been proposed to describe the effect of solvents on the composition, microstructure and propagation rate of copolymerization. In deriving each of these models, an appropriate base model for copolymerization kinetics is selected (such as the terminal model or the implicit or explicit penultimate models), and a mechanism by which the solvent influences the propagation step is assumed. The main mechanisms by which the solvent (which may be one or both of the comonomers) can affect the propagation kinetics of free-radical copolymerization reactions are as follows:

(1) Polarity effect
(2) Radical-solvent complexes
(3) Monomer-solvent complexes
(4) Bootstrap effect

In this chapter we explain the origin of these effects, show how copolymerization models for these different effects may be derived, and review the main experimental evidence for and against these models. Throughout this review the baseline model for copolymerization is taken as the terminal or Mayo-Lewis model.[30] This model can be used to derive well-known expressions for copolymer composition and copolymerization propagation kinetics. Deviations from this model have often been interpreted in terms of either solvent effects or penultimate unit effects, although the two are by no means mutually exclusive. Deviations which affect both the copolymer composition and propagation kinetics have been termed explicit effects by Fukuda[31] in deriving penultimate unit models, whereas deviations from the kinetics without influencing the copolymer composition have been termed implicit effects. In this review we use the same terminology with respect to solvent effects: that is, a solvent effect on k_p only is termed an implicit solvent effect, while a solvent effect on composition, microstructure and k_p is termed explicit. The relatively recent discovery by Fukuda and co-workers[32] of the seemingly general failure of the terminal model to predict k_p, even for bulk copolymerizations that follow the terminal model composition equation, led them to propose an implicit penultimate unit effect as a general phenomenon in free-radical copolymerization kinetics. We conclude this review with a brief examination of the possibility that a implicit solvent effect, and not an implicit penultimate unit effect, may instead be responsible for this failure of the terminal model k_p equation.

13.2.3.1 Polarity effect

13.2.3.1.1 Basic mechanism

One type of solvent effect on free-radical addition reactions such as the propagation step of free-radical polymerization is the so-called ‘polarity effect’. This type of solvent effect is distinguished from other solvent effects, such as complexation, in that the solvent affects the reactivity of the different types of propagation steps without directly participating in the reaction. The mechanism by which this could occur may be explained as follows. The transition states of the different types of propagation steps in a free-radical copolymerization may be stabilized by charge transfer between the reacting species. The amount of charge transfer, and hence the amount of stabilization, is inversely proportional to the energy difference between the charge transfer configuration, and the product and reactant configurations that combine to make up the wave function at the transition state.[33] Clearly, the stability of the charge transfer configuration would differ between the cross- and homopropagation reactions, especially in copolymerization of highly electrophilic and nucleophilic monomer pairs. Hence, when it is significant, charge transfer stabilization of the transition state occurs to different extent in the cross- and homopropagation reactions, and thus exerts some net effect on the monomer reactivity ratios. Now, it is known that polar solvents can stabilize charged species, as seen in the favorable effect of polar solvents on both the thermodynamics and kinetics of reactions in which charge is generated.[34] Therefore, when charge transfer in the transition state is significant, the stability of the charge transfer species and thus the transition state would be affected by the polarity of the solvent, and thus a solvent effect on reactivity ratios would result.

13.2.3.1.2 Copolymerization model

There are two cases to consider when predicting the effect of solvent polarity on copolymerization propagation kinetics: (1) the solvent polarity is dominated by an added solvent and polarity is thus independent of the comonomer feed ratio, or (2) the solvent polarity does depend on the comonomer feed ratio, as it would in a bulk copolymerization. In the first case, the effect on copolymerization kinetics is simple. The monomer reactivity ratios (and additional reactivity ratios, depending on which copolymerization model is appropriate for that system) would vary from solvent to solvent, but, for a given copolymerization system they would be constant as a function of the monomer feed ratios. Assuming of course that there were no additional types of solvent effect present, these copolymerization systems could be described by their appropriate base model (such as the terminal model or the explicit or implicit penultimate models), depending on the chemical structure of the monomers.

In the second case, the effect of the solvent on copolymerization kinetics is much more complicated. Since the polarity of the reacting medium would vary as a function of the comonomer feed ratios, the monomer reactivity ratios would no longer be constant for a given copolymerization system. To model such behavior, it would be first necessary to select an appropriate base model for the copolymerization, depending on the chemical structure of the monomers. It would then be necessary to replace the constant reactivity ratios in this model by functions of the composition of the comonomer mixture. These functions would need to relate the reactivity ratios to the solvent polarity, and then the solvent polarity to the comonomer feed composition. The overall copolymerization kinetics would therefore be very complicated, and it is difficult to suggest a general kinetic model to describe these systems. However, it is obvious that such solvent effects would cause deviations from the behavior predicted by their appropriate base model and might therefore account for the deviation of some copolymerization systems from the terminal model composition equation.

13.2.3.1.3 Evidence for polarity effects in propagation reactions

The idea of charge separation in the transition state of the propagation step of free radical polymerization reactions, as suggested by Price,[35] was discounted by Mayo and Walling[36] and many subsequent workers.[37] Their rejection of this idea was based upon the absence of any unambiguous correlation between the reactivity ratios of a system and the dielectric constant of the solvent. For instance, in the copolymerization of STY with MMA, it was reported that the reactivity ratios were independent of small quantities of water, ethyl benzene, dodecylmercaptans or hydroquinone, or the presence or absence of air[30,38,39] and were thus unaffected by the dielectric constant of the system. In contrast, other studies have found a relationship between dielectric constant and the reactivity ratios in specific systems.[40,41]

The apparent lack of a general relationship between the dielectric constant of the system and the monomer reactivity ratios does not necessarily discount a polarity effect on reactivity ratios. A polarity effect is only expected to occur if the charge transfer configurations of the transition state are sufficiently low in energy to contribute to the ground state wave function. Since this is not likely to occur generally, a comprehensive correlation between reactivity ratios and the solvent dielectric constant is unlikely. Furthermore, even in systems for which a polarity effect is operating, a correlation between solvent dielectric constant and monomer reactivity ratios may be obscured by any of the following causes.

- The operation of additional types of solvent effect, such as a Bootstrap effect, that would complicate the relationship between solvent polarity and reactivity ratios.
- Errors in the experimental data base from which the correlation was sought.
- The recognized inadequacy of simple reactivity - dielectric constant correlations, that take no account of specific interactions between the solvent and solute molecules.[34]

In fact, recent theoretical[33] and experimental studies[42] of small radical addition reactions indicate that charge separation does occur in the transition state when highly electrophilic and nucleophilic species are involved. It is also known that copolymerization of electron donor-acceptor monomer pairs are solvent sensitive, although this solvent effect has in the past been attributed to other causes, such as a Bootstrap effect (see Section 13.2.3.4). Examples of this type include the copolymerization of styrene with maleic anhydride[43] and with acrylonitrile.[44] Hence, in these systems, the variation in reactivity ratios with the solvent may (at least in part) be caused by the variation of the polarity of the solvent. In any case, this type of solvent effect cannot be discounted, and should thus be considered when analyzing the copolymerization data of systems involving strongly electrophilic and nucleophilic monomer pairs.

13.2.3.2 Radical-solvent complexes

13.2.3.2.1 Basic mechanism

Solvents can also interfere in the propagation step via the formation of radical-solvent complexes. When complexation occurs, the complexed radicals are more stable than their corresponding uncomplexed-radicals, as it is this stabilization that drives the complexation reaction. Thus, in general, one might expect complexed radicals to propagate more slowly than their corresponding free-radicals, if indeed they propagate at all. However, in the special case that one of the comonomers is the complexing agent, the propagation rate of the complexed radical may instead be enhanced, if propagation through the complex offers an alternative less-energetic reaction pathway. In any case, the complexed radicals would be expected to propagate at a rate different to their corresponding free-radicals, and thus the formation of radical-solvent complexes would affect the copolymerization propagation kinetics.

13.2.3.2.2 Copolymerization model

A terminal radical-complex model for copolymerization was formulated by Kamachi.[37] He proposed that a complex is formed between the propagating radical chain and the solvent (which may be the monomer) and that this complexed radical has a different propagation rate constant to the equivalent uncomplexed radical. Under these conditions there are eight different propagation reactions in a binary copolymerization, assuming that the terminal unit is the only unit of the chain affecting the radical reactivity. These are as follows.

$$RMi\cdot+Mj\xrightarrow{k_{ij}}RMiMj\cdot or\ RMiMj\cdot S\ where: i,j=1 or\ 2$$

$$RMi\cdot S+Mj\xrightarrow{k_{cij}}RMiMj\cdot or\ RMiMj\cdot S\ where: i,j=1 or\ 2$$

There are also two equilibrium reactions for the formation of the complex:

$$RMi\cdot+S\xleftrightarrow{K_i}RMi\cdot S\ where: i,j=1 or\ 2$$

Applying the quasi-steady-state and long-chain assumptions to the above reactions, Kamachi derived expressions for $\bar{r}_i$ and $\bar{k}_{ii}$, which are used in place of r_i and k_{ii} in the terminal model equations for composition and k_p:

$$\bar{k}_{ii}=k_{ii}\frac{1+\bar{s}_{ci}K_i[C_i]}{1+K_i[C_i]}\quad and\quad \bar{r}_i=r_i\frac{1+\bar{s}_{ci}K_i[C_i]}{1+(r_i/\bar{r}_{ci})\bar{s}_{ci}K_i[C_i]}$$

where: $r_i = k_{ii}/k_{ij}$; $\bar{r}_{ic} = k_{cii}/k_{cij}$; $\bar{s}_{ci} = k_{cii}/k_{ii}$; $i, j = 1$ or 2 and $i \neq j$

Variants of this model may be derived by assuming an alternative basis model (such as the implicit or explicit penultimate models) or by making further assumptions as to nature of the complexation reaction or the behavior of the complexed radical. For instance, in the special case that the complexed radicals do not propagate (that is, $\bar{s}_{ci} = 0$ for all i), the reactivity ratios are not affected (that is, $\bar{r}_i = r_i$ for all i) and the complex formation serves only removal of radicals (and monomer, if monomer is the complexing agent) from the reaction, resulting in a solvent effect that is analogous to a Bootstrap effect (see Section 13.2.3.4).

13.2.3.2.3 Experimental evidence

There is certainly strong experimental evidence for the existence of radical-solvent complexes. For instance, Russell[45-47] and co-workers collected experimental evidence for radical-complex formation in studies of the photochlorination of 2,3-dimethylbutane in various solvents. In this work, different products were obtained in aliphatic and aromatic solvents, and this was attributed to formation of a π-complex between the Cl atom and the aromatic solvent. Complex formation was confirmed by flash photolysis.[48-51] Complex formation was also proposed to explain experimental results for the addition of trichloromethane radical to 3-phenylpropene and to 4-phenyl-1-butene[52] and for hydrogen abstraction of the t-butoxy radical from 2,3-dimethylbutane.[53] Furthermore, complexes between nitroxide radicals and a large number of aromatic solvents have been detected.[54-57] Evidence for complexes between polymer radicals and solvent molecules was collected by Hatada et al.,[58] in an analysis of initiator fragments from the polymerization of MMA-d with AIBN and BPO initiators. They discovered that the ratio of disproportionation to combination depended on the solvent, and interpreted this as evidence for the formation of a polymer radical-solvent complex that suppresses the disproportionation reaction.

There is also experimental evidence for the influence of radical-solvent complexes in small radical addition reactions. For instance, Busfield and co-workers[59-61] used radical-solvent to explain solvent effects in reactions involving small radicals, such as t-butoxyl radicals towards various electron donor-electron acceptor monomer pairs. The observed solvent effects were interpreted in terms of complex formation between the t-butoxyl radical and the electron-acceptor monomer, possibly via a sharing of the lone pair on the t-butoxyl oxygen with the π-system of the acceptor monomer. Several workers have invoked frontier orbital theory to rationalize such solvent effects in terms of radical-solvent complex formation, and thus provide a theoretical base.[37,62]

Many workers have suggested radical-solvent complexes as an explanation for the influence of aromatic compounds on the homopolymerization of vinyl monomers. For instance, Mayo[63] found that bromobenzene acts as a chain transfer agent in the polymerization of STY but is not incorporated into the polymer. He concluded that a complex is formed between the solvent molecule and either the propagating polystyryl radical or a proton derived from it. The influence of halobenzenes on the rate of polymerization of MMA was detected by Burnett et al.[8,64,65] They proposed that the efficiency of a number of different initiators increased in various halogenated aromatic solvents and, since enhanced initiator or solvent incorporation into the polymer was not observed, they concluded that initiator-solvent-monomer complex participation affected the initiator efficiency. Henrici-Olive and Olive[66-71] suggested that this mechanism was inadequate when the degree of polymerization was taken into account and they proposed instead a charge transfer complex between the polymer radical and aromatic solvent. The polymer radical can form a complex with either the monomer or solvent molecule, but only the former can propagate. Bamford and Brumby,[5] and later Burnett et al.,[72,73] interpreted their solvent-effects data for k_p in terms of this donor-acceptor complex formation between aromatic solvents and propagating radicals.

Radical-solvent complexes are expected to be favored in systems containing unstable radical intermediates (such as vinyl acetate) where complexation may lead to stabilization. In this regard Kamachi et al[18] have noted that solvent effects on vinyl acetate homopolymerization result in a reduced k_p. Kamachi et al.[74] also measured the absolute rate constants of vinyl benzoate in various aromatic solvents and found that k_p increased in the order:

benzonitrile < ethyl benzoate < anisole < chlorobenzene < benzene < fluorobenzene < ethyl acetate

They argued that this trend could not be explained by copolymerization through the solvent or transfer to the solvent because there was no correlation with the solvent dielectric constant or polarity, or with the rate constants for transfer to solvent. However, there was a correlation with the calculated delocalization stabilization energy for complexes between the radical and the solvent, which suggested that the propagating radical was stabilized by the solvent or monomer, but the solvent did not actually participate in the reaction.

As noted in the introduction to this section, radical-solvent complexes may enhance the propagation rate if propagation through the complex offers an alternative, less-energetic pathway for propagation. An example of this behavior is found in the homopolymerization of acrylamide. The homopropagation rate coefficient for this monomer shows a negative temperature dependence, which has been explained in terms of radical-complex formation. Pascal et al.[11,75] suggested that propagation proceeds via a complex that enhances the propagation rate, and this complex dissociates as temperature increases, thus explaining the normal temperature dependence of the propagation rate at high temperatures. This interpretation was supported by the observation that acrylamide behaves normally in the presence of reagents such as propionamide, which would be expected to inhibit complex formation.

Given the experimental evidence for the existence of radical-solvent complexes and their influence on free-radical addition reactions such as homopropagation, it is likely that radical-solvent complexes will affect the copolymerization kinetics for certain copolymerization systems, and indeed many workers have invoked the radical-complex model in order to explain solvent effects in copolymerization. For instance, Heublein and Heublein[76] have invoked a radical complex model in combination with a partitioning idea (see Section 13.2.3.4) to explain solvent effects on the copolymerization of vinyl acetate with acrylic acid. More recently, O'Driscoll and Monteiro[77] suggested that the effect of benzyl alcohol on the copolymerization of STY-MMA was best described by an RC-type model. This was supported by pulsed-laser studies[9] on the homopropagation reactions where E_a values were found to be increased slightly by the presence of benzyl alcohol. Czerwinski (see for example reference[78] and references cited therein) has also published a variant of the RC model and has applied his model to a range of copolymerization experimental data. In conclusion, there is a strong experimental evidence for the importance of radical-solvent complexes in a number of specific copolymerization systems, especially when there is a large disparity in the relative stabilities of the different propagating radicals.

13.2.3.3 Monomer-solvent complexes

13.2.3.3.1 Introduction

A solvent may also interfere in the propagation step via complexation with the monomer. As was the case with radical-solvent complexes, complexed monomer might be expected to propagate at a different rate to free monomer, since complexation might stabilize the monomer, alter its steric properties and/or provide an alternative pathway for propagation. In examining the effect of such complexation on copolymerization kinetics, there are a number of different mechanisms to consider. In the case that the complex is formed between the comonomers, there are three alternatives: (1) the monomer-monomer complex propagates as a single unit, competing with the propagation of free monomer; (2) the monomer-monomer complex propagates as a single unit, competing with the propagation of free monomer, but the complex dissociates during the propagation step and only one of the monomers is incorporated into the growing polymer radical; (3) the monomer-monomer complex does not propagate, and complexation serves only to alter the free monomer concentrations. In the case that the complex is formed between one of the monomers and an added solvent, there are two further mechanisms to consider: (4) the complexed monomer propagates, but at a different rate to the free monomer; (5) the complexed monomer does not propagate. Models based on mechanisms (1) and (2) are known as the monomer-monomer complex participation (MCP) and dissociation (MCD) models, respectively. Mechanisms (3) and (5) would result in a solvent effect analogous to a Bootstrap effect, and will be discussed in Section 13.2.3.4. In this section, we review the MCP and MCD models, and conclude with a brief discussion of specific monomer-solvent interactions.

13.2.3.3.2 Monomer-monomer complex participation model

The use of monomer-monomer charge transfer complexes to explain deviations from the terminal model was first suggested by Bartlet and Nozaki,[79] later developed by Seiner and Litt,[80] and refined by Cais et al.[81] It was proposed that two monomers can form a 1:1 donor complex and add to the propagating chain as a single unit in either direction. The complex would be more reactive because it would have a higher polarizability due to its larger π-electron system that can interact more readily with the incoming radical. The complex would also have a higher pre-exponential factor, as a successful attack may be achieved over a wider solid angle.[80] The heavier mass of the complex would also serve to increase the pre-exponential factor.

In addition to the four terminal model reactions, four complex addition reactions and an equilibrium constant are required to describe the system.

$$RMi\cdot + Mj^{\circ} \xrightarrow{k_{ij}} RMiMj\cdot \quad where\colon i,j = 1 or\ 2$$

$$RMi\cdot + MiMj \xrightarrow{k_{iij}} RMiMiMj\cdot \quad where\colon i,j = 1 or\ 2\, and\ i \neq j$$

$$RMi\cdot + MiMj \xrightarrow{k_{iji}} RMiMjMi\cdot \quad where\colon i,j = 1 or\ 2\, and\ i \neq j$$

$$M1^{\circ} + M2^{\circ} \xleftrightarrow{K} M1M2$$

The composition and propagation rate can be expressed in terms of the following parameters.[31]

$$\frac{F_1}{F_2} = \frac{f_1^{\circ}}{f_2^{\circ}}\,\frac{(A_2B_1)r_1f_1^{\circ} + (A_1C_2)f_2^{\circ}}{(A_1B_2)r_2f_2^{\circ} + (A_2C_1)f_1^{\circ}}$$

$$\bar{k}_p = \frac{(A_2B_1)r_1\left(f_2^{\circ}\right)^2 + (A_1B_2)r_2\left(f_2^{\circ}\right)^2 + (A_1C_2 + A_2C_1)f_1^{\circ}f_2^{\circ}}{\left(A_2r_1f_1^{\circ}/k_{11}\right) + \left(A_1r_2f_2^{\circ}/k_{22}\right)}$$

where:

$A_1 = 1 + r_1s_1cQf_1^{\circ}$ and $A_2 = 1 + r_2s_2cQf_2^{\circ}$
$B_1 = 1 + s_1c(1 + r_1c^{-1})Qf_2^{\circ}$ and $B_2 = 1 + s_2c(1 + r_2c^{-1})Qf_1^{\circ}$
$C_1 = 1 + r_1s_1c(1 + r_1c^{-1})Qf_1^{\circ}$ and $C_2 = 1 + r_2s_2c(1 + r_2c^{-1})Qf_2^{\circ}$
$2Qf_i^{\circ} = \{[Q(f_j - f_i) + 1]^2 + 4Qf_i\}^{1/2} - [Q(f_i - f_j) + 1]$ and $Q = k[M]$
f_i is feed composition of Mi
$f_i^{\circ} = [Mi^{\circ}]/[M]$
$r_i = k_{ii}/k_{ij}$; $r_{ic} = k_{iij}/k_{iji}$; $s_{ic} = k_{iij}/k_{ii}$ where: i,j = 1 or 2 and $i \neq j$

The applicability of the MCP model to strongly alternating copolymerization has been a long standing point of contention. In essence, there are two opposing accounts of the strongly alternating behavior observed in copolymers of electron-donor-acceptor (EDA) monomer pairs. In the first account, this behavior has been attributed to the fact that the transition state is stabilized in cross-propagation reaction and destabilized in the homopropagation. Deviations from the terminal model are caused merely by penultimate unit effects. In the second account -the MCP model- the strongly alternating behavior is a result of propagation of a 1:1 comonomer complex which, as seen above, also leads to deviations from the terminal model. An intermediate mechanism, which will be discussed shortly, is the MCD model in which the complex dissociates during the propagation step. The main approach to discriminating between these models has been to compare their ability to describe the copolymerization data of various explicit systems, and to study the effect of added solvents on their behavior. Unfortunately, both approaches have led to inconclusive results.

As an example, the system STY with maleic anhydride (MAH) has been perhaps the most widely studied EDA system and yet there is still uncertainty concerning the role of the EDA complex in its propagation mechanism. Early studies[82,83] concluded that its behavior was best modelled by a penultimate model, despite the spectroscopic evidence for EDA complexes in this system. Later Tsuchida et al.[84,85] fitted an MCP model, based on the evidence that the rate went through a maximum at 1:1 feed ratio in benzene or CCl_4 but in strong donor solvents no such maximum occurred and instead the rate increased with the content of MAH in the feed. They argued that maximum in rate at 1:1 feed ratios was due to the fact that propagation occurred via the complex, which had a maximum concentration at this point. In strong donor solvents, the maximum rate moved to higher concentrations of MAH due to competition between the donor and STY for complexation with the MAH. However, a few years later, Dodgson and Ebdon[86,87] conducted an extensive study of STY-MAH in various solvents and discounted the MCP model on the basis of an absence of a dilution effect with the inert solvent MEK. In an MCP model a dilution effect would be expected due to the decrease in the relative concentration of the comonomer complex and the enhanced participation of the free monomer.[88] Later, Farmer et al.[89] reanalyzed this data and concluded that the composition data was consistent with both models and suggested sequence distribution may provide the answer. They also pointed out that there was a small dilution effect in MEK -greater than that predicted by the penultimate model and less than that predicted by the MCP model. Hill et al.[90] has suggested that interpretation of the effect of solvents is complicated by the fact that no solvent is truly inert, hence such results such be treated with caution. More recently Sanayei et al.[91] have performed a pulsed-laser polymerization study on STY-MAH copolymerization in butanone and acetonitrile. They concluded that whilst the complex participation model described the copolymer composition it failed to predict the average k_p data. Consequently the best description of this copolymerization was given by the penultimate unit model.

There have been many other systems for which the MCP model has been proposed as an alternative to the penultimate unit model. For instance, Litt and Seiner used the MCP model to describe the composition of a number of systems, including MAH with 1-diphenylethylene, β-cyanacrolein with styrene,[92] and vinyl acetate with dichlorotetrafluoroacetone and with hexafluoroacetone.[80] An MCP model has also been suggested for the system STY-SO_2.[39,83,93-95] In this system, the composition changes with dilution or with solvent changes, strongly alternating behavior is observed across a range of feed ratios, and one of the comonomers (SO_2) does not undergo homopolymerization. However, while the MCP model appears to be appropriate for some systems, in other strongly alternating copolymerizations it is clearly not appropriate. For instance, there are many strongly alternating copolymerizations for which there is no evidence of complex formation.[36,39,88,96] Even when complex formation is known to occur, results cannot always be explained by the MCP model. For instance, measurements of sequence distribution data revealed that, while both the MCP and penultimate model could provide an adequate description of the composition of STY with acrylonitrile (AN), only the penultimate model could account for the sequence distribution data for this system.[97] As will be seen shortly, there is evidence that in some systems the heat of propagation would be sufficient to dissociate the EDA complex and hence it could not add to the monomer as unit. In this case an MCD model would be more appropriate. Thus, it might be concluded that the MCP, MCD and the penultimate models are needed to describe the behavior of strongly alternating systems, and the selection of each model should be on a case-by-case basis. There have been many more systems for which the MCP model has been evaluated against the penultimate model on the basis of kinetic behavior. These studies have been extensively reviewed by Hill et al.[90] and Cowie[98] will therefore not be reviewed here. Instead a few additional sources of evidence for the participation of the EDA complex will be highlighted.

UV and NMR evidence for the existence of EDA complexes

There is certainly a demonstrable existence of comonomer complexes in solutions of electron donor acceptor monomer pairs. These complexes can be detected, and their equilibrium constants measured, using UV or NMR spectroscopy. Techniques for this are described in detail in reviews of comonomer complexes by Cowie[98] and Hill et al.[90] The latter review[90] also includes a listing of the equilibrium constants for the numerous EDA complexes that have been experimentally detected. The existence of comonomer complexes is not sufficient evidence for their participation in the propagation step of copolymerization, but the fact that they exist in solutions from which strongly alternating copolymers are produced suggests that they play some role in the mechanism. Furthermore, the ability to measure their strengths and quantify the effects of solvents on their observed equilibrium constants without performing kinetic experiments, may provide the key to establishing their role in the propagation mechanism. Since the alternative models for copolymerization include (or in some cases omit) the equilibrium constant for these complexes in different ways; if the equilibrium constant was to be measured separately and not treated as an adjustable parameter in the kinetic analysis, more sensitive model discrimination would be possible. To date, such an analysis does not appear to have been performed but it should be included in subsequent kinetic analyses of these explicit systems.

Temperature effects

The study of the temperature dependence of copolymerization behavior may also provide evidence for the role of comonomer complexes. As was seen previously in the study of acrylamide, complexes dissociate at high temperatures and hence, if the complex is involved in controlling an aspect of the polymerization behavior, a change in this behavior should be observed at the temperature corresponding to the complete dissociation of the complex. Such evidence has been obtained by Seymour and Garner[99,100] for the copolymerization of MAH with a variety of vinyl monomers, including STY, VA, AN, and α-MSTY. They observed that the copolymers undergo a change from strongly alternating to random at high temperatures, and these temperatures are also the temperatures at which the concentration of the EDA complex becomes vanishingly small. It is true that, since reactivity ratios have an enthalpy component, they approach unity as temperature increases. Hence, most models predict that the tendency of copolymers to form a random microstructure increases as temperature increased. Indeed, more recent work by Klumperman[101] has shown that for STY-MAH copolymerization, the reactivity ratios do follow an Arrhenius type of temperature dependence. However, further work is required to verify this for the other copolymerization listed above. Based upon the existing copolymerization data, it appears that for many systems there are sudden transition temperatures that correspond to the dissociation of the complex, which does suggest that the complex is in some way responsible for the alternating behavior.[99,100]

Stereochemical evidence for the participation of the complex

Stereochemical data may provide evidence for participation of the EDA complex. The EDA complex will prefer a certain geometry -that conformation in which there is maximum overlap between the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor.[102] If the complex adds to the propagating polymer chain as a unit, then this stereochemistry would be preserved in the polymer chain. If, however, only free monomer addition occurs, then the stereochemistry of the chain should be completely random (assuming of course that there are no penultimate unit effects operating). Hence, it is possible to test for the participation of the monomer complexes in the addition reaction by examination of the stereochemistry of the resulting polymer.

Such stereochemical evidence has been collected by a number of workers. For instance, Iwatsuki and Yamashia[103] observed an unusually high percentage of cis units in MAH/butadiene copolymers. Olson and Butler[104] studied the EDA system N-phenylmaleimide (NPM)/2-chloroethyl vinyl ether (CEVE) and found that the stereochemistry at succinimide units in NPM-CEVE copolymers is predominantly cis, and random elsewhere. Furthermore, they noted that the proportion of cis units was correlated with those variables with which the concentration of the EDA complex was also correlated. In these examples, the cis geometry is that which is most stable for the complex. However, Rätzsch and Steinert[105] have argued that this preference for cis geometry may also be explained by propagation occurring via a complex between the reacting free monomer and the chain end, as in an RC model. Thus this evidence should be used in conjunction with other evidence for model discrimination.

Further stereochemical evidence for the MCP model has been obtained by Butler et al.[106] They predicted that the usual preference for head-tail addition in free-radical polymerization would be overcome if propagation occurred via the EDA complex, and its favored geometry was a head-head conformation. They noted that for most EDA pairs head-tail geometry was favored and hence the predominance of head-tail linkages in these copolymers could not discriminate between free monomer addition and complex participation. To solve this problem, they designed and synthesized two monomer pairs for which a head-head conformation would be expected in their EDA complexes. These were the systems dimethyl cyanoethylene dicarboxylate (DMCE) with CEVE, and dimethyl cyanoethylene dicarboxylate (DMCE) with CEVE. They then showed that there were significant head-head linkages in the resulting copolymer and the proportion of these linkages was correlated with same types of variables that had previously affected the cis content of NPM/CEVE copolymers -that is, those variables which affected the concentration of the EDA complex. Thus they concluded that there was strong stereochemical evidence for the participation of the EDA complex in the propagation step.

ESR evidence for the participation of the complex

ESR studies have also been suggested as a means for providing information about the participation of the EDA complex. Since the addition of the complex is likely to occur more readily in one direction, if propagation occurs as the repeated addition of the complex then the propagating radical should be predominantly of one type. However, if free monomer addition predominantly occurs, both types of radical are likely to be present at any time. Thus ESR can be used to distinguish between the two mechanisms. This approach was used by Smirnov et al.[107] to show that, in the system phenyl vinyl ether/MAH, alternating addition of the free monomer predominates, but participation of EDA complexes is important for the system butyl vinyl ether/MAH. They argued that the difference in the behavior of the two EDA systems was a result of the different strengths of their EDA complexes. In another study, Golubev et al.,[108] used ESR to show that for dimethylbutadiene/MAH the cross-propagation of the free monomers dominated. However, Barton et al.[109] has questioned the assignments of ESR signals in the previous studies and suggested that the ESR evidence was inconclusive. Furthermore, the predominance of one type of ESR signal may also be explained without invoking the MCP model. Assuming that cross-propagation is the dominant reaction, and that one of the radicals is much less stable than the other, it might reasonably be expected that the less stable radical would undergo fast cross-propagation into the more stable radical, resulting in an ESR signal dominated by the more stable radical. Hence it appears that ESR is not able to discriminate between this and the MCP mechanism.

13.2.3.3.3 Monomer-monomer complex dissociation model

Tsuchida and Tomono[84] suggested that the monomer-monomer complex described in the MCP model may dissociate upon addition to the chain, with only one unit adding. The concept was developed by Karad and Schneider[110] who argued that the dissociation of the complex is likely since its heat of formation is typically less than the heat of propagation. As an example, they measured the heat of formation for a STY/fumaronitrile complex, and found that it was only 1.6 kcal/mol, significantly less than the heat of propagation (15-20 kcal/mol). Under a complex-dissociation mechanism, the role of the complex is merely to modify the reactivity of the reactant monomers.

A model based on the complex-dissociation mechanism was first formulated by Karad and Schneider[110] and generalized by Hill et al.[111] Again, eight rate constants and two equilibrium constants are required to describe the system.

$$RMi\cdot + Mj \xrightarrow{k_{ij}} RMiMj\cdot \quad where\!: i, j = 1 or\ 2$$

$$RMi\cdot + MjC \xrightarrow{k_{ijc}} RMiMj\cdot \quad where\!: i, j = 1 or\ 2$$

$$Mi + C \xleftrightarrow{K_i} MiC \quad where\!: i, j = 1 or\ 2$$

As for the previous models, expressions for $\bar{k}_p$ and composition can be derived in terms of these parameters by first calculating $\bar{k}_{ii}$ and $\bar{r}_i$ and then using them in place of k_{ii} and r_i in the terminal model equations. The relevant formulae are:

$$\bar{k}_{ii} = k_{ii}\frac{1+s_{ic}K_i[C_i]}{1+K_i[C_i]} \ and\ \bar{r}_i = r_i\frac{1+s_{ic}K_i[C_i]}{1+(r_i/r_{ci})s_{ic}K_i[C_i]}$$

where: $r_i = k_{ii}/k_{ij}$; $r_{ic} = k_{iic}/k_{ijc}$; $s_{ic} = k_{iic}/k_{ii}$; i,j = 1 or 2 and $i \neq j$

Efforts to compare this model with the MCP model have been hindered by the fact that similar composition curves for a given system are predicted by both models. Hill et al.[111] showed that the composition data of Dodgson and Ebdon[87] for STY/MAH at 60°C could be equally well described by the MCP, MCD or penultimate unit models. They suggested that sequence distribution would be a more sensitive tool for discriminating between these models. One study which lends some support to this model over the MCP model for describing this system was published by Rätzsch and Steinert.[105] Using Giese's[112] 'mercury method' to study the addition of monomers to primary radicals, they found that in mixtures of MAH and STY, only reaction products from the addition of free monomers, and not the EDA complex, to primary cyclohexyl radicals were found. Thus they concluded that the STY/MAH complex in the monomer solution is disrupted during the propagation step. It is likely that both the MCP and MCD mechanisms are valid and their validity in a specific system will depend on the relative strength of the EDA complex concerned. The MCD model may be useful for accounting for those systems, in which EDA complexes are known to be present but the MCP model has been shown not to hold.

13.2.3.3.4 Specific solvent effects

Several monomers are particularly susceptible to strong solvent effects via specific interactions such as hydrogen bonding, ionic strength and pH. The kinetic consequences of these specific interactions will vary from system to system. In some cases the radical and/or monomer reactivity will be altered and in other cases a Bootstrap effect will be evident. It is worth noting that monomers which are susceptible to strong medium effects will not have reliable Q-e values, a good example of this is 2-hydroxyethyl methacrylate (HEMA) where there is a large variation in reported values. The reactivity ratios of HEMA with STY have been reported to be strongly dependent on the medium,[113] similarly the copolymerization of HEMA with lauryl methacrylate is solvent sensitive;[114] behavior which has been attributed to non-ideal solution thermodynamics (cf Semchikov’s work in Section 13.2.3.4). Chapiro[115] has published extensively on the formation of molecular associates in copolymerization involving polar monomers. Other common monomers which show strong solvent effects are N-vinyl-2-pyrrolidone, (meth)acrylic acids and vinyl pyridines.

13.2.3.4 Bootstrap model

13.2.3.4.1 Basic mechanism

In the Bootstrap model, solvent effects on k_p are attributed to solvent partitioning and the resulting difference between bulk and local monomer concentrations. In this way, a solvent could affect the measured k_p without changing the reactivity of the propagation step. Bootstrap effects may arise from a number of different causes. As noted previously, when radical-solvent and monomer-solvent complexes form and the complexes do not propagate, the effect of complexation is to alter the effective radical or monomer concentrations, thereby causing a Bootstrap effect. Alternatively, a Bootstrap effect may arise from some bulk preferential sorption of one of the comonomers around the growing (and dead) polymer chains. This might be expected to occur if one of monomers is a poor solvent for its resulting polymer. A Bootstrap effect may also arise from a more localized from of preferential sorption, in which one of the monomers preferentially solvates the active chain end, rather than the entire polymer chain. In all cases, the result is the same: the effective free monomer and/or radical concentrations differ from those calculated from the monomer feed ratios, leading to a discrepancy between the predicted and actual propagation rates.

13.2.3.4.2 Copolymerization model

Copolymerization models based upon a Bootstrap effect were first proposed by Harwood[116] and Semchikov[117] (see references cited therein). Harwood suggested that the terminal model could be extended by the incorporation of an additional equilibrium constant relating the effective and ‘bulk’ monomer feed ratios. Different versions of this so-called Bootstrap model may be derived depending upon the baseline model assumed (such as the terminal model or the implicit or explicit penultimate models) and the form of equilibrium expression used to represent the Bootstrap effect. In the simplest case, it is assumed that the magnitude of the Bootstrap effect is independent of the comonomer feed ratios. Hence in a bulk copolymerization, the monomer partitioning may be represented by the following equilibrium expression:

$$\frac{f_1}{f_2} = K\left(\frac{f_{1bulk}}{f_{2bulk}}\right)$$

The equilibrium constant K may be considered as a measure of the Bootstrap effect. Using this expression to eliminate the effective monomer fractions (f_1 and f_2) from the terminal model equations, replacing them with the measurable 'bulk' fractions (f_{1bulk} and f_{2bulk}), the following equations for composition[43] and k_p[118] may be derived.

$$\frac{F_1}{F_2} = \frac{Kf_{1bulk}}{f_{2bulk}} \frac{r_1 K f_{1bulk} + f_{2bulk}}{r_2 f_{2bulk} + K f_{1bulk}}$$

$$k_p = \frac{1}{Kf_{1bulk} + f_{2bulk}} \frac{r_1 K^2 f_{1bulk}^2 + 2Kf_{1bulk} f_{2bulk} + r_2 f_{2bulk}^2}{r_1 K f_{1bulk} / k_{11} + r_2 f_{2bulk} / k_{22}}$$

Examining the composition and k_p equations above, it is seen that the Bootstrap effect K is always aliased with one of the monomer feed ratios (that is, both equations may be expressed in terms of Kf_1 and f_2). It is also seen that once Kf_1 is taken as a single variable, the composition equation has the same functional form as the terminal model composition equation, but the k_p equation does not. Hence it may seen that, for this version of the Bootstrap effect, the effect is an implicit effect - causing deviation from the terminal model k_p equation only. It may also be noted that, if K is allowed to vary as a function of the monomer feed ratios, the composition equation also will deviate from terminal model behavior - and an explicit effect will result. Hence it may be seen that it is possible to formulate an implicit Bootstrap model (that mimics the implicit penultimate model) but in order to do this, it must be assumed that the Bootstrap effect K is constant as a function of monomer feed ratios.

It should be noted that the above equations are applicable to a bulk copolymerization. When modelling solution copolymerization under the same conditions, the equations may be used for predicting copolymer composition since it is only the relationship between bulk and local monomer feed ratios that determines the effect on the composition and microstructure of the resulting polymer. However, some additional information about the net partitioning of monomer and solvent between the bulk and local phases is required before k_p can be modelled. It should be observed that in a low-conversion bulk copolymerization, knowledge of the monomer feed ratios automatically implies knowledge of the individual monomer concentrations since, as there are no other components in the system, the sum of the monomer fractions is unity. However, in a solution copolymerization there is a third component - the solvent - and the monomer concentrations depend not only upon their feed ratio but also upon the solvent concentration. Modelling k_p in a solution copolymerization could be achieved by re-writing the above equilibrium expression in terms of molar concentrations (rather than comonomer feed ratios), and including the solvent concentration in this expression.

The Bootstrap model may also be extended by assuming an alternative model (such as the explicit penultimate model) as the baseline model, and also by allowing the Bootstrap effect to vary as a function of monomer feed ratios. Closed expressions for composition and sequence distribution under some of these extended Bootstrap models may be found in papers by Klumperman and co-workers.[43,44]

13.2.3.4.3 Experimental evidence

The Bootstrap model was introduced by Harwood,[116] who studied three solvent sensitive copolymerizations (styrene/methacrylic acid, styrene/acrylic acid and styrene/acrylamide) and found that the copolymers of the same composition had the same sequence distribution irrespective of the solvent used. This meant that the conditional probabilities governing radical propagation were independent of the solvent. On this basis, he argued that composition and sequence distribution were deviating from their expected values because there was a difference between the monomer feed ratios in the vicinity of the active chain end, and those calculated on the basis of the bulk feed. In other words, the solvent was altering the rates of the individual propagation steps by affecting the reactant concentrations and not, as in the other solvent effects models, their reactivities. However, Fukuda et al.[31] have argued that the NMR evidence provided by Harwood is not conclusive evidence for the Bootstrap model, since Harwood's observations could also be described by variation of the reactivity ratios in such a way that their product (r_1r_2) remains constant. This has also been raised as an issue by Klumperman and O'Driscoll.[43] They showed mathematically that a variation in the local comonomer ratio is not reflected in the monomer sequence distribution versus copolymer composition -this relationship being governed by the r_1r_2 product only. An alternative explanation for Harwood's experimental data may be the stabilization or destabilization of the radicals by the solvent, an interpretation that would be analogous to the MCD model. Simple energy stabilization considerations, as used by Fukuda et al.[119] to derive the penultimate unit effect, also suggest the constancy of r_1r_2.

Prior to Harwood's work, the existence of a Bootstrap effect in copolymerization was considered but rejected after the failure of efforts to correlate polymer-solvent interaction parameters with observed solvent effects. Kamachi,[37] for instance, estimated the interaction between polymer and solvent by calculating the difference between their solubility parameters. He found that while there was some correlation between polymer-solvent interaction parameters and observed solvent effects for methyl methacrylate, for vinyl acetate there was none. However, it should be noted that evidence for radical-solvent complexes in vinyl acetate systems is fairly strong (see Section 3), so a rejection of a generalized Bootstrap model on the basis of evidence from vinyl acetate polymerization is perhaps unwise. Kratochvil et al.[120] investigated the possible influence of preferential solvation in copolymerizations and concluded that, for systems with weak non-specific interactions, such as STY-MMA, the effect of preferential solvation on kinetics was probably comparable to the experimental error in determining the rate of polymerization (±5%). Later, Maxwell et al.[121] also concluded that the origin of the Bootstrap effect was not likely to be bulk monomer-polymer thermodynamics since, for a variety of monomers, Flory-Huggins theory predicts that the monomer ratios in the monomer-polymer phase would be equal to that in the bulk phase.[122]

Nevertheless, there are many copolymerization systems for which there is strong evidence for preferential solvation, in particular, polymer solutions exhibiting cosolvency or where one of the solvents is a non-solvent for the polymer. Preferential adsorption and desorption are manifest where the polymer adjusts its environment towards maximum solvation. With this knowledge it may be expected that Bootstrap effects based on preferential solvation will be strongest where one of the monomers (or solvents) is a poor or non-solvent for the polymer (such as copolymerization of acrylonitrile or N-vinyl carbazole). Indeed, early experimental evidence for a partitioning mechanism in copolymerization was provided by Ledwith et al.[123] for the copolymerization of N-vinyl carbazole with MMA in the presence of a range of solvents.

Direct evidence for preferential solvation was obtained by Semchikov et al.,[124] who suggested that it could be detected by calculating, from measurements of the solution thermodynamics, the total and excess thermodynamic functions of mixing. Six monomer pairs were selected -Vac-NVP, AN-STY, STY-MA, Vac-STY, STY-BMA and MMA-STY. The first four of these monomer pairs were known to deviate from the terminal model composition equation, while the latter two were not. They found that these first four copolymerizations had positive ΔG^E values over the temperature range measured, and thus also formed non-ideal polymer solutions (that is, they deviated from Raoult's law). Furthermore, the extent of deviation from the terminal model composition equation could be correlated with the size of the ΔG^E value, as calculated from the area between the two most different composition curves obtained for the same monomer pair under differing reaction conditions (for example, initiator concentration; or type and concentration of transfer agent). For STY-MMA they obtained negative ΔG^E values over the temperature range considered, but for STY-BMA negative values were obtained only at 318 and 343K, and not 298K. They argued that the negative ΔG^E values for STY-MMA confirmed the absence of preferential solvation in this system, and hence its adherence to the terminal model composition equation. For STY-BMA they suggested that non-classical behavior might be expected at low temperatures. This they confirmed by polymerizing STY-BMA at 303K and demonstrating a change in reactivity ratios of STY-BMA with the addition of a transfer agent.

Based upon the above studies, it may be concluded that there is strong evidence to suggest that Bootstrap effects arising from preferential solvation of the polymer chain operate in many copolymerization systems, although the effect is by no means general and is not likely to be significant in systems such as STY-MMA. However, this does not necessarily discount a Bootstrap effect in such systems. As noted above, a Bootstrap effect may arise from a number of different phenomena, of which preferential solvation is but one example. Other causes of a Bootstrap effect include preferential solvation of the chain end, rather than the entire polymer chain,[121,125] or the formation of non-reactive radical-solvent or monomer-solvent complexes. In fact, the Bootstrap model has been successfully adopted in systems, such as solution copolymerization of STY-MMA, for which bulk preferential solvation of the polymer chain is unlikely. For instance, both Davis[125] and Klumperman and O'Driscoll[43] adopted the terminal Bootstrap model in a reanalysis of the microstructure data of San Roman et al.[126] for the effects of benzene, chlorobenzene and benzonitrile on the copolymerization of MMA-STY.

Versions of the Bootstrap model have also been fitted to systems in which monomer-monomer complexes are known to be present, demonstrating that the Bootstrap model may provide an alternative to the MCP and MCD models in these systems. For instance, Klumperman and co-workers have successfully fitted versions of the penultimate Bootstrap model to the systems styrene with maleic anhydride in butanone and toluene,[43] and styrene with acrylonitrile in various solvents.[44] This latter work confirmed the earlier observations of Hill et al.[127] for the behavior of styrene with acrylonitrile in bulk, acetonitrile and toluene. They had concluded that, based on sequence distribution data, penultimate unit effects were operating but, in addition, a Bootstrap effect was evident in the coexistent curves obtained when triad distribution was plotted against copolymer composition for each system. In the copolymerization of styrene with acrylonitrile Klumperman et al.[44] a variable Bootstrap effect was required to model the data. Given the strong polarity effects expected in this system (see Section 13.2.2), part of this variation may in fact be caused by the variation of the solvent polarity and its affect on the reactivity ratios. In any case, as this work indicates, it may be necessary to simultaneously consider a number of different influences (such as, for instance, penultimate unit effects, Bootstrap effects, and polarity effects) in order to model some copolymerization systems.

13.2.4 CONCLUDING REMARKS

Solvents affect free-radical polymerization reactions in a number of different ways. Solvent can influence any of the elementary steps in the chain reaction process either chemically or physically. Some of these solvent effects are substantial, for instance, the influence of solvents on the gel effect and on the polymerization of acidic or basic monomers. In the specific case of copolymerization then solvents can influence transfer and propagation reactions via a number of different mechanisms. For some systems, such as styrene-acrylonitrile or styrene-maleic anhydride, the selection of an appropriate copolymerization model is still a matter of contention and it is likely that complicated copolymerization models, incorporating a number of different phenomena, are required to explain all experimental data. In any case, it does not appear that a single solvent effects model is capable of explaining the effect of solvents in all copolymerization systems, and model discrimination should thus be performed on a case-by-case basis.

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13.3 EFFECTS OF ORGANIC SOLVENTS ON PHASE-TRANSFER CATALYSIS

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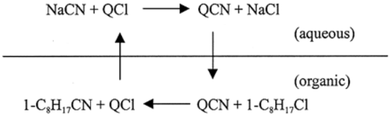
The reaction of two immiscible reactants is slow due to their low solubilities and limited contact surface area. The conventional way to improve the reaction rate or to elevate the conversion of reactants is to increase the agitation speed, temperature, or use the protic or aprotic solvent to dissolve the reactants. The increase in agitation speed can increase the contact surface area between two phases only to a certain value. Thus, the reaction rate or the conversion is limited by the increase in the agitation speed. Usually, the rate of reaction is increased by raising the temperature. However, byproducts are accompanied by elevating the solution temperature. The separation of product from byproducts or catalyst makes the cost to increase. Although protic solvent (CH_3OH, or CH_3COOH) can dissolve reactants, solvation and hydrogen bonding make the activity of the nucleophilic anion decrease significantly. Thus, the reaction rate using protic solvent is retarded. For the other case, the reaction rate is largely increased using aprotic solvent. The application of aprotic solvent is also limited because of cost and recovery difficulty. For this, the problem of two-phase reaction is not overcome until the development of phase-transfer catalysis (PTC). Phase-transfer catalytic reactions provide an effective method in organic synthesis from two immiscible reactants in recent development.[93,103,111,113]

In 1951, Jarrouse[47] found that the reaction of aqueous-soluble sodium cyanide (NaCN) and organic-soluble 1-chlorooctane (1-$C_8H_{17}Cl$) is dramatically enhanced by adding a small amount of quaternary ammonium salt ($R_4N^+X^-$, or Q^+X^-, Q^+: R_4N^+). The reaction is almost complete and a 95% conversion is obtained within two hours when a catalytic amount of tetra-n-butylammonium chloride ($(C_4H_9)_4N^+Cl^-$, or Q^+Cl^-, Q^+: $(C_4H_9)_4N^+$) is added. The mechanism of the reaction of sodium cyanide and 1-chlorooctane in organic solvent/water two-phase medium is expressed as



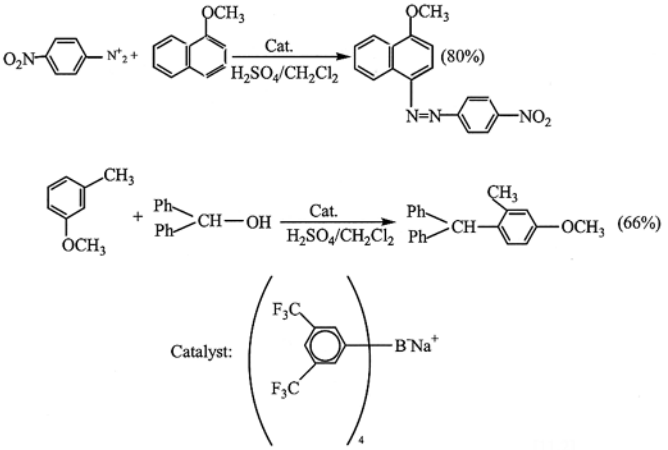
[13.3.1]

As shown in Equation [13.3.1], sodium cyanide (NaCN) and 1-chlorooctane (1-$C_8H_{17}Cl$) are soluble in aqueous phase and organic phase, respectively. In the aqueous phase, NaCN first reacts with tetra-n-butylammonium chloride ($(C_4H_9)_4N^+Cl^-$, Q^+Cl^-) to produce organic-soluble tetra-n-butylammonium cyanide ($(C_4H_9)_4N^+CN^-$, Q^+CN^-). Then, this tetra-n-butylammonium cyanide (QCN) further reacts with 1-chlorooctane (1-$C_8H_{17}Cl$) to produce 1-cyanooctane ($C_8H_{17}CN$) in the organic phase. Tetra-n-butylammonium chloride ($(C_4H_9)_4N^+Cl^-$), which is also produced from the organic-phase reaction, transfers to the aqueous phase, prepared for further regeneration. It is obvious that PTC reaction[107] involves a two-phase reaction (aqueous-phase and organic-phase reaction), transfer of QCN from aqueous phase to organic phase and transfer of QCl from organic phase to aqueous phase, and equilibrium partition of QCN and QCl between organic and aqueous phases, respectively. The overall reaction rate highly depends on the intrinsic rate constants in aqueous phase and organic phase, the mass transfer rate of QCN and QBr, and the equilibrium partition coefficient of QCN and QBr, which are all affected by the interaction of components and their environments. The organic solvent provides the environment for the interaction of reactants. Therefore, the organic solvent plays an important role in influencing the reaction rate and the conversion of reactant.

Since then, Makosza used an interfacial mechanism[65-67] to describe the behavior in the two-phase reaction. Later, Starks[107] used the extraction mechanism to explain the behavior in the two-phase reaction and selected phase-transfer catalysis (PTC) to describe this special chemical process.[14,161] The most important advantage of using PTC technique is in synthesizing specialty chemicals with almost no byproducts and moderate reaction conditions. Today, PTC is widely applied to various reactions via substitution, displacement, condensation, oxidation and reduction, polymer modification and polymerization to synthesize specialty chemicals. Based on the reaction mechanism, phase-transfer catalysis can be classified as: (1) normal phase-transfer catalysis (NPTC), (2) reverse phase-transfer catalysis (RPTC), and (3) inverse phase-transfer catalysis (IPTC). Equation [13.3.1] illustrates the typical reaction for NPTC. The phase-transfer catalyst (Q^+) brings the nucleophilic reagent (CN^-) from aqueous phase to organic phase. Quaternary ammonium salts, quaternary phosphonium salts, crown ethers, polyethylene glycols (PEGs) and tertiary amines are the common normal phase-transfer catalyst (NPTC).[17,29,94,108,109,110,128,130,152]

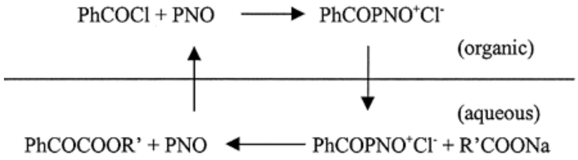
In general, the cation transfers from aqueous phase to organic phase in the RPTC. The principle of reverse phase-transfer catalysis (RPTC)[24,42-44,50] is that an ion pair is formed from catalyst and cation in the aqueous phase. This ion-paired compound then transfers to the organic phase reacting with an organic-phase reactant. Alkyl-aryl sulfonate (RSO_3Na), such as sodium 4-dodecylbenzene sulfonate (NaDBS) and tetraarylboronate such as sodium tetra(diperfluoromethyl)phenyl-boronate (TFPB) are the common reverse phase-transfer catalysts. However, few results were reported using reverse phase-transfer catalysis in synthesizing specialty chemicals.[24,42-44,50] A typical reaction mechanism in a liquid-liquid two-phase solution is given by Equation [13.3.2]

In the NPTC and RPTC, the function of the catalyst is that it first reacts with aqueous-phase reactant to produce an organic-soluble ion-pair compound. Mathias and Vaidya[69] found that an aqueous-soluble ion pair was produced in the organic phase from the reaction of alanine and benzoyl chloride catalyzed by 4-dimethylaminopyridine (DMAP). This discovery initiated the research of the field in inverse phase-transfer catalysis (IPTC), in which the catalyst first reacts with organic-phase reactant in the organic phase to produce an aqueous-soluble ion-paired intermediate. Then, this aqueous-soluble ion-paired intermediate transfers to the aqueous phase, prepared for reacting with aqueous-phase reactant to produce the desired product. Catalyst is released in the aqueous phase and transferred to the organic phase for further regeneration. A typical IPTC mechanism of the reaction of benzoyl chloride and sodium acetate to synthesize ester compound in the liquid-liquid two-phase reaction is expressed by Equation [13.3.3]



[13.3.2]

Inverse phase-transfer catalysis (IPTC) can be applied to synthesize symmetric and antisymmetric acid anhydride in organic synthesis.[26,54,69,102,148-150,153] Pyridine 1-oxide (PNO), 4-dimethylaminopyridine (DMAP), 4-pyrrolidinopyridine (PPY) and 1-methyl-2(1H)-pyridothione are usually used as the inverse phase-transfer catalysts (IPTC).[159]



[13.3.3]

The characteristics of two-phase phase-transfer catalytic (PTC) systems are: the presence of at least two phases and at least one interfacial region separating the phases.[24,26,42,43,50,69,107,109,110,152] The reactions involve: (1) transfer of an ion or compound from its normal phase into the reaction phase or interfacial region, (2) reaction of the transferred ion or compound with the non transferred reactant located in the reaction phase or interfacial region, and (3) transfer of the product from the reaction phase or interfacial region into its normal phase. For example, a successful NPTC process involves (1) the maximization of the rate of transfer of reactant anions from the aqueous or solid phase to the organic phase, (2) the maximization of the rate of transfer of product anions from the organic phase to the aqueous phase or solid phase, and (3) the related equilibrium partitioning of the reactant and product anions between organic and aqueous or solid phases. The anion must not only transfer to the organic phase, but once there the anion must be in a highly reactive form. Some organic-phase reactions are so fast that the transferred anion requires little or no activation beyond just being delivered to the organic phase. Other reactions require substantial anion activation before useful and practical reaction rates can be achieved. It is obvious that the polarity of the organic solvent affects the activation of the anion as well as the difference in the cation-anion interionic distance for the two ion pairs. In principle, anions do not have a great affinity for nonpolar solvent and prefer to reside in an aqueous phase.

Ease or difficulty of transfer of most anions into organic-phase solution is also highly affected by the organic solvent, i.e., interaction of the organic solvent and the reactant. In general, a polar solvent may be necessary to obtain an appropriate rate of the anion transfer to the organic phase for a NPTC process. Solvent may be necessary to increase the rate of the organic-phase reaction. The most common solvent, dichloromethane (CH_2Cl_2), has been extensively used as a polar solvent in the PTC work because it readily dissolves most quaternary salts and other phase-transfer agents, and because it is polar to speed both the transfer step and the organic-phase reaction step. Although the hydrocarbons suffer from lack of polarity, they have also been extensively used as solvents for PTC systems. The main reasons are that they are reasonably safe, inexpensive and easy to recover in a high purity. One strategy for selecting organic solvent is that a high boiling point solvent is selected for a reaction in which the product has a low-boiling point. In other cases, a solvent might be chosen to minimize solubility of phase-transfer agent in the organic phase to force formation of third phase (catalyst) from which the phase-transfer catalyst may be more easily separated or extracted.

The phase-transfer catalytic reactions (NPTC, RPTC or IPTC) are usually carried out in a liquid-liquid two-phase medium. They have been extensively applied to liquid-gas, liquid-solid two-phase media.[18,21,63,128-130] However, purification of product from catalyst in the liquid phase of a final solution is difficult to produce a product of high purity. In 1975, Regen and coworkers[88-92] proposed triphase catalysis (TC) in which the catalyst is immobilized on a porous solid support (usually polymer). The solid catalyst is easily separated from the final products after reaction by mechanical separation processes, such as centrifugation or filtration. The organophilicity and the hydrophilicity of the solid polymer support greatly influence the content and the imbibed composition of the organic phase and the aqueous phase within the solid porous polymer support. Hence, the reaction rates are determined by the concentrations of reactants in both the organic phase and aqueous phase, they are controlled by the organic solvents. Therefore, it is important to understand the characteristics of the organic phase in the triphase catalyst as well as the characteristics of the organic solvent in the liquid-liquid two-phase PTC reaction.

13.3.1 TWO-PHASE PHASE-TRANSFER CATALYTIC REACTIONS

13.3.1.1 Theoretical analysis of the polarity of the organic solvents and the reactions

The transfer of anions from an aqueous phase to an organic phase may be achieved by choosing a phase-transfer cation that is not strongly solvated by water, that has organic-like characteristics, and is compatible with the organic phase for NPTC. The factors that affect the mass transfer and the distribution of the phase-transfer catalyst cation-anion pair between the organic and aqueous phases include:

(1) the charge-to-volume ratio of the anion, the polarizability, and the organic structure of the cation associated with the anion,
(2) the hydrophilic-organophilic balance of the associated cation;
(3) the polarity of the organic phase;
(4) the hydration of the anion;
(5) the presence of aqueous salts and/or aqueous hydroxide ions.

Both cation and anion of phase-transfer catalyst can affect the distribution of the PTC between two phases, and hence the reaction rate. The partitioning equilibrium of the anion between organic and aqueous phases can be qualitatively estimated from the free energies of the anion transfer from water to organic phase. A large positive free energy of transfer from the aqueous phase to the organic phase clearly indicates that the anion prefers to reside in the aqueous phase. For example, the free energies of transfer of Cl^-, Br^-, and I^- from water to acetonitrile are +11.6, +8.1 and +4.8 Kcal/mol, respectively.[110] Thus, the transfer from aqueous to organic phase becomes less unfavorable as one proceeds from chloride to bromide to iodide. These trends may be understood in terms of the change in charge-to-volume ratios of the halide ions. Because chloride has the largest charge-to-volume ratio, it is the least polarizable and the most strongly hydrated. In contrast, iodide has a relatively diffuse charge and is less strongly hydrated.

A successful phase-transfer catalytic reaction occurs when the process is able to transfer the anions from the aqueous phase to the organic phase or *vice versa* for the reaction to proceed, and the transferred anions are active and prepared for reaction. An active catalyst needs to be sufficiently distributed in the organic phase for the reaction to occur. The distribution of catalysts and the associated anion in the organic phase strongly depends on the structure of the quaternary cation and the hydration of anion being transferred into the aqueous phase. Therefore, the following results are used for the reference in selective NPTC catalyst.

(1) Tetramethylammonium cation with a simple anion $(CH_3)_4N^+Y^-$ ($Y=Cl^-$, Br^-, CN^-, etc.) is not easily distributed in most organic solutions. Therefore, $(CH_3)_4N^+Y^-$ are usually not good PTCs. The only ways to increase the distribution of $(CH_3)_4N^+Y^-$ is to couple the cation with a large organic anion[13,49,78,95,155,156] or to use an organic solvent of high purity.[17,107,109,110,152]

(2) Tetraethylammonium ($(C_2H_5)_4N^+Y^-$) and tetrapropylammonium ($(C_3H_7)_4N^+Y^-$) salts are also poor catalysts for transferring small anions into most organic solutions.[51,105]

(3) Tetrabutylammonium salts show high efficiencies as phase-transfer catalysts. They are readily available in high purity on a commercial scale.

(4) Quaternary ammonium cations, R_4N^+, $R=C_5H_{11}$ to $C_{10}H_{21}$ easily extract anions into organic phase and exhibit higher catalytic activities.

(5) Higher tetraalkylammonium salts, R_4N^+X, R: $(C_{12}H_{25})_4N^+$ and higher groups, can easily extract anion into an organic phase. However, the interchange of anions between organic and aqueous phases is slow and the reaction rate decreases compared with quaternary salts where $R = C_5H_{11}$ to $C_{10}H_{21}$.

Table 13.3.1 shows the effect of catalyst structure on the rate of PTC reaction of thiophenoxide with 1-bromooctane.

In addition to the preference of anion to reside in the aqueous or organic phase, a distribution ratio (or partition coefficient), α, of phase-transfer catalyst (QX) cation between aqueous and organic phase is defined as

$$\alpha = [QX]_{org}/[QX]_{aq} \qquad [13.3.4]$$

Use of solvents having higher polarity facilitates distribution of quaternary salts into organic solvents. Hence, it also allows use of smaller quaternary salts as catalysts. With di-

Table 13.3.1. Effect of catalyst structure on the rate of the reaction of thiophenoxide and 1-bromooctane in benzene/water solution

Catalyst	$k \times 10^3$, $L mol^{-1} s^{-1}$
$(CH_3)_4N^+Br^-$	<0.0016
$(C_3H_7)_4N^+Br^-$	0.0056
$(C_4H_9)_4N^+Br^-$	5.2
$(C_8H_{17})_3MeN^+Cl^-$	31
$(C_8H_{17})_3EtP^+Br^-$	37
$(C_6H_{13})Et_3N^+Br^-$	0.015
$(C_8H_{17})Et_3N^+Br^-$	0.16
$C_{10}H_{21}Et_3N^+Br^-$	0.24
$C_{12}H_{25}Et_3N^+Br^-$	0.28
$C_{16}H_{33}Et_3N^+Br^-$	0.15
$C_{16}H_{33}Et_3N^+Br^-$	0.48

Data obtained from the work of Herriott and Picker[36]

chloromethane or solvent of a similar polarity, it is possible to use tetramethylammonium cation, $(CH_3)_4N^+$, or tetrapropylammonium cation, $(C_3H_7)_4N^+$, or cation salts as catalysts.

Wu et al.[158] measured the concentration distribution of the quaternary salt between dichloromethane (or chlorobenzene) and alkaline solution and determined the thermodynamic characteristics (the true extraction constant, the distribution coefficient, and the dissociation constant). The distribution coefficient, highly dependent on the organic solvent, increased with increasing NaOH concentration. However, the real dissociation constant decreased with increasing NaOH concentration. Konstantinova and Bojinov[52] synthesized several unsaturated 9-phenylxanthene dyes under phase transfer catalysis conditions. They determined the most favorable solvent.

The extraction constant of QX between two phases is given by equation:

$$E_{QX} = \frac{[Q^+]_{aq}[X^-]_{aq}}{[QX]_{org}} \qquad [13.3.5]$$

In addition to synthesizing specialty chemicals, the PTC technique can be used to analyze many lipid-rich samples.[106] Hydrolyzed samples were treated with phenylisothiocyanate and the phenylthiocarbamyl (PTC). Derivatives obtained were separated by reverse phase HPLC. The PTC/reverse HPLC method was used for analysis of chloroform/methanol extracts of spinal cord, lung and bile after chromatography on Lipidex 5000 in methanol/ethylene chloride, 4:1 (v/v).[106]

The extraction constant of hydroxide is about 10^4 times smaller than that of chloride.[19,20] Table 13.3.2 shows the effect of solvents on the distribution of $(C_4H_9)_4N^+Br^-$ between aqueous and organic phases. In addition to improved transfer of anion to an organic phase, more polar solvents are commonly recognized in physical organic chemistry for enhancing the rate of organic-phase reactions by providing a more ion-compatible reaction mechanism.

The polarity of the organic phase in conjunction with the structure of the anion and the catalyst cation affects the selectivity of the phase-transfer catalyst partitioning into the organic phase. Increasing the polarity and the hydrogen-bonding ability of the organic phase has a strong favorable effect on the extraction of small ions (large charge-to-volume ratios) and on anion with substantial organic structure.

The polarity of the organic phase is thus an important factor influencing the reaction rate. The polarity of the organic phase depends on the polarity of solvent and organic-phase reactant. However, there are many PTC reactions without organic phase (near organic reactant is used as the organic phase). Thus, a substantial change in the polarity of the organic

Table 13.3.2. Effect of organic solvents on the distribution of $(C_4H_9)_4N^+Br^-$ between organic and aqueous phases

Solvent	Extraction constant, E_{QBr}*
C_6H_6	>10.0
C_6H_5Cl	>10.0
o-$C_6H_4Cl_2$	>10.0
n-C_4H_9Cl	>10.0
$Cl(CH_2)_4Cl$	3.33
$Cl(CH_2)_3Cl$	0.34
$Cl(CH_2)_2Cl$	0.16
$ClCH_2Cl$	0.028
$CHCl_3$	0.021
$C_2H_5COC_2H_5$	0.91
$CH_3COC_2H_5$	0.071
n-C_4H_9OH	0.014

*E_{QBr}= $[Q^+]_{aq}[Br^-]_{aq}/[QBr]_{org}$
Data adopted from Brandstrom[4]

phase may occur as the reaction proceeds. This may have some effect on the reaction rate of the organic-phase (may raise or lower the value of the rate constant). The changes in the polarity of the organic phase may increase or decrease, causing almost all catalyst cation-anion pairs to be partitioned into the organic phase. This behavior is evidenced in the cyanide displacement on 1-bromooctane catalyzed by tetra-n-butylphosphonium bromide ($(C_4H_9)_4P^+Br^-$, or Q^+Br^-).[107,109,110,111,114] The catalyst is only sparingly soluble in 1-bromooctane, but is substantially more soluble in aqueous sodium cyanide solution, so that initially little Q^+CN^- is in the organic phase and the displacement reaction is slow. However, tetra-n-butylphosphonium salts ($(C_4H_9)_4P^+CN^-$, Q^+CN^-) are more soluble in the product 1-cyanooctane; therefore, as the conversion of 1-bromooctane to 1-cyanooctane continues, increasing quantities of the catalyst are taken into the organic phase, and the reaction rate accelerates. This behavior signals the autocatalytic character of reaction.

Not only does the solvent affect the reaction rate, but it also determines the reaction mechanism. In Starks' extraction mechanism of PTC, most reacting compound transfers to the bulk phase. However, reaction may occur at the interface of the two phases. For example: hexachlorocyclotriphosphazene has been reported to react very slowly with 2,2,2-trifluoroethanol in an alkaline solution of NaOH/C_6H_5Cl two-phase system in the absence of phase-transfer catalyst.[136-140] Since sodium 2,2,2-trifluoroethanoxide is not soluble in chlorobenzene, the process probably proceeds at the interface region of the system. Similar is the reaction of benzylation of isobutyraldehyde in the presence of tetra-n-butylammonium iodide in an alkaline solution of NaOH/toluene, which is a two-phase system.[37] Makosza interfacial mechanism[65-67] was employed to rationalize the experimental results. The main reason is that the ammonium salt of the nucleophilic reagent is not soluble in toluene.

Usually, the nucleophilic substitutions under NPTC condition are described by an S_N2-type reaction both in solid-liquid and liquid-liquid systems in which they can proceed at the interface through the formation of cyclic adsorption complexes.[160] The activity of the nucleophilic reagent in the organic phase is determined by the polarity of the organic solution and the hydration in liquid-liquid system. In the solid-liquid system, the reaction is highly affected by the organic solvent.

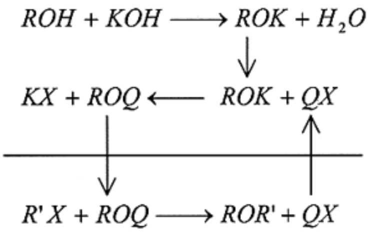
13.3.1.2 Effect of organic solvent on the reaction in various reaction systems

(A) Synthesis of ether compound catalyzed by quaternary ammonium salts (NPTC)

One of the most useful synthesis applications of phase transfer catalysis (PTC) is in the preparation of ether according to the following general equation

$$R'X + ROX + OH^- \xrightarrow{PTC} ROR' + H_2O + X^- \qquad [13.3.6]$$

where R and R' are the primary or secondary alkyl or aryl groups, X is a halide and the caustic base is usually sodium or potassium hydroxide in the aqueous solution. The generally accepted reaction mechanism is



[13.3.7]

It is important to consider that the alkoxide ion (RO^-) is a reactive nucleophilic but also a strong base. It was shown that 10^{-3} M $C_6H_5(CH_3)_3N^+OC_4H_9$ is 1000 times more basic than KOC_4H_9 (both in C_4H_9OH). Extracted alkoxide bases can be applied in principle to numerous base-catalyzed reactions, e.g., oxidations, eliminations and isomerization. Better quantitative understanding of the extraction of alkoxide into organic phase is important. Dehmlow et al.[20] investigated the extraction of aqueous sodium hydroxide solution with organic solvent containing various quaternary ammonium salts by mixing sodium hydroxide with organic solvent containing R_4NX. After phase separation, titration of the organic phase showed only traces of base presence if concentrated NaOH solution was employed and if Cl^- was the counter ion.

The Cl-OH exchange was found to be of the order 1-2% for all quaternary ammonium chloride with chlorobenzene as solvent; i.e., 98% of the salts remained in the R_4NCl form. However, upon addition of trace amounts of various alcohols, a dramatic change in the behavior of the system was observed and significant amounts of base could be detected in the organic phase. Table 13.3.3 shows the experimental results where 50% aqueous caustic solutions were extracted by equal volumes of 0.1 M $(C_8H_{17})_4NBr$ in chlorobenzene containing 0.1 M of various alcohols.

Table 13.3.3. Extraction of base by chlorobenzene solution of tetra-n-octyl-ammonium bromide and alcohols (0.1 M) from an equal volume of 50% NaOH (percent of the maximum possible basicity)

	%		%
Primary alcohols		2-tert-Butylcyclohexanol	2.0
Ethanol	4.5	3- Methylcyclohexanol	2.0
1-Propanol	5.0	**tert-Alcohols**	
2-Methyl-1-propanol	4.4	tert-Butanol	0.3
1-Pentanol	4.3	2-Methyl-2-butanol	0.2
1- Hexanol	4.3	**Diols**	
1-Heptanol	4.8	1,5-Pentanediol	< 0.02
1-Octanol	2.0	2,5-Hexanediol	5.2
1-Dodecanol	0.8	2,2-dimethyl-1,3-propanediol	18.4
Secondary alcohols		2-Methyl-2,4-propanediol	28.0
2- Propanol	1.9	2,3-Dimethyl-2,3-butanediol	25.8
2-Pentanol	1.2	2,5-Dimethyl-2,5-hexanediol	32.0
2-Hexanol	1.1	**Diol monoethers**	
2-Octanol	0.7	Ethylene glycol monoethylether	8.9
Cyclohexanol	0.5	Diethylene glycol monobutylether	8.7
4-tert-Butylcyclohexanol	1.5	Glycerol isopropylideneacetal	13.0

Data obtained from Dehmlow et al.[20]

It is apparent that the order of decreasing alkoxide extraction with monohydric alcohols is primary > secondary > tertiary. The better extractivity of diol anions can be attributed to the relatively high acidity of these alcohols in part, but it seems that the main factors are the distance between the two hydroxyl groups and the skeletal structure. In general, the concentration of the extracted base depends on the amount of alcohol added.[20] The concentration of aqueous sodium hydroxide is also an important factor in the extraction processes.

Herriott and Picker[36] carried out the reaction of thiophenoxide ion with 1-bromooctane in a two-phase system. They found that an increase in the ionic strength of the aqueous phase or change to a more polar organic solvent increased the reaction rate. The effect of organic solvent on the reaction rate under NPTC is given in Table 13.3.4. Correlations between the rate constants and the partition coefficients indicate that the major function of the catalyst is simply the solubilization of the nucleophilic in the organic phase. Conventional methods of synthesizing ethers, i.e., Williamson synthesis and alkoxymercuration have been well developed in organic chemistry.[76,96] The synthesis of formaldehyde acetal were carried out from the reaction of alcohol and dichloromethane in a 50% sodium hydroxide solution applying Tixoget VP clay as a catalyst. However, completing the reaction for such a low reaction rate takes long time. Dehmlow and Schmidt[15] first used PTC technique to synthesize formaldehyde acetals from alcohol and dichloromethane in the aqueous phase. Wang and Chang[144-146] employed the PTC technique to synthesize formaldehyde acetals from the reaction of alcohol and dibromomethane in an alkaline solution of KOH/organic solvent. Alcohol (ROH) first reacted with KOH so as to form potassium alkoxide (ROK) in the aqueous phase. ROK further reacted with quaternary ammonium salt (QBr) in the aqueous phase to produce quaternary ammonium alkoxide (QOR) which is more soluble in the organic solvent. Dibromomethane reacted with QOR in the next step to form the desired product dialkoxymethane $CH_2(OR)_2$ in the organic phase, as shown in Equation [13.3.7].

Dibromomethane, which possesses weak dipole moment, may form a weak dipole-dipole bond with the organic solvent. However, this bond does not significantly affect the reaction rate. QOR solvates in a polar organic solvent. This solvation results in less energy in the nucleophilic agent than that in the transition state compound. The activation energy therefore becomes high due to the solvation of QOR with a highly polar solvent which is unfavorable in the present reaction system. The low polarity solvent neither solvates QOR, nor separates tetra-n-butylammonium ion (Q^+) from the alkoxide ion (^-OR). Thus, the reactivity in low polar solvent is low. Organic solvents of appropriate polarity, such as chlorobenzene or dibutyl ether, are the best solvents to obtain a high yields of various alcohols, as shown in Table 13.3.5. As shown in Figure 13.3.1, similar results were obtained in synthesis of unsymmetric acetals under PTC conditions.[144-146] The values of k_{app}, in which the reaction follows a pseudo-first-order kinetic rate law, are 4.59×10^{-3}, 4.58×10^{-3}, 8.17×10^{-3}, and 1.47×10^{-2} min^{-1} for reaction of CH_2Br_2 with butanol and octanol in cyclohexane, n-decane, dibutyl ether and chlorobenzene, respectively.

Table 13.3.4 Effect of solvent on the rate of reaction of thiophenoxide and bromooctane

Catalyst	Solvent	$k\times10^3$ $M^{-1}s^{-1}$
$(C_4H_9)_4N^+I^-$	C_7H_{16}	0.02
$(C_4H_9)_4N^+I^-$	$C_6H_4Cl_2$	88
$(C_3H_7)_4N^+Br^-$	$C_6H_4Cl_2$	0.45
$C_6H_5CH_2(C_2H_5)_3N^+Br^-$	$C_6H_4Cl_2$	0.04
$C_8H_{17}(C_2H_5)_3N^+Br^-$	$C_6H_4Cl_2$	28
$(C_6H_5)_4P^+Br^-$	C_7H_{16}	0.0093
$(C_6H_5)_4P^+Br^-$	$C_6H_4Cl_2$	47
$(C_6H_4)_4P^+Cl^-$	$C_6H_4Cl_2$	180

Data obtained from Herriott and Picker[36]

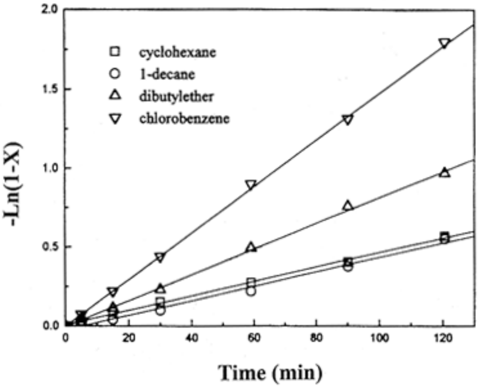


Figure 13.3.1 Effects of the organic solvents on the conversion of CH_2Br_2; 6.88×10^{-2} mol of 1-butanol, 1.5 molar ratio of 1-butanol/1-octanol, 30 g of KOH, 2.76×10^{-2} mol of CH_2Br_2, 3.11×10^{-3} mol of TBAB catalyst, 10 mL of water, 50 mL of organic solvent, 1020 rpm, 50°C (Adapted from Ref. [145], by permission.)

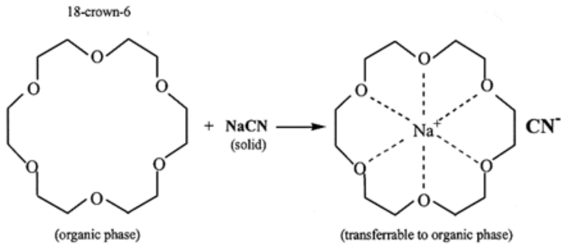
Table 13.3.5. Effects of the organic solvents on the conversion of alcohols

Reactant	Organic solvent			
	chlorobenzene	dibutyl ether	xylene	benzene
	Conversion, X, %			
1-Butanol	83.22	58.94	49.65	55.48
1-Heptanol	81.44	50.16	41.94	44.90
1-Octanol	82.17	52.00	46.49	49.35
Cyclohexanol (2 h)	81.37	53.60	48.94	47.89
2-Ethoxyethanol (0.5 h)	92.82	87.86	79.61	73.86
2-(2-Ethoxyethoxy)-ethanol (0.5 h)	98.58	98.87	96.21	92.21
Dielectric constant	5.62	3.08	2.27	2.28

Data obtained from Wang and Chang;[145] 9.17×10^{-2} mol of alcohols, 10 mL of H_2O, 0.028 mol of CH_2Br_2, 30 g of KOH, 1 g of TBAB catalyst, 50 mL of organic solvent, 1020 rpm, 50°C

(B) Synthesis of ether compound catalyzed by crown ether (NPTC)

The other type of phase transfer catalyst is crown ether, cryptands, polyethylene glycol (PEG) and their derivatives, and other nonionic phase-transfer agents. The phase transfer agent complexes with inorganic cation, along with the anion, can be transferred to the organic phase, preparing for reaction with organic-phase reactant. For example: with 18-crown-6 ether as a phase transfer agent for sodium cyanide:



[13.3.8]

The function of crown ether is that it can chelate with metal ion, such as: lithium, sodium or potassium. Czech et al.[12] noted that crown ethers are a better phase-transfer catalyst for solid-liquid reactions, whereas quaternary salts are better for a liquid-liquid system. Table 13.3.6 shows the solubilities of potassium salts in acetonitrile at 25°C in the presence and absence of 18-crown-6 ether. The solubility of potassium salts in CH_3CN highly depends on the addition of 18-crown-6 ether.

Table 13.3.6. Solubilities of potassium salts in CH_3CN at 25°C in the presence and absence of 18-crown-6 ether

Potassium salt	Solubility of potassium salt		
	in 0.15 M crown in CH_3CN (A)	in CH_3OH (B)	Enhancement factor (A/B)
KF	4.30×10^{-3}	3.18×10^{-4}	13.52
KCl	5.55×10^{-2}	2.43×10^{-4}	228.40
KBr	1.35×10^{-1}	2.08×10^{-1}	64.90
KI	2.02×10^{-1}	1.05×10^{-1}	1.92
KCN	1.29×10^{-1}	1.19×10^{-3}	108.40
KOAc	1.02×10^{-1}	5.00×10^{-4}	204
KSCN	8.50×10^{-1}	7.55×10^{-1}	1.13

Data adopted from the work of Liotta[60]

Table 13.3.7. Rates of reaction of benzyl chloride with potassium cyanide at 85°C in the presence and absence of 18-crown-6 ether as a function of added water

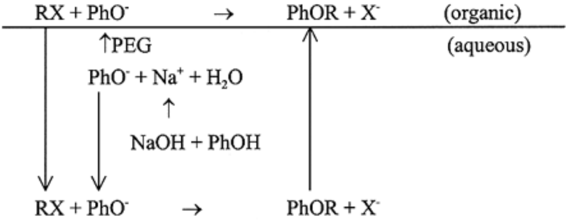
Water	$k\times10^5\ s^{-1}$ (crown)	$k\times10^5\ s^{-1}$ (no crown)
0.0	3.2	0.0
0.36	9.2	0.0
0.50	9.4	0.0
1.00	11.6	0.0
2.00	14.7	0.0
10.0	10.2	0.0
20.0	5.8	1.3
40.0	3.9	1.9
75.0	4.8	3.2

Data obtained from the work of Liotta;[61] 0.05 mol of benzyl chloride, 0.01 mol of 18-crown-6 ether, 0.15 mol of KBr, and 0.015 mol of KCN

The rates of reaction of benzyl bromide and benzyl chloride with potassium cyanide were studied as a function of added water in the presence and absence of crown ether in toluene at 85ºC,[61] as shown in Table 13.3.7. The reaction is highly affected by the addition of 18-crown-6 ether. In addition to enhancing the reaction rate, it is important to note that in the absence of added water, the rates followed zero-order kinetics, while in the presence of added water, the rates followed first order kinetics.

(C) Synthesis of ether compound catalyzed by polyethylene glycols (NPTC)

Similar to quaternary ammonium salts, polyethylene glycols (PEGs) act as the phase transfer catalyst. There are two majors effects of PEG on the two-phase reactions. First, part of the PEG, existing in the organic phase, forms a complex with metal cation. The formation of a complex leads to an increase in the solubility of sodium alkoxide (RONa) or sodium phenoxide (PhONa) for the synthesis of ether in the organic phase. Hence, the reaction rate in the organic phase is promoted. Second, PEG acts as an excellent organic solvent, but it can also dissolve in water. Thus, part of the alkyl halide that is dissolved by PEG is brought into the aqueous phase from the organic phase. The dissolved alkyl halide directly reacts with phenoxide (PhO^-) or alkoxide (RO^-) ion in the aqueous phase, as shown in Figure 13.3.2.[143] The reaction rate in the aqueous phase is also enhanced. The mechanism of the reaction rate of alkyl halide (or allyl halide, RX) and phenoxide (PhO^-), both existing in the aqueous phase with PEG help, is different from that in presence of quaternary ammonium salt.



[13.3.9]

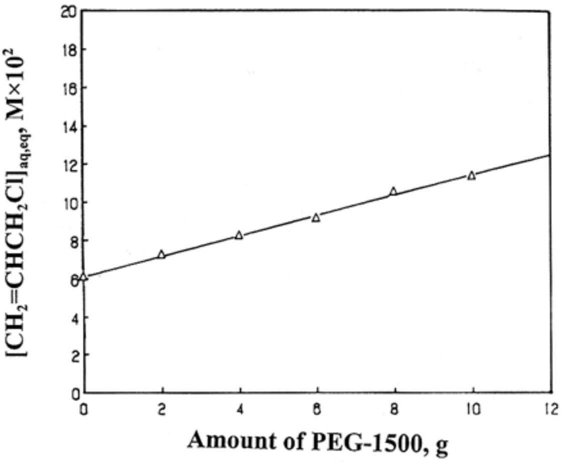


Figure 13.3.2 Dependence of the concentration of allyl chloride in the aqueous phase on the amount of PEG-1500 added, $V_{org}=V_{aq}=50$ mL, 30°C (Adapted from Ref. [143], by permission.)

The reaction catalyzed by PEG can be carried out either in a homogeneous phase or in a two-phase solution. The alkyl halide usually serves as the reactant as well as the solvent. The reaction proceeds because organic-phase reactant dissolves in an organic solvent in the presence of PEGs. Dichloromethane, chlorobenzene, ethyl ether, cyclohexane and n-decane are frequently used solvents.

The reaction mechanism of two-phase catalytic reaction by PEG includes formation of a complex of PEG with cation.[141,142] This is different than the reaction catalyzed by quaternary salts. Table 13.3.8 shows the initial reaction rate using PEG, ($(-r)_{i,PEG}$) and the initial reaction rate without using PEG, ($(-r)_{i,B}$) in various organic solvents. Both $(-r)_{i,B}$ and $(-r)_{i,PEG}$ decrease when the polarity of the organic solvent increases. The maximum reaction rate is obtained with n-decane, which has the lowest polarity, as the protic solvent. Same results were obtained from the work of Landini et al.[55] on the reaction of n-octylmethylene sulfonate and bromide ion in a homogeneous phase with $C_{16}H_{33}P^+(C_4H_9)_3Y^-$ as PTC. Wang and Chang[142] made a reasonable explanation for this peculiar phenomena, i.e., the transition state possesses a higher degree of dispersity of electric charge than does the ground state. Increasing the polarity of the solvent increases the relative activation energy between the transition state and the reactants. Hence the reaction rate is decreased.

Table 13.3.8. Effect of the aprotic solvent on the initial reaction rate of the allylation of phenoxide

Solvents	Dielectric constant (20°C)	Initial reaction rate×10^3 Mh^{-1}		$(-r)_{i,PEG}/(-r)_{i,B}$
		$(-r)_{i,B}$	$(-r)_{i,PEG}$	
n-decane	1.991	171.77	355.62	2.07
cyclohexane	2.023	127.5	277.68	2.16
ethyl ether	4.335	98	205.83	2.10
cyclobenzene	5.708	75.25	174.56	2.32
dichloromethane	9.080	45.61	86.31	1.89

Data obtained from the work of Wang and Chang[142]

13.3.1.3 Effects of the organic solvents on the reactions in other catalysts

(A) Quaternary ammonium salts as NPTC

The effects of the organic solvents on the reaction rate are given in Table 13.3.9.[121] The rates of the reactions of the tetra-n-butylammonium and potassium salts of phenoxide with 1-chlorobutane and 1-bromobutane in pure solvents and solvent mixtures varying in dielectric constant from 2.2 to 39 were obtained by Uglestad et al.[121]

Table 13.3.9. Effect of organic solvent on the reaction of tetra-n-butylammonium salts of phenoxide and potassium salts of phenoxide with halobutane

Reactants Solvents	Rate constant×10^5, $Lmol^{-1}s^{-1}$				Dielectric constant (ε)
	1-C_4H_9Cl	1-C_4H_9Cl	1-C_4H_9Br	1-C_4H_9Br	
	$K^{+-}OC_6H_5$	$Bu_4N^{+-}OC_6H_5$	$K^{+-}OC_6H_5$	$Bu_4N^{+-}OC_6H_5$	
Dioxane 10%			0.01	330	2.2
CH_3CN 50%	0.0025	2.8	0.22	400	6
CH_3CN	0.084	4.0	12	600	
Acetonitrile	0.33	2.2	40	300	39

Data obtained from Uglestad et al.,[121] 0.2 M $C_6H_5O^-$, 0.05 or 0.1 M C_4H_9X, 25°C

The rates of reaction of potassium phenoxide vary over three orders of magnitude with the changes in the dielectric constant of solvent, whereas the corresponding rates with the tetra-n-butylammonium salt vary by approximately a factor of 6.

(B) Tertiary amines as NPTC

Quaternary ammonium salts, PEGs and crown ethers are the common compounds, employed as PTC. The inexpensive tertiary amines have also been used as the phase transfer catalysts (PTC) in recent years. The synthetic process for producing 2-mercaptobenzimidazole (MBI) is a reaction of o-phenylene diamine ($C_6H_4(NH_2)_2$) and carbon disulfide (CS_2) in a two-phase medium affected by appropriate choice of solvent.[128-130]

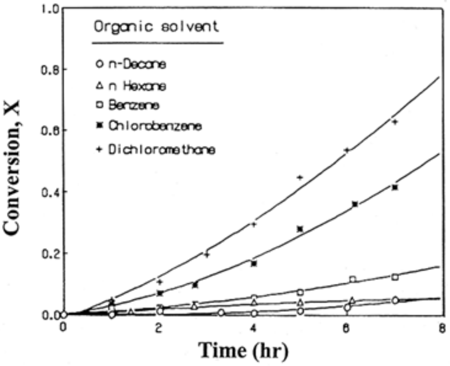


Figure 13.3.3. Effect of solvents on the conversion of o-phenylene diamine in the two-phase catalyzed reaction; 3.17×10^{-3} mol of $C_6H_4(NH_2)_2$, 2.50×10^{-2} mol of CS_2, 1.679×10^{-3} mol of tributylamine (TBA), 1000 rpm, 30°C. (Adapted from Ref. [128], by permission.)

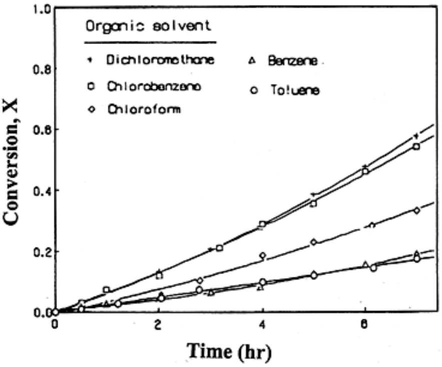


Figure 13.3.4. Effect of solvents on the conversion of o-phenylene diamine; 0.4 g of $C_6H_4(NH_2)_2$, 4.003 g of CS_2, 0.4 mL of tributylamine (TBA), 50 mL of organic solvent, 600 rpm, 30°C. (Adapted from Ref. [129], by permission.)

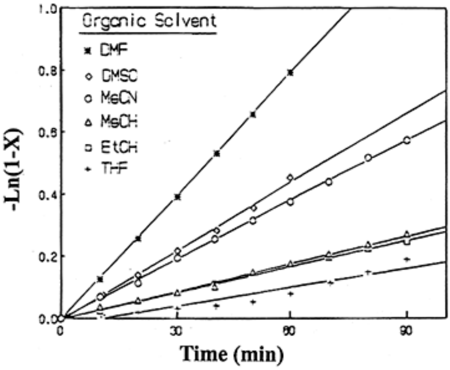


Figure 13.3.5. Effect of solvents on the conversion of o-phenylene diamine; 3.18×10^{-3} mol of o-phenylene diamine, 8 molar ratio of $CS_2/C_6H_4(NH_2)_2$, 0.01 M of triethylamine (TEA), and 50 mL of CH_3CN, 600 rpm, 40°C. (Adapted from Ref. [130], by permission.)

Several solvents, such as: n-decane, n-hexane, benzene, chlorobenzene and dichloromethane, which are immiscible with water, were used. The effect of solvent on conversion is shown in Figure 13.3.3.[128] The order of the conversion of o-phenylene diamine $C_6H_4(NH_2)_2$ in various organic solvents is: dichloromethane > chlorobenzene > benzene > n-hexane > n-decane, which is consistent with the order of solvent polarity, i.e., the greater the polarity of solvent the higher the conversion of o-phenylene diamine.

Results for the reaction of o-phenylene diamine and carbon disulfide in a homogeneous phase (organic solvent) are given in Figure 13.3.4.[129] The order of the reactivities is: dichloromethane (8.91) > chlorobenzene (5.6) > chloroform (4.8) > toluene (2.4) > benzene (2.3). The reaction rate is related to the dielectric constant of the organic solvent. A larger conversion of o-phenylene diamine was obtained using solvent with a higher dielectric constant.

In choosing a polar organic solvent, such as: MeCN, MeOH, EtOH, DMSO, DMF and THF, a homogeneous solution was used for the reaction.[130] Figure 13.3.5 shows the effects of organic solvents (protic or aprotic) on the conversion of o-phenylene diamine. The order of the reactivities for these six organic solvents is: DMF > DMSO > > MeCN > MeOH > EtOH >THF. The corresponding dielectric constants of solvents are: DMF (37.71), DMSO (46.45), MeCN (35.94), MeOH (32.66), EtOH (24.55) and THF (7.58), respectively. The protic solvents, such as MeOH and EtOH, containing hydroxyl group possess acidic properties. The unpaired electrons on the oxygen atom associate with the anions. A relatively lower conversion is obtained in MeOH or EtOH solvent. This result indicates that the acidic hydrogen bond does not have a strong catalytic capability.

The aprotic solvents, which do not possess hydrogen bond, are highly polar. Therefore, the aprotic solvents possess high alkalinity and nucleophilicity required to obtain a high conversion of o-phenylene diamine in the synthesis of mercaptobenzimidazole (MBI). A larger conversion is obtained when using a protic solvent or aprotic solvent of high polarity. However, the structure of DMF, which is an amide, is similar to that the tertiary amine. It possesses similar catalytic property to dimethylaminopyridine (DMAP). The effect of DMF on the conversion of o-phenylene diamine is more pronounced than that of DMSO. The Arrhenius rate equations in various solvents for the reaction of o-phenylene diamine and carbon disulfide catalyzed by tributylamine are as follows:

$$\begin{aligned} &\mathit{DMF:} && k_{app} = 1.06\text{x}10^{15}\exp(-1.20\text{x}10^{4}/T) \\ &\mathit{DMSO:} && k_{app} = 7.82\text{x}10^{8}\exp(-7.78\text{x}10^{3}/T) \\ &\mathit{MeCN:} && k_{app} = 1.39\text{x}10^{13}\exp(-1.09\text{x}10^{4}/T) \qquad [13.3.10] \\ &\mathit{MeOH:} && k_{app} = 9.62\text{x}10^{14}\exp(-1.24\text{x}10^{4}/T) \\ &\mathit{EtOH:} && k_{app} = 3.84\text{x}10^{10}\exp(-9.29\text{x}10^{3}/T) \\ &\mathit{THF:} && k_{app} = 3.25\text{x}10^{38}\exp(-2.99\text{x}10^{4}/T) \end{aligned}$$

k_{app} is the apparent rate constant in which the reaction follows pseudo-first-order rate law.

In two-phase phase-transfer catalytic reactions, the solvents significantly affect the reaction rate. The main reason is that the distribution of regenerating catalyst QX and the active catalyst QY between two-phases is highly dependent upon the polarity of the solvent. It is desirable for most of the intermediate products to stay in the organic phase and react with the organic-phase reactant. Therefore, a solvent with high polarity will be preferred for the reaction.

(C) Pyridine 1-oxide (PNO) as IPTC

The substitution reaction of benzoyl chloride (PhCOCl) and sodium acetate (CH_3COONa) using pyridine 1-oxide (PNO) as the inverse phase-transfer catalyst (IPTC) in a two-phase system of organic solvent and water was investigated by Wang, Ou and Jwo.[148-150] They found that the polarity of the organic solvent strongly affected conversion of benzoyl chloride, the yield of the main product (acetic benzoic anhydride ($PhCOOCOCH_3$)), and the reaction rate. The reaction follows a pseudo-first-order kinetic rate law. Dichloromethane, chloroform, tetrachloromethane and cyclohexanone ($C_6H_{10}O$) were used as the organic modifier in the two-phase reaction system. The results are given in Table 13.3.10. A linear reaction rate was observed for a more polar organic solvent. The order of relative reactivities in these solvents is cyclohexanone > dichloromethane > chloroform > tetrachloromethane, consistent with their polarities. Kuo and Jwo[54] obtained similar results. Wang, Ou and Jwo[148] also found that the conversion was substantially increased with initial concentration of PNO increasing in the aqueous phase with CH_2Cl_2 present as the organic solvent. The reason is that the concentration of carboxylate ion[54] influences the concentration of PNO in the organic phase.

Table 13.3.10. Effect of the composition of organic solvent on the PNO-catalyzed $PhCOCl-CH_3COONa$ reaction in a two-phase medium

Organic phase	$k_{app}\times10^{-3}$ min^{-1} at T=				
	5°C	10°C	18°C	25°C	33°C
CH_2Cl_2	24.7	32.3	48.5(5.73)[b]	65.8(12.0)[b]	
$CH_2Cl_2+CCl_4$					
$[CCl_4]$=1.00 M	18.8	26.6	38.3	51.5	72.8
$[CCl_4]$=3.00 M			17.9	26.8	
$[CCl_4]$=5.00 M		5.13	9.06	18.1	
$CH_2Cl_2+C_6H_5NO_2$					
$[C_6H_5NO_2]$=1.00 M	28.0(2.93)[b]	36.4(6.42)[b]	62.7(14.6)[b]	83.0	124
$CH_2Cl_2+CHCl_3$					
$[CHCl_3]$=5.00 M		26.9	37.6	49.0	
$CH_2Cl_2+C_6H_{10}O$					
$[C_6H_{10}O]$=3.00 M		35.0(4.49)[b]	57.2(9.38)[b]	91.4(20.4)[b]	
$CHCl_3$		14.6	19.5	26.7	
CCl_4			16.2		
$C_6H_{10}O$		68.7	106	170	

Data obtained from Wang et al.[148] 2.00×10^{-4} M of PNO, 1.00×10^{-2} M of PhCOCl, 0.500 M of CH_3COONa, 18°C, 1200 rpm, 50 mL of H_2O, 50 mL of organic solvent, [b]No PNO added; $C_6H_{10}O$, cyclohexanone

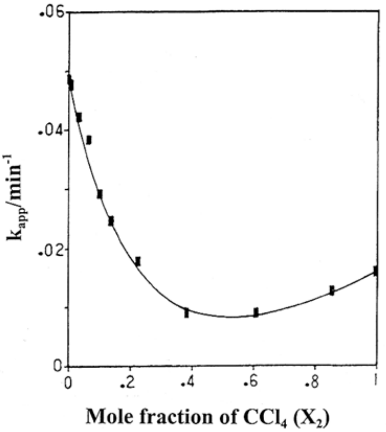


Figure 13.3.6. Effect of the mole fraction of CCl_4 in the mixed organic solvent on the k_{app} value in the two-phase $H_2O/(CH_2Cl_2+CCl_4)$ medium; 1.00×10^{-2} M of PhCOCl 0.500 M of CH_3COONa, 2.00×10^{-4} M of PNO, 50 mL of H_2O, 50 mL of organic solvent ($CH_2Cl_2+CCl_4$), 18°C. (Adapted from Ref. [148], by permission.)

In the studies on the inverse phase-transfer catalytic reaction, Wang, Ou and Jwo[148] conducted two independent experiments in order to evaluate the effect of polarity of the organic phase on the reaction. In the first experiment, a relatively inert organic substances such as $C_6H_5CH_2CN$, C_6H_5CN, $C_6H_5N(Et)_2$, $C_6H_5NO_2$, $CH_3COOC_2H_5$ or $C_3H_7COOC_2H_5$ were individually added to the organic phase (CH_2Cl_2) as the mixed organic solvent in the two-phase reaction system. The reactions of these compounds with PhCOCl or PNO were negligibly slow compared to the reaction of PhCOCl and PNO. The results are given in Tables 13.3.11 and 13.3.12, respectively. It is shown that k_{app} increased with added inert substance of high polarity,

Table 13.3.11. Effect of the inert organic substance on the PNO-catalyzed CH_3COONa-PhCOCl reaction in a two-phase H_2O/CH_2Cl_2 medium

Organic substance, R	$k_{app}\times10^3$ min^{-1}	Dipole moment, D
$C_6H_5CH_2CN$	61.2	
C_6H_5CN	60.5	4.18
$C_6H_5N(Et)_2$	56.8	
$C_6H_5NO_2$	57.0	4.22
$CH_3COOC_2H_5$	53.1	1.78
$C_3H_7COOC_2H_5$	48.5	
CH_2Cl_2	48.5	1.60
CCl_4	42.5	0

Data obtained from Wang et al.[148] 1.00×10^{-2} M of PhCOCl, 0.500 M of CH_3COONa, 0.500 M of R, 2.00×10^{-4} M of PNO, 50 mL of H_2O, 50 mL of CH_2Cl_2, 18°C

such as nitrobenzene and ethyl acetate or basic organic substance, such as diethylaniline. The k_{app}-value increased to a greater extent with added highly polar and basic organic substance, such as benzyl cyanide and benzonitrile. In the second set of experiments, reactions were carried out with nonpolar CCl_4 added to the CH_2Cl_2 as the mixed organic solvent. As shown in Figure 13.3.6, that due to decreased polarity, the value of k_{app} also decreased with increased amount of added CCl_4 to a minimum.[148] Then, it increased slightly on further addition of CCl_4 due to the increased rate of PNO-catalyzed hydrolysis of PhCOCl. Since the distribution of PhCOCl in the CH_2Cl_2 decreases with increased amount of CCl_4, the reaction rate of PhCOCl with PNO in the aqueous phase leads to the hydrolysis of PhCOCl. Wang, Ou and Jwo[148] observed that the yields of $PhCOOCOCH_3$ decrease with increased content of CCl_4.

Table 13.3.12. Effect of the amount of inert organic substance on the PNO-catalyzed CH_3COONa-PhCOCl reaction in a two-phase H_2O/CH_2Cl_2 medium

Inert organic Substance $[R]_{org}$	$k_{app}\times10^3$ min^{-1} with $[R]_{org}$, M						
	0.100	0.300	0.500	0.800	1.00	1.50	2.00
$C_6H_5CH_2CN$	57.3		61.3		62.4	71.8	
$C_6H_5NO_2$	49.0		57.0		62.7	60.7	60.9
$C_6H_5N(Et)_2$	55.1	61.1	56.8	54.9			
CCl_4	47.6		42.1		38.3	28.5	24.7

Data obtained from Wang et al.[148] 1.00×10^{-2} M of PhCOCl, 0.500 M of CH_3COONa, 2.00×10^{-4} M of PNO, 50 mL of H_2O, 50 mL of CH_2Cl_2, 18°C

In Table 13.3.12, k_{app} approached a constant value when nitrobenzene (1.0 M) was added. This result indicates that solvation of the transition structure for the reaction of benzoyl chloride with sodium nitrate reached an upper limit. Benzyl cyanide is a polar solvent. The value of k_{app} increased with increased content of benzyl cyanide. Further, highly basic diethylaniline ($C_6H_5N(Et)_2$) could increase the concentration of free PNO and also the reaction rate. However, this compound is less polar than dichloromethane and the polarity decreased with increased proportion of diethylaniline, which caused the value of k_{app} to decrease. Therefore, the value of k_{app} reached a maximum, as shown in Table 13.3.12. In general, the value of k_{app} increased with an increased proportion of highly polar inert organic substance, such as $C_6H_5CH_2CN$ and $C_6H_5NO_2$, and decreased with increased proportion of slightly polar inert organic substance, such as $C_6H_5N(Et)_2$ and CCl_4. In the case of CCl_4, the greater the proportion of nonpolar or less polar compound, the smaller the reaction rate. The results are due to a combination of the hydrolysis of benzoyl chloride, the distribution of PNO between two phases, and the mass transfer of PNO from organic phase to aqueous phase.

(D) Electrophile reaction by NaDBS

Although the electrophile transferred to the organic phase from the aqueous phase by phase transfer catalysis (PTC), the role of organic solvent was still important. Ellwood and Griffiths[24] carried out the coupling reactions between 4-nitrobenzendiazonium chloride and N-ethylearbazole or N,N-diphenylamine in aqueous media. The coupling reactions were accelerated by using a two-phase water-dichloromethane containing sodium 4-dodecylbenzene sulfonate (NaDBS) as a transfer catalyst for the diazonium ion. Effects of solvents and catalyst (NaDBS) on the rate constants are given in Table 13.3.13. The NaDBS (0.05 molar proportions) increases the rate coupling in dichloromethane-water by a factor of at least 20 relative to the reaction in water-acetic acid. A part of this increase is attributed to incomplete solubility of N-ethyl carbazole in the latter solvent. Also, the polarity of the organic phase is important (cf. CH_2Cl_2, $C_6H_5NO_2$ have much higher dielectric constants than toluene and ethyl acetate). This may be attributed to the covalent character of diazonium arylsulfonates. Its ionization is greater in the former solvents. Crown ethers act as transfer agents for the diazonium ion, but the resultant complexes have low coupling reactivity.

Table 13.3.13. Initial rates of coupling between 4-nitrobenzene diazonium chloride and N-ethylcarbazole at 0°C in various solvent mixtures in the presence and absence of additives

Solvent[a]	Additve[b]	Rate[c]$\times 10^9$, $mol^{-1}dm^{-3}$
CH_2Cl_2-H_2O	none	1.25
CH_2Cl_2-H_2O	NaDBS	11.1
CH_2Cl_2-H_2O	18-crown-C-6 ether	0.28
CH_2Cl_2-H_2O	Lissapol NX[d]	0.56
Toluene-H_2O	none	< 0.1
Toluene-H_2O	NaDBS	< 0.1
EtOAc-H_2O	none	0.89
EtOAc-H_2O	NaDBS	1.03
$PhNO_2$-H_2O	none	1.39
$PhNO_2$-H_2O	NaDBS	10.5
AcOH-H_2O[e]	none	0.47[f]
DMF-H_2O[g]	none	0.53[f]
1,4-Dioxane-H_2O[h]	none	1.33

Data obtained form the work of Ellwood and Griffths;[24] [a]v/v=1/1 except where stated, [b]0.05 mmol except where stated, [c]initial rate of formation of azo dye, [d]commercial (ICI) non-ionic detergent, 0.05 mmol, [e]95% H_2O v/v, containing $NaOAc\cdot 3H_2O$, [f]suspension of N-ethylcarbazole, [g]60% H_2O v/v, [h]60% H_2O v/v homogeneous solution containing 1.0 mmol diazonium ion and 1.0 mmol N-ethyl carbazole 100 mL solvent

(E) Oxidation by dimethyl polyethylene glycol and oxidant

Dimethyl polyethylene glycol solubilizes potassium permanganate in benzene or dichloromethane and can thus be used as a phase-transfer agent for permanganate oxidation. The reaction is highly dependent on the organic solvent. If benzene is used as solvent, dimethyl polyethylene glycol does not efficiently extract $KMnO_4$ from an aqueous solution, but it solubilizes the solid reagent when CH_2Cl_2 is used as the solvent, $KMnO_4$ may be transferred from either aqueous solution or from the solid phase. The effect of organic solvent on the distribution of products is given in Table 13.3.14.[58]

Table 13.3.14. Oxidation of cyclododecene

Solvent system	Oxidation ratio[a]	Phase transfer agent	Products (%)
Benzene+17% acetic acid	3.3	Polyether[b]	1,2-Cyclododecanedione (16), dodecanedioic acid (59), cyclododecane (23)
Benzene+17% acetic acid	3.3	Crown ether[c]	1,2-Cyclododecanedione (22), dodecanedioic acid (56), cyclododecane (12)
Benzene+17% acetic acid	3.3	Adogen 464	1,2-Cyclododecanedione (8), dodecanedioic acid (58), cyclododecane (9)
Dichloromethane+17% acetic acid	3.3	Polyether	1,2-Cyclododecanedione (8), dodecanedioic acid (77), cyclododecane (1)
Dichloromethane+17% acetic acid	3.3	Crown ether	1,2-Cyclododecanedione (7), dodecanedioic acid (83), cyclododecene
Dichloromethane+17% acetic acid	3.3	Adogen 464	1,2-Cyclododecanedione (7), dodecanedioic acid (83), cyclododecene (2)
Dichloromethane+17% acetic acid	2.2	Adogen	1,2-Cyclododecanedione (18), dodecanedioic acid (63), 2-hydroxycyclododecanone (6)
Dichloromethane+17% acetic acid	1.6	Agogen 464	1,2-Cyclododecanedione (14), dodecanedioic acid (40), 2-hydroxycyclododecanone (6), cyclododecene (23)
Dichloromethane+17% acetic acid	2.2	Adogen 464	1,2-Cyclododecanedione (19), dodecanedioic acid (27), 2-hydroxycyclododecone (7), cyclododecene (23)
Dichloromethane+10% acetic acid	2.2	Adogen 464	1,2-Cyclododecanedione (69), dodecanedioic acid (13), 2-hydroxycyclododecane (3), cyclododecene (9)
Dichloromethane/water +10% acetic acid	2.2	Polyether	1,2-Cyclododecanedione (16), dodecanedioic acid (82)
Dichloromethane/aqueous NaOH	1.0	Benzyl triethyl ammonium chloride	1,2-Cyclododecanediol (50)

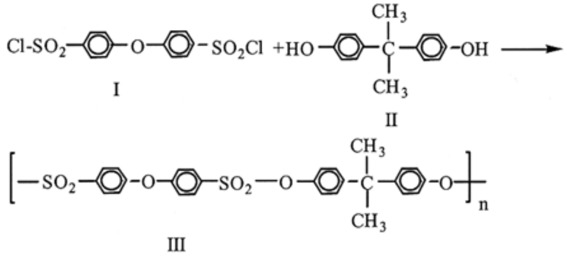
Data obtained from Lee and Chang;[58] [a]number of moles of potassium permanganate per mole of alkene, [b]dimethylpolyethylene glycol, [c]dicyclohexano-18-crown-6 ether

(F) Polymerization by PTC

Poly(ethylene glycol)-block-poly(butylacrylate), synthesized by radical polymerization,[56] were obtained by PTC in the Williamson reaction. The morphology and the crystallinity of the cast film of the block polymer were significantly affected by the organic solvent.

The technique of phase-transfer catalysis has been extensively applied to the two-phase polycondensation using various phase-transfer catalysts, such as quaternary ammonium and phosphonium salts, crown ethers and poly(ethylene glycol)s.[8,11,30,46,53,75,87,119,151] Various types of condensation polymers such as aromatic polysulfonates and polysulfides, aromatic polyethers, aliphatic and aromatic polysulfides, and carbon-carbon chain polymers of high molecular weights by the phase-transfer catalyzed polycondensation from combinations of aromatic disulfonyl chlorides, phosphonic dichlorides, activated aromatic dichlorides, and aliphatic dihalides, with bisphenol, aliphatic and aromatic dithiols, and active ethylene compounds. The two-phase polycondensation was generally carried out in a water-immiscible organic solvent-aqueous alkaline solution system at room temperature. The method of polycondensation offers a highly versatile and convenient synthetic method for a variety of condensation polymers.

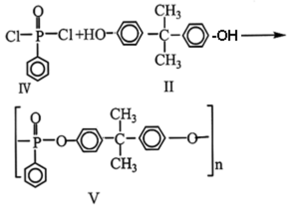
Aromatic polysulfonates of high molecular weights can be prepared from aromatic disulfonyl chlorides and alkaline salts of bisphenols by interfacial polycondensation technique using onium salt accelerators. In the absence of the catalyst, only low molecular polysulfonate **III** was obtained, even though the reaction was continued for 254 hours, whereas the addition of these quaternary ammonium salts and crown ethers increased the average molecular weight of the polymer remarkably.



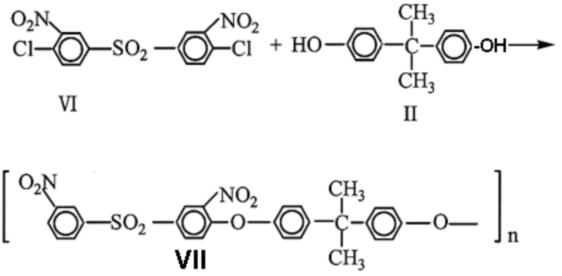
[13.3.11]

Among the catalysts, TBAC and DC-18-C-6 were found to be highly efficient, leading to the formation of the polysulfonate with an inherent viscosity [η] of as high as 1.4 dLg^{-1}.

Similarly, aromatic polysulfonates and aromatic polyether were synthesized from the polycondensation of phenylphosphonic dichloride (**IV**) with bisphenol A (**II**) leading to a polyphosphonate (**V**), aromatic dihalides (**VI**) with alkaline salts of bisphenols (**VII**), under various phase transfer catalysis in two-phase system, i.e.,



[13.3.12]



[13.3.13]

The effect of organic solvent on the two-phase polycondensation is shown in Table 13.3.15. Chloroform, 1,2-dichloroethane, nitrobenzene, acetophenone and anisole were all effective as the polymerization media to produce moderate molecular weight polymer (VII).

Table 13.3.15. Synthesis of aromatic polyether VII in various organic solvent/water system with DC-18-C-6 catalyst

Solvent	Reaction temp., °C	Reaction time, h	Polymer [η], dLg^{-1}*
CH_2Cl_2	20	24	0.84
$CHCl_3$	20	24	0.53
CH_2ClCH_2Cl	20	24	0.42
$C_6H_5NO_2$	20	24	0.47
$C_6H_5NO_2$	80	2	0.51
$C_6H_5NO_2$	100	1	0.42

Data obtained from the work of Imai;[41] Reaction conditions: 2.5 mmol of II, 2.5 mmol of VI, 0.05 mmol of DC-18-C-6 in 3.5 mL of solvent, and 5 mL of KOH (1.01 M) solution, *Measured at a concentration of 0.5 dLg^{-1} in DMF at 30°C

A convenient method for the preparation of polysulfides by the two-phase polycondensation in a KOH solution is known.[41] Polycondensation of 1,4-dibromobutane (**VIII**) and 1,6-hexanedithiol (**IX**) leading to polysulfide (**X**) was carried out in various organic solvent/H_2O system with DC-18-C-6 catalyst.

$$\underset{VIII}{Br(CH_2)_4Br} + \underset{IX}{HS(CH_2)_6SH} \rightarrow \underset{X}{\left[-(CH_2)_4-S-(CH_2)_6-S-\right]_n} \qquad [13.3.14]$$

The results of the polycondensation are given in Table 13.3.16. All polymerization media employed produced polysulfide with moderately high inherent viscosities; whereas the polymer with the highest viscosity was produced in the absence of organic solvents. Polycondensation conducted in the presence of any catalyst in this system led to the formation of a polymer with moderately high molecular weight.

Table 13.3.16. Synthesis of aliphatic polysulfide X in various organic solvent-water system with DC-18-C-6 catalyst

Solvent	Reaction temp. °C	Polymer [η], dLg^{-1}*
CH_2Cl_2	20	0.30
$CHCl_3$	80	0.31
C_6H_6	80	0.30
$C_6H_5NO_2$	80	0.58
CH_3CN	80	0.58
None	80	0.73

Data obtained from Imai;[41] Polymerization conditions: 2.5 mmol of VIII and IX, 0.05 mmol of DC-18-C-6 in 2.5 mL of solvent and 5 mL of 1.01 M KOH solution for 48 h, *measured at a concentration of 0.5 gdL^{-1} in chloroform at 30°C

Several polycarbonates[59] were synthesized by two-phase polycondensation of bisphenols and brominated with trichloromethyl chloroformate in a system of an organic solvent and aqueous alkaline solution of quaternary ammonium salts. Chlorinated hydrocarbons, dichloromethane (DCM), tetrachloromethane (TCM), tetrachloromethane (TCM) and nitrobenzene (NB) served as organic solvents. The effects of solvents on the reaction yields are given in Table 13.3.17.[59] Although polymers with a high yield were obtained using nitrobenzene (NB) as an organic solvent, the inherent viscosities were low. Polycarbonates were prepared by a two-phase condensation of TCF with bisphenol S. They precipitate from chlorinated hydrocarbon solvents such as DCM, TCM and DCE. According to both the yield and the inherent viscosity of these polymers, the use of BTEAC as a phase-transfer catalyst, sodium hydroxide as a base and DCE as an organic solvent was suitable to prepare a polycondensate having a large molar mass and a high yield.

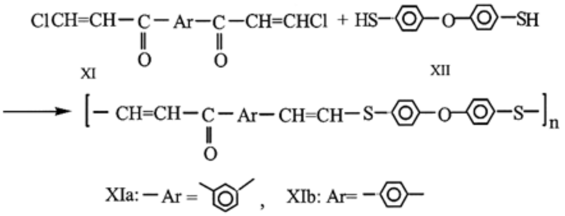
Table 13.3.17 Synthesis of bisphenol S-based homopolycarbonate by two-phase polycondensation catalyzed by PTC[a]

Reaction conditions		Polymer yield		
Solvent[b]	Catalyst	%	[η], dLg^{-1}*	State
DCM	TBAB	76.7	0.21	ppt.
DCM	TBAC	76.6	0.10	ppt.
DCM	BTEAC	78.7	0.13	ppt.
DCM	BTEAB	79.3	0.20	ppt.
TCM	TBAB	60.0	0.11	ppt.
TCM	BTEAC	83.4	0.12	ppt.
DCE	TBAB	88.9	0.28	ppt.
DCE	TBAC	76.4	0.12	ppt.
DCE	BTEAC	86.5	0.32	ppt.
DCE	BTEAB	89.3	0.21	ppt.
NB	TBAB	85.0	0.17	solution
NB	TBAC	90.6	0.11	solution

Reaction conditions		**Polymer yield**		
Solvent[b]	Catalyst	%	[η], dLg^{-1}*	State
NB	BTEAC	92.2	0.19	solution

Data obtained from Liaw and Chang;[59] [a]Polymerization was carried out with bisphenol S (5.00 mmol) and TCF (7.50 mmol) in the organic solvent (37.5 mL) and water (30 mL) in the presence of catalyst (3.15 mmol) and sodium hydroxide (28.5 mmol) at room temperature for 2 h. [b]Abbreviations: DCM, dichloromethane; TCM, tetrachloromethane; DCE, 1,2-dichloroethane; NB, nitrobenzene. *Measured at a concentration of 0.5 gdL^{-1} in DMF at 25°C

Another type of polysulfide (**XIII**) was synthesized by the two-phase polycondensation of bis-(3-chloroacryloy)benzenes (**XI**a and **XI**b) with 4,4'-oxybisbenzenethiol (**XII**). The polycondensation was carried out in a chloroform-water system at room temperature with some phase transfer catalysts.



[13.3.15]

Table 13.3.18 shows the results of polycondensation. The polysulfides having inherent viscosities above 0.5 dLg^{-1} were readily obtained from two bis(2-chloroacryloyl)benzene with or without use of phase transfer catalysts. These activated dichlorides are highly reactive, almost comparable to ordinary dicarboxylic acid chlorides. The use of catalysts, such as DC-18-C-6, was not essential to this type of polycondensation for producing high molecular weight of polysulfides **XIII**.

Table 13.3.18. Synthesis of polysulfides XIII in organic solvent-water system[a]

Dichloride	Solvent	Catalyst	Reaction time, min	Polymer, [η], dLg^{-1}*
XIa	chloroform	none	15	0.21
XIa	chloroform	none	60	0.61
XIa	chloroform	DC-18-C-6	10	0.62
XIa	chloroform	TBAC	60	0.72
XIa	dichloromethane	DC-18-C-6	60	0.55
XIb	chloroform	none	60	0.55
XIb	dichloromethane	none	15	0.42
XIb	dichloromethane	DC-18-C-6	15	0.51

Data obtained from Imai;[41] [a]Reaction conditions: 2.5 mmol of XI, 2.5 mmol of XII, 0.05 mmol of catalyst, 5 mL of solvent, 5 mL of 1.01 M KOH at 15°C under nitrogen, *Measured at a concentration of 0.5 gdL^{-1} in concentrate sulfuric acid at 30°C

13.3.1.4 Effect of the volume of organic solvent and water on the reactions in various reaction systems

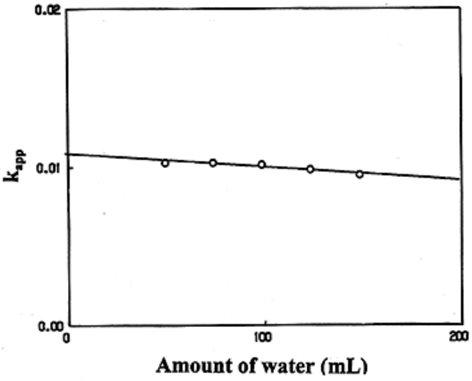


Figure 13.3.7. Effect of the amount of water on the apparent rate constant (k_{app}); 4 g of 2,4,6-tribromophenol, 0.9 g of KOH, 0.6 mL of benzyl bromide, 50 mL of H_2O, 50 mL of chlorobenzene, 40°C. (Adapted from Ref. [147], by permission.)

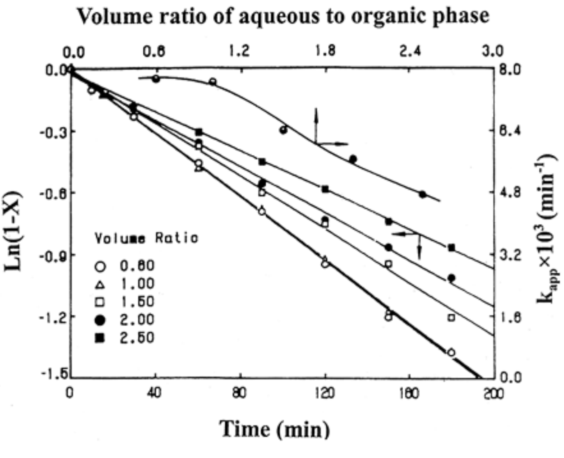


Figure 13.3.8. Effect of the volume ratio of water to chlorobenzene on the conversion; 1.568 g of 4-bromophenol, 1.0 g of KOH, 0.7 g of allyl bromide, 0.2 g of TBAB catalyst, 50 mL of chlorobenzene, 50°C. (Adapted from Ref. [135], by permission.)

In general, the concentration of reactants in the aqueous phase is decreased by increased amount of water. The addition of water probably also decreases the concentration of the intermediate product in the organic phase. Hence, both the mass transfer rate and the degree of hydration with the anion are decreased, which also decreases the reaction rate. However, this argument is not necessarily correct. Figure 13.3.7 indicates that the conversion in the two-phase reaction is not affected by the amount of water added.[147] Wang and Yang[135] studied the effects of the volume ratio of water to chlorobenzene on the conversion for the reaction of 4-bromophenol and allyl bromide in an alkaline solution of KOH/chlorobenzene at 50°C under phase-transfer catalytic conditions. The reaction followed the pseudo-first-order rate law and the corresponding apparent rate constant decreased gradually when the water content was increased, as shown in Figure 13.3.8.[135] The reason was that the concentration of the intermediate product tetra-n-butylammonium phenoxide (ArOQ, or the active catalyst) in the aqueous phase decreased with the increase in the amount of water. The mass transfer rate of the intermediate product (or the active catalyst) from the aqueous phase to the organic phase decreased when a large amount of water was used. In addition, the dilution effect led to reduction of the reaction rate in the aqueous phase.

In general, a higher concentration of the intermediate product (tetra-n-butylammonium alkoxide, or the active catalyst, ArOQ) in the aqueous phase enhances the reaction rate. This is due to a large concentration gradient across the interface in transferring the species from the aqueous phase to the organic phase. For the reaction of allyl bromide and 2,4-dibromophenol in synthesizing 2,4-dibromophenyl allyl ether in an

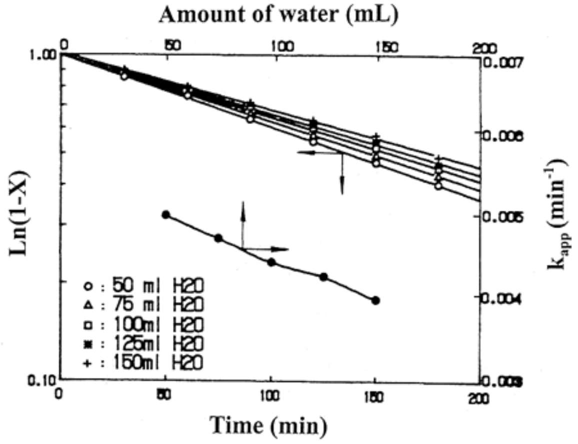


Figure 13.3.9. Effect of the water content on the conversion; 2.28 g of 2,4-dibromophenol, 0.2 g of TBAB catalyst, 0.7 g of allyl bromide, 1.0 g of KOH 50 mL of chlorobenzene, 50°C. (Adapted from Ref. [132], by permission.)

alkaline solution of KOH/chlorobenzene two-phase medium under PTC conditions,[132] the conversion increases with the increase in the concentration of ArOQ in the aqueous phase (or decreasing content of water). However, this change is small, reflecting a small mass transfer resistance, as shown in Figure 13.3.9.[132] The influence of the amount of water on the conversion in the reaction of carbon disulfide and o-phenylene diamine catalyzed by tertiary amine in a two-phase medium was studied. The conversion decreased with the increase in the amount of water. Therefore, the value of apparent rate constant (k_{app}), in which the reaction follows pseudo-first-order-rate law, decreases with the increase in the volume of water.[128] Wang and Chang[144-146] found that the conversion increases with the increase in the volume ratio of water to organic solution up to 1/5. The conversion is independent of the volume ratio of water to organic phase (chlorobenzene), greater than 1/5. The reason is that the reaction is carried out in a large amount of KOH (solid form). Probably, the omega phase is generated for the volume ratio of water to chlorobenzene less than 1/5. However, this change in the conversion vs. the volume ratio of water to chlorobenzene is not significant.

(A) Omega phase reaction

It is found that 92% of the 18-crown-6 ether added to a salt (KCN and KCl) and toluene system resided in the organic phase. However, all but approximately 1-2% of the crown ether was translocated onto the surface of the salt upon addition of small quantities of water. The results of Liotta et al.[62] are given in Table 13.3.19. The initial water added to the system coats the surface of the salt particles and it was this aqueous salt coating that extracted the crown from the organic phase. Liotta et al.[61,62] called this new region of the reaction system the omega phase. The 8% of the crown located on the surface of the salt particles prior to the addition of water was probably due to the presence of water already present in the salt. The distribution of 18-crown-6 ether between the organic phase and the omega phase was determined.[62] The amount of crown ether in the organic phase remained low and relatively constant (0.06-0.07 milimoles of 18-crown-6 ether in organic phase). The omega phase adsorbed most of added crown ether. For the accompanying pseudo first-order kinetics reaction of benzyl bromide with potassium cyanide, the results are given in Table 13.3.20.[122] There is a slight increase in the rate as the number of millimoles of 18-crown-6 ether increases, but the rate remains essentially constant with the increase of crown ether.

Table 13.3.19 Effect of added water on the concentration of 18-crown-6 ether in toluene at room temperatures

Water, μL	Equiv. of water, mole of H_2O/mole of crown	Percent crown in toluene, %
0	0.00	91.5
10	0.14	81.4
15	0.21	77.3
22	0.31	50.0
25	0.35	34.6
30	0.42	17.7
45	1.25	2.5
50	1.39	2.0
80	2.22	1.0

Data obtained from Liotta et al.[62] 0.0040 mole of 18-crown-6, 0.027 mol of KCN, 10 mL of toluene

Table 13.3.20 18-Crown-6 catalyzed reactions of benzyl bromide with KCN as a function of added crown ether

Millimoles of 18-crown-6	$k\times10^5$ sec^{-1}
3.0	2.16, 2.47
5.0	3.97, 3.63
7.0	3.86, 3.99
10.0	3.75, 4.00
12.0	3.80, 3.60

Data obtained from Vladea and Simandan;[122] 1.0 mL of H_2O, 0.15 mole KBr, 0.15 mol of KCN, 50 mL of toluene, 25°C

(B) Reaction catalyzed by PEGs

The structure of polyethylene glycol ($HO(CH_2CH_2O)_nH$, PEG) is similar to that of crown ether. Polyethylene oxide chains (CH_2CH_2O) form complexes with cations, much like crown ethers, and these complexes cause the anion to be transferred into the organic phase and to be activated.[122] Table 13.3.21 shows the binding constant, K, for PEG complexes with sodium cation depend on both the value of n (i.e., average molecular weight of PEG or number of (CH_2CH_2O) unit) and on the end-group substituents.[112,114,115] Gokel and coworkers[31,32] determined the binding strength for Na^+ in anhydrous methanol solution with PEGs and obtained the binding constant K=1.4. They concluded that the strength of complexation is a function of the total number of binding sites present and not the number of polymer chains, suggesting that a long PEG chain may be involved in binding more than one cation.

PEGs and their derivatives have been extensively investigated as phase transfer catalysts and are used in many commercial processes. In the absence of strong acids, PEGs are nontoxic, inexpensive, and thermally stable. For some reactions such as with hydroxide transfer, PEGs are excellent catalysts, sometimes better than crown ethers, especially when used in liquid-solid PTC reactions with potassium salts, and with little or no added water, and with at least moderately polar organic solutions. PEGs are water soluble and if the organic phase is not sufficiently polar the PEG will reside almost completely in the aqueous phase; or with concentrated aqueous solutions of organic salts, the PEG may form a third catalyst-rich phase, a change that normally leads to a high level of catalytic activity.

PEGs are themselves soluble in water. To obtain partitioning of PEG into an organic solution may require use of a mono- or diether derivative. Harris and Case[34] found that with exception of dichloromethane as an organic-phase solvent, most PEGs are themselves partitioned into the aqueous phase, depending also on the concentration of dissolved salts in the aqueous phase.[35] To improve organic-phase solubility of PEG, several dialkyl ethers of PEGs as permanganate-PTC catalysts are suggested in Table 13.3.22.

Table 13.3.21 Binding constants for complexation of PEGs and some symmetrical derivatives with sodium cation Na^+ + PEG = $[Na^+{\cdot}PEG]$ complex

PEG Avg. MW	Log K (binding constant) with various sodium salts					
	Avg. n	HO-	CH_3O-	C_2H_5O-	PhO-	$cyC_5H_{10}N$-
200	4.1	1.64			0.5	
300	6.4	2.02	1.55	1.25	1.05	1.16
400	8.7	2.26			1.49	1.51
600	13.2	2.59	2.09	1.99	1.87	
1000	22.3	2.88	2.55	2.48	2.37	2.46
1500	33.7	3.09	2.86	2.80	2.68	
2000	45.0	3.28	3.08	3.05	2.81	3.08

Data obtained from Szabo et al.[112,114,115]

Table 13.3.22 Partition of PEG-dialkyl ethers between C_6H_6 and H_2O

PEG Ether	Partitioning, % in C_6H_6/% in H_2O
C_4-PEG1500-C_4	14
C_6-PEG1500-C_6	84
C_{18}-PEG6000-C_{18}	Emulsion
C_{18}-PEG750-Me	108
C_{18}-PEG1900-Me	39
C_{18}-PEG5000-Me	37
C_8-PEG5000-Me	12
C_4-PEG5000-Me	13
PEG6000	<1

Data obtained from Harris et al.[34,35] C_4-PEG1500-C_4 represents a PEG of MW 1500, capped by a butyl group at both ends

Aliphatic hydrocarbons are immiscible with PEGs. Therefore, it is important to select a good organic-phase solvent such as aromatic hydrocarbons, chlorinated hydrocarbons, or acetonitrile.[80] In toluene, PEGs are more effective catalysts than crown ethers for the reaction of benzyl chloride and solid potassium acetate. In butanol, the effectiveness of PEGs and crown ethers as phase-transfer catalysts were the same for the reaction of benzyl chloride and solid potassium acetate.[27]

13.3.1.5 Effects of organic solvents on other phase-transfer catalytic reactions

(A) Liquid-liquid-liquid three phase reaction

Not only will the organic solvent influence the NPTC reaction, but it also affects the character of NPTC. Another type of transfer mechanism takes place when the quaternary salt catalyst is not highly soluble in either the aqueous or the organic phase, but instead forms a third phase.[154] For example, tetrabutylammonium salts in the presence of highly concentrated aqueous solutions, and with toluene as solvent for the organic phase, form a third (quaternary compound) phase.[126] Jin et al.[48] investigated the relationship between the properties and the catalytic activity of the liquid-liquid-liquid three-phase phase-transfer catalytic system. The condition of formation of the third phase are investigated by changing the kind of PTC and organic solvent. With tetra-n-butylammonium bromide $Bu_4N^+Br^-$ is used as the phase transfer catalyst, the third phase is formed with both dodecane and toluene as the organic solvents. On the other hand, when tetra-n-hexylammonium bromide $(Hex)_4N^+Br^-$ is used as the phase transfer catalyst, the third phase forms with dodecane but not with toluene. In such situations, most of the reaction actually occurs in the third phase with both aqueous and organic reagent transferring to this phase for conversion. Third-phase reactions of this type may be faster than simple PTC reactions. Because formation of the third phase offers simplified catalyst removal and recovery procedures, third-phase catalyst is highly attractive for commercial operations.

In the conversion of benzyl chloride to benzyl bromide using tetra-n-butylammonium bromide as the catalyst, a third phase was also observed.[126] More rapid reaction rates were obtained in the presence of this additional phase. The kinetics associated with the base-catalyzed isomerization of p-allylanisole in the presence of a variety of polyethylene glycols (PEGs) has been reported.[79] The reaction followed first-order kinetics in p-allylanisole and the reaction system was characterized by three phases consisting of an organic solvent phase, an aqueous base phase, and a complex liquid phase consisting of PEG and potassium hydroxide. It was suggested that the isomerization reaction took place in the complex third phase.

PEG forms a third phase between toluene and aqueous KOH when some methanol is added.[39] Some methanol must be added to reduce the amount of PEG that otherwise would dissolve in the toluene phase. Thus, dehydrobromination of 2-bromooctane in toluene, using PEG as catalyst, could be accomplished by removal and replacement of the organic and aqueous phases after completion of reaction, and recycle of the catalyst phase. After four cycles no catalyst was lost. Reaction rates for KOH dehydrohalogenation of 2-bromooctane in toluene with PEG catalysts were increased by a maximum factor of 126 by addition of methanol.[38,40] The base efficiency (moles base per mole of catalyst) PEGs with molecular weights 3000 and 20,000 exceeded unity and reached a maximum of 12 on addition of methanol. Hydrogenative dehalogenation of polychlorinated aromatic halides can be accomplished by hypophosphite reduction using a quaternary ammonium salt as a phase-transfer catalyst in conjunction with a palladium-on-carbon co-catalyst.[68] The quaternary salt, being insoluble in both reactant phases, coats the Pd/C catalyst forming a third phase. The strongly alkaline medium and the phase-transfer agent are synergistic.

In principle, formation of a third catalyst could be accomplished either by (1) use of a phase-transfer catalyst that has limited solubility in both the organic and aqueous phase, or (2) by use of a special solvent, perhaps a fluorocarbon, having great affinity for the catalyst but only modest affinity for both of the reactants. Tetra-n-butyl-ammonium salts frequently form third layer when used in conjunction with an organic phase that has little polarity (e.g., neat 1-chlorooctane, toluene, or cyclohexane as solvent, but only dichloromethane) and with a concentrated aqueous solution of inorganic salts.

The catalyst may form a third layer during the PTC reaction, when using high salt concentrations and nonpolar organic solvents. Wang and Weng[123-126,154] found that a third layer phase was built when using a low polarity organic solvent in the PTC reaction system. This has been observed for PEGs, quaternary onium salts and crown ether. In such cases, catalyst recovery involves a simple phase separation. In industrial kettles (with limited visibility in the reactor) or when a "rag" layer distorts an otherwise sharp phase boundary, a phase separation operation may not be simple. Nevertheless, choosing conditions in which the catalyst separates as a third layer is usually advantageous. A dehydrohalgenation was performed four times consecutively, with no loss in catalytic activity by simply replacing the organic phase and replenishing the aqueous base phase after each use, leaving the third phase containing PEG in the reactor.

(B) Electrochemical and PTC reaction

The combination of phase transfer catalysis (PTC) with other processes, such as supercritical fluid extraction[22] and electrochemical process[5-7,23,120] have been investigated in detail. Do and Chou[23] carried out the anodic oxidation of benzyl alcohol in the two-phase system containing both the redox mediator, ClO^-/Cl^-, and a phase-transfer catalyst (PTC). The reaction mechanism and the factors which affect the efficiency of benzaldehyde production were explored. The current efficiency is mainly governed by the pH value and the nature of the organic solvent as well as the types and the concentration of phase transfer catalyst (PTC). When ethyl acetate and chlorinated hydrocarbons were used as solvents, the current efficiencies were between 64 and 86%, respectively as shown in Table 13.3.23.[23] With ethyl acetate as solvent, the current efficiency was less than for chlorinated hydrocarbons. The results indicate that the chlorinated hydrocarbons have a higher extraction capacity for $Bu_4N^+ClO^-$ from the aqueous phase than has ethyl acetate. Similar results were obtained by Dehmlow and Dehmlow.[16] The current efficiencies change slightly when different chlorinated hydrocarbons were used as organic solvents.

Table 13.3.23 Effect of organic solvent on current efficiency

Organic solvent	Current efficiency, %
CH_2Cl_2	80
CH_2ClCH_2Cl	75
$CHCl_3$	86
$CH_3COOC_2H_5$	64

Data obtained from the work of Do and Chou;[23] 0.5 M of $C_6H_5CH_2OH$ in the organic phase; 25°C, 600 rpm, 20 mAcm^{-2} of current density, 70 mL of organic phase, 70 mL of aqueous phase, 0.005 M of Bu_4NHSO_4, 1.0 M of NaCl, pH=6.9, electricity passed 2 Fmol^{-1} of benzyl alcohol

Tsai and Chou[120] carried out the indirect electrooxidation of cyclohexanol by using a double mediator consisting of ruthenium and chlorine redoxes in the multiphase system. Table 13.3.24 shows that the current efficiency had the highest value at 83% using carbon tetrachloride as organic solvent.[120] The current density decreased in order, carbon tetrachloride > chloroform > toluene > cyclohexane. The selectivity was 100% except when toluene was used as organic solvent. For this case, the concentration of cyclohexanol in carbon tetrachloride is higher than that of the other solvents.

Table 13.3.24. Effect of organic solvent on the conversion and selectivity

Solvent	Conversion, %	Selectivity, %	C.E., %	Energy consumption, KWH/mole
CCl_4	42	100	83	0.226
$CHCl_3$	38	100	70	0.268
Toluene	17	81	34	3.154
Cyclohexane	12	100	23	4.662

Data obtained from Tasi and Chou;[120] Reaction conditions: 0.8 M of cyclohexanol, 15 $mAcm^{-2}$ of current density, graphite cathode and graphite anode, 0.007 M of RuO_2, pH=4, 0.99 $Fmol^{-1}$ electricity passed, NaCl saturated solution as electrolyte, 1275 rpm, 5°C

13.3.1.6 Other effects on the phase-transfer catalytic reactions

Simple mechanical separation such as filtration, centrifugation or phase separation can be used to separate the product and the phase-transfer catalyst by use of insoluble catalysts. However, the more frequently encountered technical problems in use of PTC for industrial applications is the need to separate the product and the phase-transfer catalyst by chemical equilibrium separation method in the liquid-liquid two-phase phase transfer catalytic reaction. The most commonly used methods for separation of products and PTC catalysts on an industrial scale are extraction and distillation. Other separation methods include sorption[3,33,57] and reaction.[45]

The principle of extraction method used to separate PTC and product is based on solubility of quaternary ammonium salt in alkaline aqueous solution.[2,25,104] For example, tetrabutylammonium bromide is soluble to the extent of 27% in dilute (1% NaOH) aqueous solutions, but when the solution is made more concentrated (15% NaOH), the solubility of $Bu_4N^+Br^-$ decreases to 0.07%. When the products are obtained in PTC system, they can be usually separated from PTC by distillation method. PTC catalyst in the distillation residue may sometimes be reusable. With quaternary ammonium salts as catalysts, temperatures above 100-120°C usually result in partial or total decomposition of the quaternary salts to trialkylamines and other products. Mieczynska et al.[70] and Monflier et al.[72] investigated the hydrogenation and hydroformylation under phase transfer catalytic conditions. They found that the yield of aldehydes obtained in hydroformylation of 1-hexene strongly depends on solvent: 24% in toluene, 53-86% in toluene-water-ethanol mixture and 77-94% in water-ethanol solution. The mixture of water-ethanol as a solvent was also found to be the best for hydrogenation of 1-hexene (96% of hexane). Conversion of $Ph_2PCH(CH_3)(COOH)$ phosphine into sodium salt $Ph_2PCH(CH_3)(COONa)$ yields aldehyde in toluene, 92% in toluene-water and 94% in toluene-water-ethanol mixture.

In principle, hydroxide anion is very difficult to transfer from aqueous to organic phases, yet it is one of the most valuable and most commonly used anions in the PTC systems. Addition of small amounts of alcohols to PTC systems requiring hydroxide transfer causes a dramatic increase in rates. Therefore, addition of alcohol enhances the PTC reaction as the cocatalytic effect. For example: formation of alkoxide anions, RO^-, which are more readily transferred than the highly hydrated hydroxide anion, and which can serve as a strong base just as well as OH^-, and solvation of the hydroxide with alcohol rather than with water, making the hydroxide anion more organophilic and more easily transferred.[99,100]

Cyanide displacements catalyzed by quaternary ammonium salts usually do not proceed without the presence of water to facilitate exchange and transfer of anions. However, PTC displacement depends on alcohol structure. Benzyl alcohol is about 1.5-2 times as effective as either methanol or ethanol.

In the synthesis of BTPPC (benzyltriphenylphosphonium chloride) from benzyl chloride and triphenylphosphine, second-order rate constants and activation parameters for the reaction of benzyl chloride and triphenylphosphine were measured in several protic and aprotic solvents covering a wide range of dielectric constant were obtained by Maccarone et al.[64] Wang, Liu and Jwo[127] also used eight solvents in studying their effect on the reaction of triphenylphosphine and benzyl chloride. They classified these solvents into two categories depending on the solubility of benzyltriphenylphosphonium chloride (BTPPC). Solvents that dissolve BTPPC are acetic acid, dichloromethane, methanol and water. Solvents that do not dissolve BTPPC are acetone, benzene, toluene and ether. In general, triphenylphosphine (TP) does not dissolve in methanol or water. The effect of solvents on the reaction rate was measured by the apparent rate constant in which the reaction follows pseudo-first-order rate law. The order of relative activities of solvents is methanol (0.34 h^{-1}) > acetic acid (0.176 h^{-1}) > dichloromethane (0.0468 h^{-1}) > acetone (0.0114 h^{-1}) > diethyl ether (0.0043 h^{-1}) > benzene (0.0018 h^{-1}) > toluene (0.0008 h^{-1}).

Table 13.3.25. Second-order rate constants and activation parameters for the reaction of benzyl chloride with triphenylphosphine in various solvents

Solvent	Dielectric constant (20°C)	k×10^4, Lmol^{-1}s^{-1}				
		60°C	70°C	80°C	90°C	100°C
Decalin	2.26	0.00134				0.0355
Toluene	2.38	0.0169		0.0843	0.181	0.353
Anisole	4.33	0.0569		0.260	0.466	1.15
Bromobenzene	5.40	0.0933		0.276	0.457	0.909
Chlorobenzene	5.62	0.0512		0.243		1.13
Benzyl alcohol	13.1	8.94		38.7		107
1-Butanol	17.1	4.93		19.5		43.7
Acetopnenone	17.39	0.300		1.32		9.19
1-Propanol	20.1	4.41	9.86			
Acetone	20.3	0.166	0.417			
Ethanol	24.3	3.60	7.73			
Benzonitrile	25.2	0.545		1.71		6.38
Nitroethane	28.06	0.470		3.05		12.9
Methanol	32.65	8.86				
N,N-dimethylformanide	36.7	0.460		1.88		6.59
Acetonitrile	37.5	1.20	2.79			

Solvent	Dielectric constant (20°C)	$k \times 10^4$, $Lmol^{-1}s^{-1}$				
		60°C	70°C	80°C	90°C	100°C
N,N-Dimethylacetamide	37.8	0.29		1.06		4.29
N-Methylformamide	189.5	6.08		28.7		86.5

Data obtained from the work of Maccarone et al.[64]

The BC-TP reaction shows better reactivity in protic or polar solvent since the activated complex is more polar than both reactant molecules.

13.3.2 THREE-PHASE REACTIONS (TRIPHASE CATALYSIS)

As stated, the solid PTC is suitable for the industrial processes concerning the removal of the catalyst from the reaction mixture and its economic recycle. The real mechanism of reaction in a triphase catalysis is not completely understood. However, the reaction rate and the conversion of reactant in a triphase catalysis (TC) is highly dependent on the organiphilicity (hydrophilicity or hydroprobicity) of the polymer support of the catalyst and the polarity of the organic solvent. Not only the partition of the organic to the aqueous solutions is affected by the organophilicity of the polymer-supported catalyst, but also the concentration distribution of the catalyst between two phases is influenced by the organophilicity of the polymer-supported catalyst.

Ohtani et al.[82-86] used polystyrene-supported ammonium fluoride as a phase transfer catalyst (triphase catalysis) for several base-catalyzed reactions, such as cyanoethylation, Knoevenage reaction, Claisen condensation and Michael addition. The catalytic activity of the polystyrene-supported ammonium fluid was comparable to that of tetrabutylammonium fluoride (TBAF). The ionic loading and the ammonium structure of the fluoride polymers hardly affected the catalytic efficiency. The reaction was fast in a non-polar solvent (e.g., octane or toluene) from which the rate-determining step of the base-catalyzed reaction is very similar to that of the S_N^2 nucleophilic substitution reactions.

The solvent may affect the catalytic activity in several ways. The greater its swelling power, the larger the volume fraction of catalytic occupied by the more mobile liquid, and the swollen volume fraction of the more rigid polymer network. The degree of swelling and the viscosity within the polymer matrix affect intraparticle diffusion rates. The solvent may also affect intrinsic reactivity at the active sites. Experimentally, it is difficult to distinguish solvent effect on diffusivity from solvent effects on reactivity. Tomoi and Ford[116] found that the triphase catalysis followed pseudo-first-order rate law. The corresponding apparent rate constant k_{app} decreases with solvent in the order: chlorobenzene > toluene > decane over wide ranges of particle sizes and polymer crosslinking. The ability of the solvent to swell the catalysts decreases in the same order.

13.3.2.1 The interaction between solid polymer (hydrophilicity) and the organic solvents

In triphase catalysis, solvated resin supports are important carriers for solid-phase organic synthesis in combinatorial chemistry. The physical properties of resin, resin swelling, dynamic solvation, and solvated supports are important factors in affecting the synthesis.[160] However, these factors are also affected by solvent. Selective solvation of resin alters the local reactivity and accessibility of the bound substrate and the mobility of the entrapped reagent. Resin solvation changes during the course of the reaction when the attached substrate changes its polarity or other physicochemical properties.

The basic steps involved in reactions with resin-supported PTC catalysts differ from ordinary two-phase PTC reactions in one important respect: ordinary PTC reactions require only one reagent to be transferred from their normal phase to the phase of the second reactant. Use of resin-supported catalysts requires that both reagents diffuse to active PTC sites on the catalyst surface, or for reactions with slow intrinsic rates, both reagents must also diffuse to the active sites inside the resin bulk phase. The need for diffusion processes with solid catalysts also means that both reagents are required to diffuse to and penetrate the stagnant outer layer of liquid(s) (the Nernst layer), coating the catalyst particle.

Ford and Tomoi[28] carried out the reaction of 1-bromooctane with aqueous sodium cyanide, catalyzed by tributylphosphonium groups bound into beads of an insoluble styrene-divinylbenzene resin,

$$1-C_8H_{17}Br_{(org)} + NaCN_{(aq)} \xrightarrow{polymer-C_8H_5PBu_3Br} 1-C_8H_{17}CH_{(org)} + NaBr_{(aq)} \quad [13.3.16]$$

The reaction includes the following steps:

(a) Diffusion of aqueous sodium cyanide through the bulk phase and through the resin bulk to active sites

(b) Equilibrium exchange of CN^- for Br^- at the active sites

(c) Diffusion of Br^- out of the catalyst particle and into the aqueous bulk phase

(d) Diffusion of RBr ($1\text{-}C_8H_{17}Br_{(org)}$) through the organic bulk phase and through the bulk resin phase to active sites. Some reactions may occur at sites on the catalyst surface, but since the number of surface sites is small compared to the number of sites within the bulk of the catalyst, most of the reaction occurs inside the catalyst bulk.

(e) Chemical reaction (intrinsic reaction) between RBr and Resin-$PR_3^+CN^-$ at active sites to produce RCN and Br^-

(f) Diffusion of RCN out of the catalyst particle and into the organic phase.

A schematic diagram of the general resin-bound PTC catalyst is given in Figure 13.3.10. As indicated in Figure 13.3.10, spacer chains can increase some reactions by removing the active site away from the polymer chain, and from other active sites. When active sites, particularly quaternary onium salts, are located close to one another, they join to form doublets, triplets, and higher aggregates that are less active catalyst centers, and that tend to present an "aqueous" face to the reactants. Thus, the use of spacer chains increases the rates of some reactions, such as nucleophilic displacements, two-to-four-fold.[1,9,73] When the spacer chain also contains complexable ether oxygen atoms, using 15-crown-5 ether as the PTC functional group, catalyst activity is even greater, as observed in halide exchange of KI with 1-bromooctane.[10]

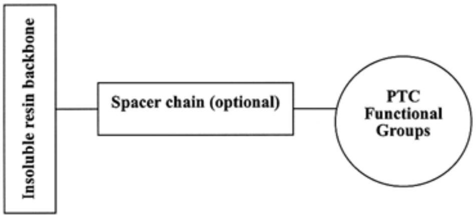


Figure 13.3.10. Schematic diagram of the general resin-bound PTC catalysts.

Preparation of phase transfer catalyst (PTC) functional groups bound to insoluble resins and their activity for catalyzing two-phase reactions has been extensively stud-

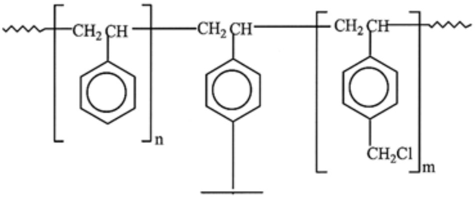


Figure 13.3.11. Crosslink to other polymer chains.

ied.[82,83,97,101] Much work has been done on the preparation and testing of phase-transfer catalysts supported on resins including extensive work by Montanari and co-workers[71,74] and by Ford and Tomoi[28] and their co-workers. Most published works on resin-bound phase-transfer catalysts use a styrene-divinylbenzene resin (SDV) and related resins, taking advantage of the huge amount of technology available on these resins due to their use as ion-exchange resin supports (Figure 13.3.11).

Tomoi and co-workers[117] suggest that solvents may affect rates of triphase-catalyzed reaction in three ways: intrinsic chemical reactivity; solvent effect on ion-exchange rate; and overall activity, including diffusion effects due to swelling of polymer-supported phosphonium salts under three-phase conditions. First, the intrinsic activity of the catalysts, as well as of soluble phosphonium salts, depended slightly on organic solvents for cyanide displacement reactions. Second, the exchange rate of chloride ion in the catalysts vs. that of acetate depends on the solvents when the degree of ring substitution is less than 16%. With 30% ring-substituted catalysts, the rate increases and hardly depends on the solvents. Third, the overall catalyst reactivity for the reaction of organic halides with NaCN depends on the substrate and organic solvents. For 1-bromooctane, the catalysts were more reactive in good solvents (e.g., chlorobenzene) than in poor solvent (e.g., octane). Shan and co-workers,[98] Wang and Wu[136,137] examined the effects of solvents and other resin-bound catalysts parameters (macroporosity, microporosity, crosslink density and size of catalyst pellet). They all show that the swelling in organic solvents is an important factor affecting the conversion of the reactant, as shown in Table 13.3.26.[98]

Table 13.3.26. Effect of the organic solvent on the yield of ester from benzyl bromide and aqueous KOAc under standardized conditions

Catalyst[a]	Solvent (dielectric constant, ε)[b]	Yield of ester, %
Macro (6%)-400	Cyclohexane (2.02) Toluene (2.38) Chlorobenzene (5.62) Benzyl ethyl ketone (17.4) Nitrobenzene	13.2 16.5 23.3 94.5 100.0
Micro (6%)-400	Cyclohexane (2.02) Toluene (2.38) Chlorobenzene (5.62) Benzyl ethyl ketone (17.4) Nitrobenzene	9.2 13.5 18.2 86.0 100.0

Data obtained from Shan, Kang and Li;[98] [a]6% crosslinking; [b]PEG-400 used for active sites on catalyst

13.3.2.2 Effect of solvents on the reaction in triphase catalysis

The disadvantage of using liquid-liquid phase-transfer catalysis (ll-PTC) is in the separation of catalyst from product after reaction. This problem can be overcome using the immobilized catalyst on a solid support (e.g., porous polymer pellet). Simple mechanical separation processes, such as filtration or centrifugation, can be employed to separate the solid catalyst from the product in liquid form. A detailed investigation of the effect of polymer particle on the reaction rate was conducted by Wang and coworkers.[131,133-137] Wang and Wu[136] studied the reaction of substitution of hexachlorocyclotriphosphazene and 2,2,2-trifluoroethanol in an organic solvent/alkaline solution by triphase catalysis. The polymer, which was prepared from the polymerization of styrene monomer and chloromethylstyrene monomer, served as the support for the immobilization of the catalyst.

The effects of the structure of the polymer support, which can be related to the factors of the degree of crosslinking, ring substitution (RS), lipophilicity of the polymer, the chloride density and solvents on the imbibed compositions[84,118] on the reaction rate or conversion were investigated. This imbibed composition, influenced by the internal structures of the triphase catalyst particles, affected the reactivities. The interaction of the polymer support pellet and the organic solvents play an important role in determining the reaction rate and the conversion of the reactant. The reaction could be improved to obtain a high reaction rate by using a polar solvent.

For investigating the degree of crosslinking of the polymer, the resistance of mass transfer within the catalyst pellet is small. When a smaller degree of crosslinking of the polymer support is used. This is due to the fact that a larger value of the swell of the polymer was obtained when a small degree of crosslinking of the polymer was used. Wang and Yu[131] have similar observations for the reaction of allyl bromide and 2,4-dibromophenol under triphase catalysis. A maximum value exists for the degree of swell and the imbibed composition, as shown in Table 13.3.28 for the degree of crosslinking.[136]

In Table 13.3.27,[136] the degree of swell for the polymer support with a 6% crosslinking is larger than that for the two other degrees of crosslinking. This implies that greater amounts of $NaOCH_2CF_3$ were imbibed into the catalyst pellet with a 6% crosslinking. The reaction rate is directly related to the amount of the imbibed composition. Also, in Table 13.3.27, the imbibed compositions are affected by the structure of the polymer support. The reactivity of the triphase catalysis can also be determined from the composition imbibed by the particles. It can be observed that the reactivities were highly affected by the lipophilicity of the catalyst pellet for the substitution reaction in the organic phase and the hydrophilicity of the catalyst pellet of the ion exchange in the aqueous phase. For example, the reaction rate in the organic phase was promoted by using a lipophilic polymer support catalyst when the substitution reaction rate was slow. In Table 13.3.27, the amount of chlorobenzene and water imbibed in the macroporous pellet was greater than that in the microporous pellets for most cases.[136] However, the macroporous pellet with 10% degree of crosslinking had the least lipophilicity and degree of swelling; therefore, the reactivity was the lowest for the macroporous pellet with a 10% crosslinking among the polymer-support catalysts. The reactivity environments which were created by the lipophilicity and the hydrophilicity of the polymer support plays an important role in determining the reactivity.

It is known that the distribution of organic phase and aqueous phase existing in the porous pellet is affected by a change of the ring substitution (RS) of the polymer support.[84] Wang and Wu[136] prepared three kinds of polymer supports with different numbers of ring substitution, such as 10%RS, 20%RS and 49%RS, to analyze the lipophilicity of the polymer support. The order of the lipophilicity was 10%RS > 20%RS> 49%RS, which is the same as the order of swelling. However, a maximum value of the apparent rate constant was obtained for using a 20%RS pellet catalyst among the three kinds of ring substitution polymer pellet. Therefore, it is concluded that the lipophilicity of the polymer cannot be too large to enhance the reaction rate. This is due to the fact that the ion exchange rate is retarded to lower the reaction rate because of using a high lipophilic polymer support. It is concluded that the lipophilicity and the hydrophilicity highly influence the reactivity in triphase catalysis.

For a two-phase PTC, it is recognized that the polarity of the organic solvent affects the reaction rate. In general, the reaction rate increases with the augmentation of the polarity of the solvents. Table 13.3.28 shows the effects of the organic solvents on the apparent rate constant, $k_{o,app}$ and $k_{a,app}$.[136] A higher value of the apparent rate constant was obtained using solvent of high polarity. This result is consistent with the swelling and the imbibed compositions that are given in Table 13.3.29.[136]

Table 13.3.27. Compositions of the imbibed solvents and swelling volume of the triphase catalyst pellet with various polymer structures

Triphase catalyst	Conditions	ClC_6H_5 g	H_2O g	$NaOCH_2CF_3$, g (calcd value, g)	Swelling volume ratio
microporous 2%	ClC_6H_5	1.31			2.4
	H_2O/ClC_6H_5	1.23	0.33		2.7
	2.8M $NaOCH_2CF_3/ClC_6H_5$	1.92	0.67	0.40 (0.29)	3.6
microporous 6%	ClC_6H_5	1.19			2.2
	H_2O/ClC_6H_5	1.17	0.62		2.8
	2.8M $NaOCH_2CF_3/ClC_6H_5$	1.90	0.50	0.60 (0.22)	3.4
microporous 10%	ClC_6H_5	1.06			2.0
	H_2O/ClC_6H_5	0.96	0.29		2.1
	2.8M $NaOCH_2CF_3/ClC_6H_5$	1.40	0.50	0.19 (0.22)	2.9
macroporous 2%	ClC_6H_5	1.28			
	H_2O/ClC_6H_5	1.33	0.73		3.1
	2.8M $NaOCH_2CF_3/ClC_6H_5$	2.29	0.50	0.34 (0.22)	3.8
macroporous 6%	ClC_6H_5	1.54			2.5
	H_2O/ClC_6H_5	1.25	0.82		3.1
	2.8M $NaOCH_2CF_3/ClC_6H_5$	2.2	0.59	0.42 (0.25)	3.8
macroporous 10%	ClC_6H_5	0.76			
	H_2O/ClC_6H_5	1.05	0.63		2.7
	2.8M $NaOCH_2CF_3/ClC_6H_5$	1.28	0.38	0.17 (0.16)	2.6

Data obtained from Wang and Wu;[136] 50 mL of chlorobenzene, 20 mL of water, 0.059 mole of $(NPCl_2)_3$, 0.7 meq of catalyst was used, 20°C

Table 13.3.28. Effects of the concentrations of $NaOCH_2CF_3$ and kind of solvent on the apparent intrinsic rate constants, $k_{o,app}$ and $k_{a,app}$

Solvent	$k_{o,app}$ for $[NaOCH_2CF_3]$ (M), $(min.meq)^{-1}$			$k_{a,app}$ for $[NaOCH_2CF_3]$ (M), $(min.meq)^{-1}$		
	1.6 M	2.2 M	2.8 M	1.6 M	2.2 M	2.8 M
CH_2Cl_2	0.25	0.33	0.58	0.036	0.028	0.036
C_6H_5Cl	0.063	0.12	0.19	0.017	0.015	0.014
$C_6H_5CH_3$	0.027	0.056	0.15	0.0055	0.006	0.011
n-C_6H_{14}	0.015	0.031	0.092	0.0008	0.0008	0.018

Data obtained from Wang and Wu;[136] 50 mL of solvent, 20 mL of water, 0.0059 mol of $(NPCl_2)_3$, 0.18 meq of macroporous catalyst, 20°C, 40-80 mesh of particle

Table 13.3.29. Effects of solvents on the composition of the imbibed solvents and swelling volume of the triphase catalyst pellet

Solvent	Conditions	Solvent g	H_2O g	$NaOCH_2CF_3$, g (calcd value, g)	Volume ratio
CH_2Cl_2	CH_2Cl_2	2.75			3.2
	H_2O/CH_2Cl_2	2.24	0.96		3.8
ClC_6H_5	ClC_6H_5	1.28			2.2
	H_2O/ClC_6H_5	1.33	0.73		3.1
	2.8M $NaOCH_2CF_3/ClC_6H_5$	2.29	0.50	0.34 (0.18)	3.8
$CH_3C_6H_5$	$CH_3C_6H_5$	0.57			1.7
	$H_2O/CH_3C_6H_5$	0.61	0.29		2.1
	2.8M $NaOCH_2CF_3/CH_3C_6H_5$	0.37	0.30	0.01 (0.10)	1.8
n-C_6H_{14}	n-C_6H_5	0			1
	H_2O/n-C_6H_5	0.10	0.30		1.4
	2.8M $NaOCH_2CF_3$/n-C_6H_5	0.10	0.15	0.01 (0.05)	1.24

Data obtained from Wang and Wu;[136] 30 mL of solvent, 0.80 meq of catalyst (1 g), 40-80 mesh of macroporous particle, 20°C

The overall kinetics can be divided into two steps by virtue of the presence of the two practically immiscible liquid phases, i.e.,

(1) a chemical conversion step in which the active catalyst sites (resin with 2,2,2-trifluoroethanoxide ions) react with hexachlorocyclotriphosphazene in the organic solvent, i.e.,

$$yResin^{+-}OCH_2CF_{3(s)} + (NPCl_2)_{3(org)} \rightarrow$$

$$yResin^{+}Cl^{-}_{(s)} + N_3P_3Cl_{6-y}(OCH_2CF_3)_{y(org)},\ y=1\text{-}6 \qquad [13.3.17]$$

(2) the ion exchange step in which the attached catalyst sites are in contact with the aqueous phase, i.e.,

$$Resin^{+}Cl^{-}_{(s)} + NaOCH_{2}CF_{3(aq)} \rightarrow$$

$$Resin^{+}OCH_{2}CF^{-}_{3(s)} + Na^{+}Cl^{-}_{(aq)} \qquad [13.3.18]$$

The total moles of the catalyst active sites are S; thus

$$S = [Resin^{+-}OCH_{2}CF_{3(s)} + Resin^{+}Cl^{-}_{(s)}] \qquad [13.3.19]$$

The reaction rates for $(NPCl_2)_3$ in the organic phase and for $NaOCH_2CF_3$ in the aqueous phase follow pseudo-first-order kinetics and can be written as

$$-\frac{d\left[(NPCl_{2})_{3}\right]_{0}}{dt} = k_{0,app}S\left[(NPCl_{2})_{3}\right]_{(org)} \qquad [13.3.20]$$

$$-\frac{d[NaOCH_{2}CF_{3}]_{a}}{dt} = k_{a,app}S[NaOCH_{2}CF_{3}]_{(org)} \qquad [13.3.21]$$

where $k_{0,app}$ and $k_{a,app}$ are the apparent rate constants of $(NPCl_2)_3$ per unit amount of catalyst (molar equivalent) in the organic phase for triphase catalysis and the apparent rate constant of $NaOCH_2CF_3$ per unit amount of catalyst (molar equivalent) in the aqueous phase for triphase catalysis, respectively.

Wang and Yang[134] carried out the reaction of 2,4,6-tribromophenol and allyl bromide catalyzed with tributylamine immobilized on the solid styrene-chloromethylstyrene polymer support in an alkaline solution of KOH/chlorobenzene. The experimental results indicate that the swelling power is enhanced in an organic solvent of high polarity. Thus, the reactivity of the reaction is increased with the increase in the polarity of the organic solvents.

13.3.2.3 Effect of volume of organic solvent and water on the reactions in triphase catalysis

In investigating the effect of the amount of water, the contents of other components are fixed. Changing the amount of water affects the volume ratio of organic phase to aqueous phase and the concentration of nucleophile in the aqueous phase. For the reaction of hexacyclotriphosphazene and sodium 2,2,2-trifluoroethanoxide catalyzed by tributylamine immobilized on the solid styrene-chloromethylstyrene polymer support catalyst.[138-140,157] As shown in Figure 13.3.12,[140] the reaction rate is decreased with the increase in the amount of water up to a concentration of sodium 2,2,2-trifluoroethanoxide at 2.8 M. However, the reaction rate is then increased with further increase in the amount of water larger than 2.8 M sodium 2,2,2-trifluoroethanoxide. This result indicates that a high concentration of sodium 2,2,2-trifluoroethanoxide reaction will decrease the reaction rate. The main reason is that the intraparticle diffusion is also affected by the concentration of sodium 2,2,2-trifluoroethanoxide due to changing the amount of water (or the volume ratio of organic phase to aqueous phase).

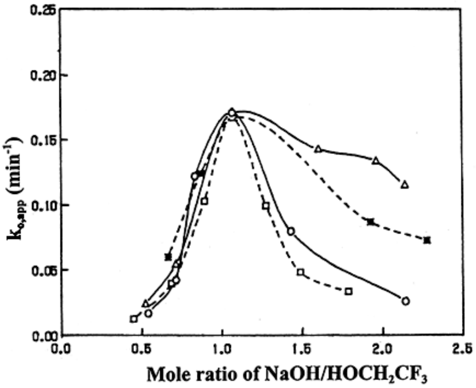


Figure 13.3.12. The apparent rate constants vs. the molar ratios of NaOH/HOCH$_2$CF$_3$; 0.059 mol of (NPCl$_2$)$_3$, 9.6×10^{-5} mol of TBAB catalyst, 50 mL of chlorobenzene, 20 mL of H$_2$O, 20°C; and (Δ) 0.07 mol of HOCH$_2$CF$_3$, (*) 0.058 mol of HOCH$_2$CF$_3$, (O) 0.075 mol of NaOH, (□) 0.063 mol of NaOH (Adapted from Ref. [138], by permission.)

The other experiments, in which the concentrations of the components in the aqueous phase are fixed, were carried out by Wu[157]. The volume of organic phase is also fixed at 50 mL, in which the amount of catalyst and phosphazene are also fixed. A generalized apparent rate constant (pseudo-first-order rate law) $k'_{i,app}$ is defined as

$$k'_{i,app} = k_{i,app} / \left[\text{Resin}_{(s)} / V_a\right]; \quad i = r,f \qquad [13.3.21]$$

where $\text{Resin}_{(s)}$ and V_a indicate the total molar equivalent active sites and the volume of water. The results are given in Table 13.3.30.[157] The apparent rate constants $k'_{r,app}$ and $k'_{f,app}$ are increased with the increase in the volume of aqueous phase. These results are explained by low concentration of sodium 2,2,2-trifluoroethanoxide in the organic phase because HOCH$_2$CF$_3$ and NaOCH$_2$CF$_3$ are all insoluble in chlorobenzene. After 4 hours of reaction, only 8% of hexacyclotriphosphasene is reacted. The increase in reaction rate by increasing the volume of aqueous solution is not due to the increase in the concentration of NaOCH$_2$CF$_3$ in the organic phase. However, the mass transfer rate within the particles is obviously affected by increasing the concentration of NaOCH$_2$CF$_3$ in the aqueous phase.

Table 13.3.30. Apparent rate constants in various NaOCH$_2$CF$_3$ concentration under constant amount of water or constant amount of NaOCH$_2$CF$_3$

NaOCH$_2$ CF$_3$ (M)	Variation of NaOCH$_2$CF$_3$				Variation of water			
	NaOCH$_2$CF$_3$ (mole)	$k_{r,app}$^{a}	$k_{f,app}$^{a}	$k'_{f,app}$^{b}	Volume of water (mL)	$k_{r,app}$^{a}	$k_{f,app}$^{a}	$k'_{f,app}$^{b}
1.3					50	0.033	0.0031	8.61
1.6	0.035	0.025	0.005	5.56	40	0.038	0.0033	7.33
2.2	0.0525	0.041	0.005	5.56	30	0.044	0.0041	6.83
2.8	0.07	0.055	0.005	5.56	20	0.055	0.0050	5.56

Data obtained from Wang and Wu;157 ^{a}min^{-1}, ^{b}Lmin^{-1}meq×10^{-4}; Reaction conditions: 50 mL of chlorobenzene, 0.0059 moles of (NPCl$_2$)$_3$, 0.175 meq of catalyst, 20°C

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13.4 EFFECT OF POLYMERIZATION SOLVENT ON THE CHEMICAL STRUCTURE AND CURING OF AROMATIC POLY(AMIDEIMIDE)

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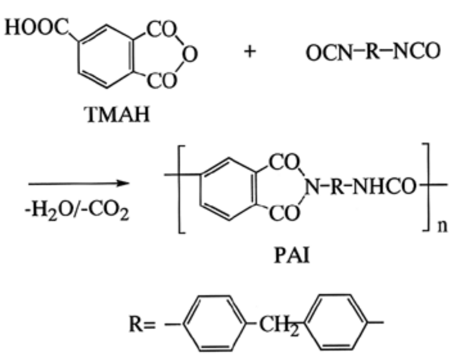
13.4.1 INTRODUCTION

Aromatic poly(amide-imide) (PAI) has an outstanding resistance not only to the thermal operations but also mechanical, electrical, and chemical operations. Although the properties of PAI are inferior to those of aromatic polyimide (PI), which is one of the most heat-resistant polymers, PAI has been widely utilized as a high performance heat resistant polymer as well as PI, because PAI is superior to PI in its workability in industry.[1,2]

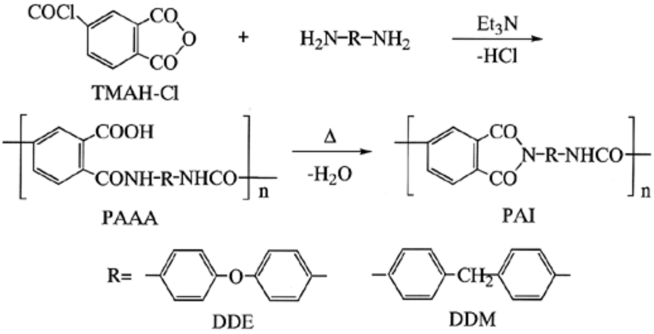
In general, PAI is prepared by the following two processes: diamine process and diisocyanate process. Diisocyanate process is achieved by the direct polycondensation of trimellitic anhydride (TMAH) with aromatic diisocyanate, such as 4,4'-diphenylmethane diisocyanate, in a polar solvent such as N-methyl-2-pyrrolidone (NMP) as shown in Eq. [13.4.1].[1-3] On the other hand, the diamine process is achieved by a two-step reaction:[1]

(1) the polymerization (polycondensation and polyaddition) of trimellitic anhydride chloride (TMAH-CI) with aromatic diamine, such as 4,4'diaminodiphenylether (DDE) or 4,4'diaminodiphenylmethane (DDM) in a polar solvent such as N,N-dimethylacetamide (DMAc), to give poly(amic acid-amide) (PAAA) and

(2) the imidation of PAAA by heating as shown in Eq. [13.4.2].



[13.4.1]



[13.4.2]

PAI is supposed to be a linear polymer containing equivalent amounts of amide and imide bonds. Therefore, PAI is soluble in polar solvents such as NMP, DMAc, and N,N-dimethylformamide (DMF). However, it is well known that PAI becomes insoluble and infusible when it is heated over 200°C. We have pointed out that some remaining carboxyl groups of PAI play an important role in the curing of PAI by heating.[4,5] Because of such a thermosetting property, PAI solution is used as a heat resistant temperature coating or an insulating enamel of magnet wire.

In the following section, the effect of polymerization solvent, DMAc and mixed solvent of methyl ethyl ketone (MEK) with water,[6] on the chemical structure and curing of PAIs prepared by diamine process will be summarized.[7]

13.4.2 EFFECT OF SOLVENT ON THE CHEMICAL STRUCTURE OF PAI

13.4.2.1 Imide and amide bond content of PAI

Four kinds of PAAA, as precursor of PAI, were prepared by the polycondensation of TMAH-Cl with DDE or DDM in DMAc and MEK/water mixed solvent (MEK containing 30 vol% of water) at room temperature. The results are shown in Table 13.4.1. It was found that the conversions reached 78-96% within 2 h at room temperature and the rate of the polycondensation of TMAHCl with diamine in MEK/water mixed solvent was much larger than that in DMAc.

Table 13.4.1. Polymerization conditions and conversion of samples [Data from reference 7]

Sample No.	Solvent	Diamine	Time, h	Conversion, %
PAAA-1	MEK/H_2O	DDE	0.5	90.3
PAAA-2	DMAc	DDE	2.0	89.6
PAAA-3	MEK/H_2O	DDM	0.5	78.4
PAAA-4	DMAc	DDM	2.0	96.8

TMAH-Cl=diamine=0.06 mol ; solvent, 172 ml; TEA, 5.0 ml; room temp.

These PAAAs, PAAA-1, PAAA-2, PAAA-3, and PAAA-4, were heated at 180°C for 2 h to give PAI-1, PAI-2, PAI-3, and PAI-4, respectively. Figure 13.4.1 shows the infrared spectra of (A) PAAA-1, (B) PAI-1, and (C) PAI-3.

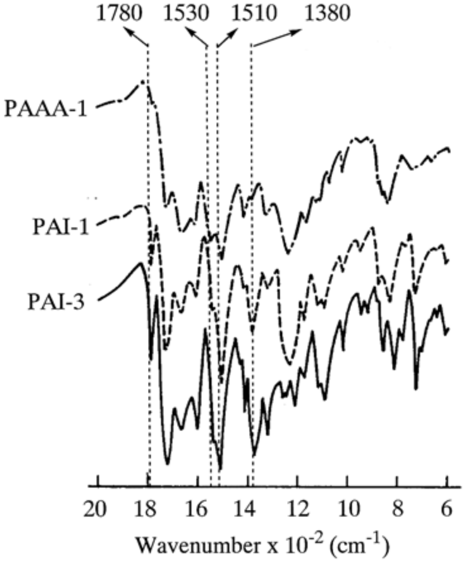
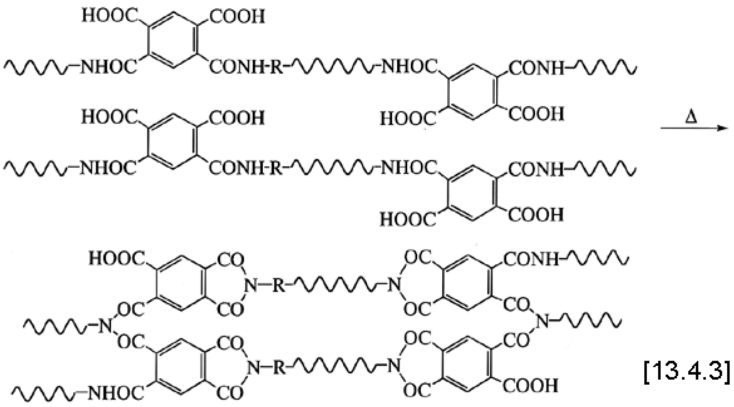


Figure 13.4.1 IR spectra of PAAA-1, PAI-1, and PAI-3 [Data from reference 7]

IR spectra of PAAA-1 show absorptions at 1530 and 1660 cm^{-1}, which are characteristic of amide bond, 1510 and 1590 cm^{-1} which are characteristic of benzene nuclei, and 1230 cm^{-1}, which is characteristic of ether bond, but the absorption at 1380 and 1780 cm^{-1}, which are characteristic of imide bond, are hardly observed. On the other hand, IR spectra of PAI-1 and PAI-3, obtained by heating of PAAA-1 and PAAA-3, respectively, show new absorptions at 1380 and 1780 cm^{-1}.

Among the adsorptions of imide bond, the absorption at 1380 cm^{-1} is assigned to C-N stretching vibrations of all imide bond (cyclic and acyclic imide bond as shown in Eq. [13.4.3] and 1780 cm^{-1} is assigned to C=O stretching vibrations of five-member imide rings (cyclic imide bond). The absorption at 1530 cm^{-1} is assigned to N-H stretching vibrations of amide bond. Furthermore, the absorption at 1510 cm^{-1} is assigned to benzene nuclei that is stable to heat treatment.



[13.4.3]

Therefore, the content of cyclic imide, amide and all imide bond of PAI was estimated by the absorbance ratio, D_{1380}/D_{1510} (the absorbance ratio of absorbance at 1380 cm^{-1} to that of benzene nuclei), D_{1780}/D_{1510}, and D_{1530}/D_{1510}, respectively.

Table 13.4.2 shows the absorbance ratio of cyclic imide, amide, and all imide bond before and after heat treatment of PAAAs. The considerable increase of cyclic and all imide bond content of PAAAs and the decrease of amide bond were observed by heating. But the effect of solvent on the imidation of PAAAs was hardly observed.

Table 13.4.2. IR absorbance ratio of PAAA and PAI [Data from reference 7]

Sample No.	Heat treatment		Absorbance ratio		
	Temperature ^oC	Time h	Cyclic imide	Amide	All imide
			D_{1780}/D_{1510}	D_{1530}/D_{1510}	D_{1380}/D_{1510}
PAAA-1			0.05	0.68	0.37
PAI-1	180	2	0.24	0.43	0.57
PAAA-2			0.10	0.59	0.36
PAI-2	180	2	0.26	0.45	0.58
PAAA-3			0.08	0.98	0.66
PAI-3	180	2	0.26	0.69	0.82
PAAA-4			0.04	0.86	0.29
PAI-4	180	2	0.27	0.63	0.79

13.4.2.2 Intrinsic viscosity and carboxyl group content

Table 13.4.3 shows the effect of solvent on the intrinsic viscosity, [η], and carboxyl group content of PAIs. The carboxyl content was determined by potentiometric titration. It is interesting to note that intrinsic viscosity of PAI from PAAA prepared in DMAc is larger than that in MEK/water mixed solvent. This suggests that the polymerization degree decreases with decreasing activity of TMAH-Cl in MEK/water mixed solvent because of the hydrolysis of TMAH-Cl by water.

Table 13.4.3. Properties of PAI samples [Data from reference 7]

Sample No.	Solvent	Diamine	Conversion, %	[η], dl/g[a]	COOH, eq/g[b]
PAI-1	MEK/H_2O	DDE	90.3	0.36	214
PAI-2	DMAc	DDE	89.6	0.54	44
PAI-3	MEK/H_2O	DDM	78.4	0.26	328
PAI-4	DMAc	DDM	96.8	0.32	73

[a]Solvent, NMP ; 30.0°C. [b]Determined by potentiometric titration

In addition, the content of carboxyl groups in PAIs prepared in MEK/water mixed solvent was considerably larger than that prepared in DMAc. This also suggests the hydrolysis of TMAH-Cl in MEK/water mixed solvent.

13.4.3 EFFECT OF SOLVENT ON THE CURING OF PAI BY HEAT TREATMENT

13.4.3.1 Chemical structure of PAI after heat treatment

Table 13.4.4 shows the effect of solvent on the change of chemical structure and formation of insoluble part of PAI-1 and PAI-2 after heat treatment. It became apparent that the content of cyclic imide bond and all imide bonds of PAI-1 and PAI-2 further increased by heating of the corresponding PAAAs at 180°C for 2 h followed by heat treatment at 260°C for 2 h. The content of amide bond decreased by heating of PAAA at 180°C for 2 h, but increased by post-heating at 260°C for 2 h.

Table 13.4.4. IR absorbance ratio and insoluble part of samples after heat treatment in air [Data from reference 7]

Sample No.	Heat treatment		Absorbance ratio			Insoluble part %
	Temperature °C	Time h	Cyclic imide	Amide	All imide	
			D_{1780}/D_{1510}	D_{1530}/D_{1510}	D_{1380}/D_{1510}	
PAAA-1			0.05	0.68	0.37	0
PAI-1	180	2	0.24	0.43	0.57	0
PAI-1	260	2	0.33	0.56	0.71	76.7
PAAA-2			0.10	0.59	0.36	0
PAI-2	180	2	0.26	0.45	0.58	0
PAI-2	260	2	0.31	0.50	0.64	16.8

13.4.3.2 Curing PAI by post-heating

The formation of the insoluble part in NMP was observed and the amount of insoluble part formed by heating of PAI-1 (obtained in MEK/water mixed solvent) was larger than that by heating of PAI-2 (obtained in DMAc).

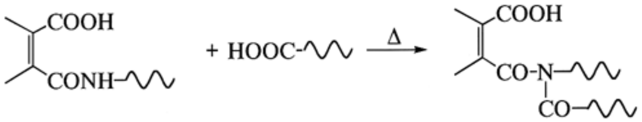
The increase of imide and amide bond content by post-heating at 260°C is considered as follows: the imidation of amic acid structure may be proceeded by both intermolecular and intramolecular imidation. The latter produces cyclic imide bond, but the former produces acyclic imide bond to give crosslinking material as shown in Eq. [13.4.3].

Since PAIs obtained by heating of PAAAs at 180°C are completely soluble in NMP, the intramolecular imidation preferentially proceeds at 180°C, but intermolecular imidation scarcely proceeds.

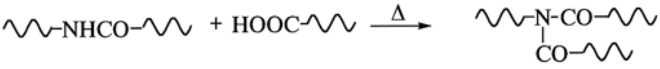
On the other hand, by post-heating at 260°C, the crosslinking reaction proceeds by the intermolecular imidation of terminal carboxyl groups of PAI with remaining amic-acid structure (Eq. [13.4.4]) and the amide bond in main chain of PAI (Eq. [13.4.5]) to give the insoluble part in NMP. The reaction induced the increase of imide bond content of PAI after post-heating. The increase of amide bond after post-heating may be due to the formation of crosslinking structure by the amidation of terminal amino groups of PAI with carboxyl groups of PAI in main chain (Eq. [13.4.5]-[13.4.8]).

Therefore, PAI obtained from the heating of PAAA obtained in MEK/water mixed solvent, which has many carboxyl groups, produces more insoluble part by post-heating.

Figure 13.4.2 shows the effect of heating temperature on the curing of PAI obtained by heating of PAAA at 180°C in MEK/water mixed solvent and DMAc. As shown in Figure 13.4.2, by post-heating at 280°C for 2 h in air, insoluble part in NMP reached 100%, indicating the almost complete curing of PAIs. It is interesting to note that PAIs formed by heating of PAAA obtained in MEK/water mixed solvent (PAI-1 and PAI-3) were found to be cured

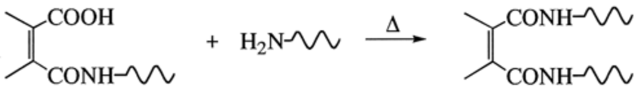


[13.4.4]

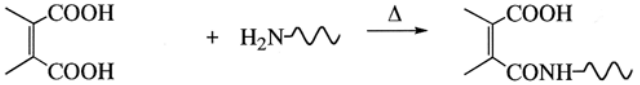


[13.4.5]

[13.4.6]



[13.4.7]



[13.4.8]

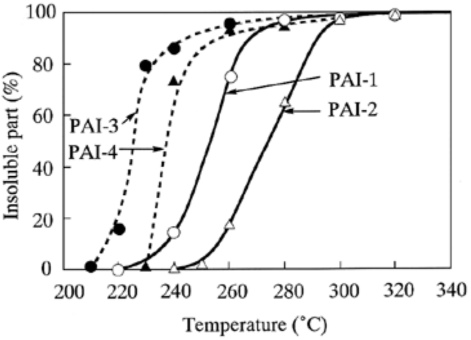


Figure 13.4.2. Relationship between heating temperature and insoluble part of PAI samples after heating (2h) in air [Data from reference 7].

more easily than in DMAc (PAI-2 and PAI-4). This is due to the fact that PAI-1 and PAI-3 contains more carboxyl groups than PAI-2 and PAI-4.

13.4.4 CONCLUSIONS

The effects of polymerization solvent on the curing of PAIs were investigated and the following results were obtained:

(1) The carboxyl group content of PAIs from PAAAs prepared in MEK/H_2O mixed solvent was larger than that in DMAc.

(2) The curing of PAIs prepared in MEK/H_2O proceeded easier than those in DMAc.

(3) The curing of PAIs by heating was due to the intermolecular reaction between functional groups of PAIs, such as carboxyl and amino groups.

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