Mixed Solvents

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9.1 INTRODUCTION

One of the basic problems in conducting a chemical process in solution is control of the process parameters. The most important is the yield of the reaction products and process rates. The equilibrium constants and the rate constants of processes in solutions are multi-factor dependencies, that is, they depend on temperature and many solvent properties. The realization of the process in individual solvent often complicates such controls, and in some cases makes it completely impossible. At the same time, it is possible to choose properties determining the process characteristics in mixed solvents directly. Such properties relate, first of all, to the density, ρ, viscosity, η, permittivity, ε, and specific solvation energy.

In this chapter, the term "mixed solvent" refers to binary solvents - regardless of the relation of their components.

The use of mixed solvents in scientific and industrial practice began at the beginning of the 20th century. But systematic theoretical-experimental research began in the sixties, and its intensity has been growing ever since. There are two basic reports on physical properties of mixed solvents. One is the published in four-volume reference edition by Timmermans[1] in the fifties and published at that period by Krestov and co-author's monograph.[2] The detailed substantiation of information as well as the corresponding bibliography are included in the monograph.[3]

9.2 CHEMICAL INTERACTION BETWEEN COMPONENTS IN MIXED SOLVENTS

The developments in physical chemistry and chemical physics of liquid state substantiated common viewpoint that liquids are associated. Assuming this approach as a limit, we may consider the individual solvent as divided into non-associated molecules having smaller energy of intermolecular interaction than the energy of molecules in thermal motion, and to molecules, having energy higher than kT.

9.2.1 PROCESSES OF HOMOMOLECULAR ASSOCIATION

In mixed solvents formed of associated component A and non-associated component B (does not interact with component A), the following equilibrium takes place:

$$mA \xleftrightarrow{B} 2A_{m/2} \xleftrightarrow{B} \cdots \xleftrightarrow{B} A_m \qquad\qquad [9.1]$$

where:

        m   number of molecules A forming the homomolecular associate (in subscript - association degree)

The systems alcohol-carbon tetrachloride or carbon acids-cyclohexane are examples of mixed solvents of this type. Interesting examples of such mixed solvents are the systems formed of liquid tetraammonium salts, R_4NA, and various liquids that are solvate-inert towards such compounds.

The values of homomolecular association constants of alcohols and acids are high, typically in the range of 10^3-10^4. Therefore concentration of the component A is rather low, even at high content of solvate-inert component B, and may be neglected.

The relative degree of the decomposition of heteromolecular associates into aggregates of a smaller association degree increases with increased permittivity of the non-associated solvate-inert component. In solutions of equal concentration of the two mixed solvents, acetic acid-cyclohexane (ε=1,88) and acetic acid-chlorobenzene (ε=5,6), the relative degree of acid heteromolecular association is higher in the first system than in the second system.

In mixed solvents, formed of two associated components in individual states A_m and B_n that do not interact with each other into specific solvation, the chemical equilibrium of mixed heteromolecular associates is established:

$$A_m + B_n \leftrightarrow x\left(A_{m/x}B_{n/x}\right) \qquad\qquad [9.2]$$

where:
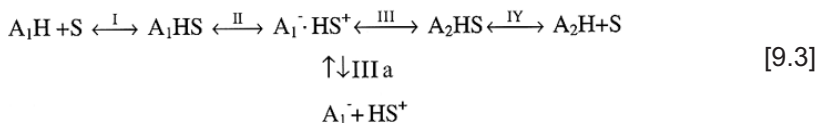
        x   number of molecules of heteromolecular associate

Whether to consider these heteromolecular associates as real chemical adducts is more terminology than a chemical problem. In most cases investigators truly assume that in systems formed of two alcohols or of two carboxylic acids, specific interaction does not exist. In the case of mixed solvents formed of two carbon acids, that is true only when components have similar proton affinity, as is the case of a system such as acetic acid-propionic acid (see further paragraph 9.2.8).

9.2.2 CONFORMIC AND TAUTOMERIC EQUILIBRIUM. REACTIONS OF ISOMERIZATION

Various conformers of the same compound differ in their dipole moments. Thus, in the mixed solvents A-B, where A is a liquid whose molecules give conformer equilibrium, and B is solvate-inert towards A, the A conformer ratio changes on addition of B component.

In binary solvents A-B where component A can exist in two tautomeric forms A_1 and A_2 the ratio of concentrations of these forms changes on addition of component B. Common theory of this influence has been worked out by Kabachnic[4,5] who proposed the common scheme of equilibrium in systems of such type:

$$A_1H + S \xleftrightarrow{I} A_1HS \xleftrightarrow{II} A_1^- \cdot HS^+ \xleftrightarrow{III} A_2HS \xrightarrow{IY} A_2H + S$$

$$\updownarrow III\,a \qquad\qquad [9.3]$$

$$A_1^- + HS^+$$

The scheme [9.3] includes the following stages occurring in sequence:

I   interaction of the first tautomeric form, A_1H, with the solvent that leads to formation of a addition product, A_1HS, (the solvate composition may be more complicated)

II   ionization of solvate with formation of ionic couple, $A_1^-HS^+$

III   ionic couple may decompose into ions (stage III a), transfer of ionized complex into a product of solvent addition already in the second tautomeric form

IV   formation of the free tautomeric form, $A_2H\ A_2H$.

The nature of the chemical type of influences on keto-enol equilibrium is obvious: the more basic the solvent, the higher the degree of keto-enol transformation into enol form. If solvent is indifferent with enough degrees of approximation, the well-defined dependence of the constants of keto-enol equilibrium on solvent permittivity is encountered. The difference in dipole moments of tautomeric forms is the basis of these relationships.

In mixed solvents such as ACR-B, the first component may undergo rearrangement reactions:

$$ACR \leftrightarrow ARC \qquad\qquad\qquad [9.4]$$

These occur under the solvent influence or even with its direct participation:

$$ACR \xleftarrow{\ +B\ }\rightarrow \cdots \xleftarrow{\ +B\ }\rightarrow ARC \qquad\qquad\qquad [9.4a]$$

9.2.3 HETEROMOLECULAR ASSOCIATION

When components of the binary solvent A-B are solvent-active to one another, the sum of chemical equilibrium is established:

$$mA + nB \leftrightarrow A_mB_n \qquad\qquad\qquad [9.5]$$

In most scenarios, the interaction proceeds in steps, i.e., equilibrium solution represents the mixture of heteroassociates of different stoichiometry: AB, AB_2, A_2B, etc. Systems formed by O-, S-, N-, P-bases with various H-donors (e.g., amines-carboxylic acids, esters-carboxylic acids (phenols), dimethylsulfoxide-carboxylic acid) refer to this type of interaction.

The systems having components which interact by means of donor-acceptor bond (without proton transfer) belong to the same type of solvents (e.g., pyridine-chloracetyl, dimethylsulfoxide-tetrachloroethylene, etc.). Components of mixed solvents of such type are more or less associated in their individual states. Therefore, processes of heteromolecular association in such solvents occur along with processes of homomolecular association, which tend to decrease heteromolecular associations.

9.2.4 HETEROMOLECULAR ASSOCIATE IONIZATION

In some cases, rearrangement of bonds leads to formation of electro-neutral ionic associate in binary solvents where heteromolecular associates are formed:

$$A_mB_n \leftrightarrow K_p^{q+}L_q^{p-} \qquad\qquad\qquad [9.6]$$

In many cases, ionic associate undergoes the process of ionic dissociation (see paragraph 9.2.5). If permittivity of mixture is not high, interaction can limit itself to formation of non-ionogenic ionic associate, as exemplified by the binary solvent anisol-m-cresol, where the following equilibrium is established:
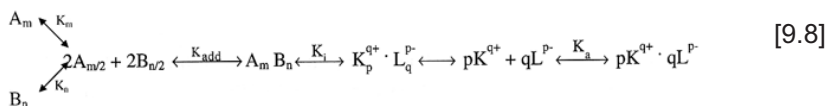
$$C_6H_5OCH_3 + CH_3C_6H_4OH \leftrightarrow C_6H_5OCH_3 \bullet CH_3C_6H_4OH \leftrightarrow [C_6H_5OCH_3 \bullet H]^+ \bullet CH_3C_6H_4O^-$$

9.2.5 ELECTROLYTIC DISSOCIATION (IONIC ASSOCIATION)

In solvents having high permittivity, the ionic associate decomposes into ions (mostly associated) to a variable degree:

$$K_p^{q+}L_q^{p-} \leftrightarrow K_{p-1}^{q+}L_{q-1}^{p-} + K^{q+} + L^{p-} \leftrightarrow \cdots \leftrightarrow pK^{q+} + qL^{p-} \qquad [9.7]$$
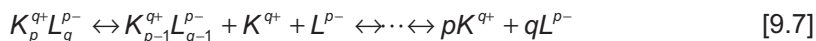
Electrolyte solution is formed according to eq. [9.7]. Conductivity is a distinctive feature of any material. The practice of application of individual and mixed solvents refers to electrolyte solutions, having conductivities $> 10^{-3}$Cm/m. Binary systems, such as carbonic acids-amines, cresol-amines, DMSO-carbonic acids, hexamethyl phosphorous triamide acids, and all the systems acids-water, are the examples of such solvents.

The common scheme of equilibrium in binary solvents, where components interaction proceeds until ions formation, may be represented by the common scheme:

$$\begin{array}{c}A_m \searrow^{K_m} \\ 2A_{m/2} + 2B_{n/2} \xleftarrow{K_{add}} A_m B_n \xleftarrow{K_i} K_p^{q+} \cdot L_q^{p-} \longleftrightarrow pK^{q+} + qL^{p-} \xleftarrow{K_a} pK^{q+} \cdot qL^{p-} \\ B_n \nearrow_{K_n}\end{array} \qquad [9.8]$$

where:

K_m, K_n	the constants of homomolecular association; respectively
K_{add}	the constant of the process formation of heteromolecular adduct
K_i	the ionization constant
K_a	the association constant.

The system acetic acid-pyridine[4] may serve as an example of binary solvent whose equilibrium constants of all stages of the scheme [9.8] have been estimated.

9.2.6 REACTIONS OF COMPOSITION

As a result of interaction between components of mixed solvents, profound rearrangement of bonds takes place. The process is determined by such high equilibrium constant that it is possible to consider the process as practically irreversible:

$$mA + nB \rightarrow pC \qquad [9.9]$$

where:

m, n, p	stoichiometric coefficients
C	compound formed from A and B

Carbonic acid anhydrides-water (e.g., $(CH_3CO)_2O + H_2O \rightarrow 2CH_3COOH$), systems isothiocyanates-amines (e.g., $C_3H_5NCS + C_2H_5NH_2 \rightarrow C_2H_5NHCNSC_3H_5$) are examples of such binary solvents.

It is pertinent that if solvents are mixed at stoichiometric ratio (m/n), they form individual liquid.

9.2.7 EXCHANGE INTERACTION

Exchange interaction

$$mA + nB \leftrightarrow pC + qD \tag{9.10}$$

is not rare in the practice of application of mixed solvents. Carbonic acid-alcohol is an example of the etherification reaction. Carbonic acid anhydride-amine exemplifies acylation process $(CH_3CO)_2O + C_6H_5NH_2 \leftrightarrow C_6H_5NHCOCH_3 + CH_3COOH$; carbonic acid-another anhydride participate in acylic exchange: $RCOOH + (R_1CO)_2O \leftrightarrow RCOOCOR_1 + R_1COOH$. The study of the exchange interaction mechanism gives forcible argument to believe that in most cases the process goes through formation of intermediate - "associate":

$$mA + nB \leftrightarrow [A_m B_n] \leftrightarrow pC + qD \tag{9.11}$$

9.2.8 AMPHOTERISM OF MIXED SOLVENT COMPONENTS

The monograph of one of the authors of this chapter[7] contains a detailed bibliography of works related to this paragraph.

9.2.8.1 Amphoterism of hydrogen acids

In the first decades of the 20th century, Hanch ascertained that compounds which are typical acids show distinctly manifested amphoterism in water solutions while they interact with one another in the absence of solvent (water in this case). Thus, in binary solvents H_2SO_4-CH_3COOH and $HClO_4$-CH_3COOH-acetic acid accepts proton forming acylonium, CH_3COOH^{2+}, cation. At present time, many systems formed by two hydrogen acids are being studied. In respect to one of the strongest mineral acids, CF_3SO_3H, all mineral acids are bases. Thus, trifluoromethane sulfuric acid imposes its proton even on sulfuric acid, forcing it to act as a base:[8]

$$CF_3SO_3H + H_2SO_4 \leftrightarrow CF_3SO_3^- \bullet H_3SO_4^+$$
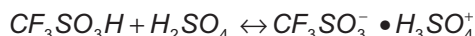
Sulphuric acid, with the exception of the mentioned case, and in the mixtures with perchloric acid (no proton transfer), shows acidic function towards all other hydrogen acids.

The well-known behavior of acidic function of absolute nitric acid towards absolute sulphuric acid is a circumstance widely used for the nitration of organic compounds.

Trifluoroacetic acid reveals proton-acceptor function towards all strong mineral acids, but, at the same time, it acts as an acid towards acetic and monochloroacetic acids.

In mixed solvents formed by two aliphatic carbonic acids, proton transfer does not take place and interaction is usually limited to a mixed associate formation, according to the equilibrium [9.2].

9.2.8.2 Amphoterism of L-acids

In binary liquid mixtures of the so-called aprotic acids (Lewis acids or L-acids) formed by halogenides of metals of III-IV groups of the periodic system, there are often cases when one of the components is an anion-donor (base) and the second component is an anion-acceptor (acid):

$$M_I X_m + M_{II} X_n \leftrightarrow M_I X_{m-1}^+ + M_{II} X_{n+1}^- \tag{9.12}$$

The following is an example of eq. [9.12]: In the mixture $AsCl_3$ - $SnCl_4$, stannous tetrachloride is a base and arsenic trichloride is an acid:

$$2AsCl_3 + SnCl_4 \leftrightarrow \left(AsCl_2^+ \right)_2 \bullet SnCl_6^{-2}$$
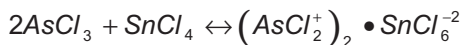
9.2.8.3 Amphoterism in systems H-acid-L-acid

Amphoterism phenomenon is the mechanism of acid-base interaction in systems formed by H-acids or two L-acids in binary systems. For example, in stannous tetrachloride-carboxylic acid system, acid-base interaction occurs with $SnCl_4$ being an acid:

$$SnCl_4 + 2RCOOH \leftrightarrow \left[SnCl_4 (RCOO)_2 \right] H_2$$
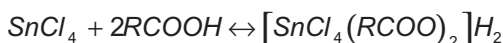
The product of this interaction is such a strong hydrogen acid that it is neutralized by the excess of RCOOH:

$$\left[SnCl_4 (RCOO)_2 \right] H_2 + RCOOH \leftrightarrow \left[SnCl_4 (RCOO)_2 \right] H^- + RCOOH_2^+$$
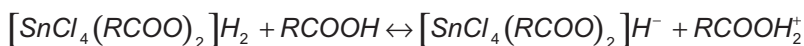
The mechanism of acid-base interaction in binary solvents of the mentioned type depends often on component relation. In systems such as stannous pentachloride-acetic acid, diluted by $SbCl_5$ solutions, interaction proceeds according to the scheme:
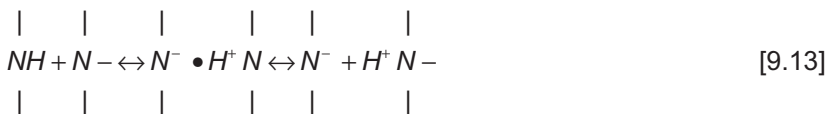
$$2SbCl_5 + 4HAc \leftrightarrow SbCl_3 Ac_2 + SbCl_6^- + Cl^- + 2H_2 Ac^+$$

In solutions of moderate concentrations, the following scheme is correct:

$$2SbCl_5 + 2HAc \leftrightarrow SbCl_4 Ac + Cl^- + H_2 Ac^+$$

9.2.8.4 Amphoterism in binary solutions amine-amine

If amines differ substantially in their energies of proton affinity, one of them has a proton-donor function in binary mixtures of these amines, so that it acts as an acid:

$$\begin{matrix} | & & | & & | & & | & & | & & | \\ NH & + & N & - & \leftrightarrow & N^- & \bullet & H^+ & N & \leftrightarrow & N^- & + & H^+ & N & - \\ | & & | & & | & & | & & | & & | \end{matrix} \qquad [9.13]$$

In the overwhelming majority of cases, this acid-base interaction limits itself only to the first stage - formation of heteromolecular adduct. Interactions occurring in all stages of the scheme [9.13] are typical of binary solvents such as triethylene amine-pyridine or N-diethylaniline. Proton-donor function towards the amine component reveals itself distinctly in the case of diphenylamine.

To conclude the section discussing amphoterism in binary solvents, we have constructed a series of chemical equilibria that help to visualize the meaning of amphoterism as a common property of chemical compounds:

base		acid		
Et_3N	+	$PhNH_2$	$\leftrightarrow$	$Et_3N \cdot PhNH_2$
$PhNH_2$	+	Ph_2NH	$\leftrightarrow$	$PhNH_2 \cdot Ph_2NH$
Ph_2NH	+	H_2O	$\leftrightarrow$	$Ph_2NH \cdot H_2O$
H_2O	+	HAc	$\leftrightarrow \cdots \leftrightarrow$	$H_3O^+ + Ac^-$
HAc	+	CF_3COOH	$\leftrightarrow \cdots \leftrightarrow$	$H_2Ac^+ + CF_3COO^-$
CF_3COOH	+	HNO_3	$\leftrightarrow$	$CF_3COOH \cdot HNO_3$
HNO_3	+	H_2SO_4	$\leftrightarrow$	$H_2NO_3^+ + HSO_4^-$ *
H_2SO_4	+	CF_3SO_3H	$\leftrightarrow$	$H_3SO_4^+ + CF_3SO_3^-$

*The first stage of absolute sulfuric and nitric acids

9.3 PHYSICAL PROPERTIES OF MIXED SOLVENTS

9.3.1 THE METHODS OF EXPRESSION OF MIXED SOLVENT COMPOSITIONS

In the practice of study and application of mixed solvents the fractional (percentage) method of composition expression, according to which the fraction, Y, or percentage, Y*100, of i-component in mixed solvent are equal, is the most common:

$$Y_i = c_i \, / \sum_{i=1}^{i=i} c_i \qquad\qquad [9.14]$$

$$Y_i = \left(c_i \, / \sum_{i=1}^{i=i} c_i \right) \times 100\% \qquad\qquad [9.14a]$$

where:
$\quad$ c $\qquad$ a method of composition expression.

The volume fraction, V, of a given component in the mixture equals to:

$$V_i = v_i \, / \sum_{i=1}^{i=i} v_i \qquad\qquad [9.15]$$

where:
v $\qquad$ initial volume of component
$\quad$ Molar fraction, X, equals

$$X = m_i \, / \sum_{i=1}^{i=i} m_i \qquad\qquad [9.16]$$

where:

    m   the number of component moles.

    Mass fraction, P, equals to:

$$P = g_i \ / \sum_{i=1}^{i=i} g_i \qquad\qquad [9.17]$$

where:

    g   mass of a component.

It is evident that for a solvent mixture, whose components do not interact:

$$\sum V = \sum X = \sum P = 1 \qquad\qquad [9.18]$$

and expressed in percent

$$\sum V_{100} = \sum X_{100} = \sum P_{100} = 100 \qquad\qquad [9.19]$$

Fractions (percentage) [9.19] of mixed solvents, since they are calculated for initial quantities (volumes) of components, are called analytical. In the overwhelming majority of cases, analytical fractions (percentages) are used in the practice of mixed solvents application.

However, in mixed solvents A-B, whose components interact with formation of adducts, AB, AB$_2$, it is possible to use veritable fractions to express their composition. For example, if the equilibrium A+B $\leftrightarrow$ AB establishes, veritable mole fraction of A component equals to:

$$N_A = m_A \ / \left(m_A + m_B + m_{AB}\right) \qquad\qquad [9.20]$$

where:

    m$_i$ number of moles of equilibrium participants

In the practice of mixed solvents application, though more seldom, molar, c_M, and molal, c_m, concentrations are used. Correlations between these various methods of concentration expression are shown in Table 9.1.

Table 9.1. Correlation between various methods of expression of binary solvent A-B concentration (everywhere - concentration of component A)

Function	Argument				
	x	**V**	**P**	**c$_M$**	**c$_m$**
x		$V\theta_B / (\theta_A - \sigma_\theta V)$	$PM_B / (M_A - \sigma_M P)$	$c_M\theta_B / (10^3\rho - c_M\sigma_M)$	$c_m M_B / (10^3 + c_m M_B)$
V	$x\theta_A / (\sigma_\theta x + \theta_B)$		$P\rho_B / (\rho_A - \sigma_\rho P)$	$c_M\theta_A / 10^3$	$c_m M_B\theta_A / (10^3\theta_B + c_m M_B\theta_A)$
P	$xM_A / (\sigma_M x + M_B)$	$V\rho_A / (\sigma_\rho V + \rho_B)$		$c_M M_A / 10^3\rho$	$c_m M_A / (10^3 + c_m M_A)$
c$_M$	$10^3\rho x / (\sigma_M x + M_B)$	$10^3 V / \theta_A$	$10^3\rho P / M_A$		$10^3\rho c_m / (10^3 + c_m M_A)$
c$_m$	$10^3 x / M_B(1 - x)$	$10^3\theta_B V / M_B\theta_A(1 - V)$	$10^3 P / M_A(1 - P)$	$10^3 c_M / (10^3\rho - M_A c_M)$	

σ is the difference between the corresponding properties of components, i.e., $\sigma_y = y_A - y_B$, ρ is density, and θ is molar volume.

9.3.1.1 Permittivity

In liquid systems with chemically non-interacting components, molar polarization, P_M, according to definition, is additive value; expressing composition in molar fractions:

$$P_M = \sum_{i=1}^{i=i} P_{M_i} x_i \qquad [9.21]$$

where:

$\quad$ x_i $\qquad$ molar fraction of corresponding mixture component

In the case of binary solvent system:

$$P_M = P_{M_1} x + P_{M_2} (1-x) = \left(P_{M_1} - P_{M_2}\right) x + P_{M_2} \qquad [9.21a]$$

where:

$\quad$ x $\qquad$ molar fraction of the first component.

Here and further definitions indices without digits relate to additive values of mixture properties and symbols with digits to properties of component solvents. As

$$P_M = f(\varepsilon) M / \rho = f(\varepsilon) \theta$$

then $\qquad f(\varepsilon)\theta = \sum_{1}^{i} f(\varepsilon_i)\theta_i x_i \qquad [9.22]$

or for binary solvent

$$f(\varepsilon)\theta = f(\varepsilon_1)\theta_1 x + f(\varepsilon_2)\theta_2 (1-x) \qquad [9.22a]$$

where:

$\quad$ M $\qquad$ an additive molecular mass
$\quad$ ρ $\qquad$ density
$\quad$ θ $\qquad$ molar volume
$\quad$ $f(\varepsilon)$ $\qquad$ one of the permittivity functions, e.g., $1/\varepsilon$ or $(\varepsilon - 1)/(\varepsilon + 2)$

In accordance with the rules of transfer of additive properties from one way of composition expression to another[3] based on [9.22], it follows that

$$f(\varepsilon) = \sum_{1}^{i} f(\varepsilon_i) V_i \qquad [9.23]$$

and for a binary system

$$f(\varepsilon) = f(\varepsilon_1) V + f(\varepsilon_2)(1-V) \qquad [9.23a]$$

where:

$\quad$ V $\qquad$ the volume fraction.

Substituting $f(\varepsilon)$ function into [9.23], we obtain volume-fractional additivity of permittivity

$$\varepsilon = \sum_{1}^{i} \varepsilon_i V_i \qquad \qquad [9.24]$$

or for binary solvent

$$\varepsilon = \varepsilon_1 V + \varepsilon_2 (1 - V) \qquad \qquad [9.24a]$$

Vast experimental material on binary liquid systems[1,2,3] shows that the equation [9.24] gives satisfactory accuracy for systems formed of components non-associated in individual states. For example, dielectric permittivity describes exactly systems n-hexane-pyridine, chlorobenzene-pyridine by equation [9.24a]. For systems with (one or some) associated components, it is necessary to consider fluctuations, which depend on concentration, density, orientation, etc. Consideration of ε fluctuations shows that calculation of dielectric permittivity for mixture of two chemically non-interacting liquids requires $\Delta\varepsilon$-values determined from equation [9.24a] and substituted to equation:

$$\Delta\varepsilon = (\varepsilon_1 - \varepsilon_1)^2 (\Delta\bar{\rho}) / [\varepsilon(2 + \delta_\varepsilon)] \qquad \qquad [9.25]$$

where:

$\Delta\bar{\rho}$	fluctuation of density
δ_ε	$= (\partial\varepsilon_{Add}/\partial V)/(\partial\varepsilon_{exp}/\partial V)$
$\varepsilon_1, \varepsilon_2$	dielectric permittivities of individual components
ε_{Add}	additive value
ε_{exp}	experimental value

The $\Delta\varepsilon$ value may be calculated from a simplified equation. For equal volume mixtures (V=0.5) of two solvents:

$$\Delta\varepsilon_{V=0.5} = 0.043(\varepsilon_1 - \varepsilon_2)^2 / \varepsilon_{V=0.5} \qquad \qquad [9.25a]$$

Thus, permittivity of equivolume mixture of two chemically non-interacting solvents can be calculated from the equation

$$\varepsilon_{V=0.5} = 0.5(\varepsilon_1 - \varepsilon_2) + \varepsilon_2 - \Delta\varepsilon_{V=0.5} \qquad \qquad [9.26]$$

Having ε values of both initial components and the ε value for the mixture, it is not difficult to interpolate these values for mixtures for any given composition.

For systems formed of two associated liquids, there are no reliable methods of ε isotherms calculation. An empirical method has been proposed, which is based on the assumption that each associated component mixed with the other associated component that does not interact chemically with the first one introduces the rigorously defined contribution into ε deviation from the volume-fractional additivity. The extent of these deviations for the first representatives of the series of aliphatic carbonic acids and alcohols of normal structure, as well as for some phenols, are given elsewhere.[3]

Permittivity of mixtures at different temperatures can be calculated with high accuracy from absolute temperature coefficients of permittivity and their values using equations identical in form to [9.24]- [9.26]. For example, the calculation of temperature coefficients

of permittivity, α_ε, of the equivolume mixture of two chemically non-interacting associated solvents is carried out using the equation identical in its form to [9.26].

$$\Delta\alpha_{\varepsilon,V=0.5} = 0.5\left(\alpha_{\varepsilon_1} - \alpha_{\varepsilon_2}\right) + \alpha_{\varepsilon_2} - \Delta\alpha_{\varepsilon,V=0.5} \qquad [9.27]$$

where

$$\Delta\alpha_{\varepsilon,V=0.5} = 0.043\left(\alpha_{\varepsilon_1} - \alpha_{\varepsilon_2}\right) / \alpha_{\varepsilon,V=0.5} \qquad [9.28]$$

9.3.1.2 Viscosity

There are a great number of equations available in literature intended to describe viscosity of mixtures of chemically non-interacting components. All these equations, regardless of whether they have been derived theoretically or established empirically, are divided into two basic groups. The first group includes equations relating mixture viscosity, η, to viscosity of initial components, η_i, and their content in mixture, c, (c in this case is an arbitrary method of concentration expression):

$$\eta = f\left(\eta_1, \eta_2, \cdots \eta_i; \quad c_1, c_2, \cdots c_{i-1}\right) \qquad [9.29]$$

The equations of the second group include various constants k_1, k_2, etc., found from experiment or calculated theoretically

$$\eta = f\left(\eta_1, \eta_2, \cdots \eta_i; \quad c_1, c_2, \cdots c_{i-1}; \quad k_1, k_2, \cdots\right) \qquad [9.30]$$

The accuracy of calculation of solvents mixture viscosity from [9.30] type of equations is not higher than from equations of [9.29] type. We, thus, limit discussion to equations [9.29].

The comparison of equations of type [9.29] for binary liquid systems[3] has shown that, in most cases, viscosity of systems with chemically non-interacting components is described by the exponential function of molar-fractional composition

$$\eta = \prod_1^i \eta_i^{x_i} \qquad [9.31]$$

or for binary solvent:

$$\eta = \eta_1^x \eta_2^{1-x} \qquad [9.31a]$$

where:

x_i molar fractions of components of the binary system

Empirical expressions for calculation of viscosity of the system of a given type, which permit more precise calculations, are given in monograph.[3]

From [9.31], it follows that the relative temperature coefficient of viscosity $\beta_\eta = \partial\eta / \eta\partial T = \partial\ln\eta / \partial T$ for mixtures of chemically non-interacting liquids is described by equation:

$$\beta_\eta = x\beta_{\eta_1} + (1-x)\beta_{\eta_2} \qquad [9.32]$$

9.3.1.3 Density, molar volume

According to the definition, a density, ρ, of system is the volume-additive function of composition:

$$\rho = \sum_1^i \rho_i V_i \qquad\qquad [9.33]$$

or for binary system:

$$\rho = \rho_1 V_1 + \rho_2 (1-V_1) \qquad\qquad [9.33a]$$

From [9.33], it follows that molar volume of ideal system is a molar-additive function of composition:

$$\theta = \sum_1^i \theta_i x_i \qquad\qquad [9.34]$$

Molar mass of mixture, according to the definition, is a molar-additive function too:

$$M = \sum_1^i M_i x_i \qquad\qquad [9.35]$$

For two-component mixture of solvents, these relations are as follows:

$$\theta = \theta_1 x + \theta_2 (1-x) \qquad\qquad [9.36]$$

$$M = M_1 x + M_2 (1-x) \qquad\qquad [9.37]$$

Non-ideality of the system leads to relative deviations of density and molar volume, as well as of other volumetric properties, having magnitude of about 1%. Here, contraction and expansion of solutions are approximately equiprobable. In systems in conditions close to separation, considerable contraction is possible. However, two component systems formed from the most common solvents, used in practical applications, form solutions far from separation at usual temperature range.

Taking into account the linear density dependence on temperature in equations [9.33] and [9.34], it is possible to calculate values of density and molar volume at any given temperature.

9.3.1.4 Electrical conductivity

High conductivity of solvent mixture formed from chemically non-interacting components may be related to the properties of only one or both components. Very high conductivity of mineral acids, carboxylic acids, some complexes of acids with amines, stannous chloride, and some tetraalkylammonium salts increases conductivity of their mixtures with other solvents.[3]

Normal practice does not often deal with mixed solvents of such high conductivity. Therefore, the theory of concentration dependence of conductivity of binary solvents is briefly discussed here.[3,10]

Two basic factors which influence conductivity of binary solvent mixture are viscosity and permittivity. The influence of these factors on specific conductivity is quantitatively considered in empirical equation:

$$\kappa = 1/\eta \exp\left[\ln \kappa_1 \eta_1 - L(1/\varepsilon - 1/\varepsilon_1)\right]$$ [9.38]

where:

κ	conductivity (symbols without index belong to the mixture properties, index 1 belongs to electrolyte component)
L	$= a\varepsilon_1\varepsilon_2 / (\varepsilon_1 - \varepsilon_2)$
a	proportionality coefficient

and in non-empirically equation:

$$\ln \kappa = const_1 + 1/\varepsilon(const_2 + const_3 + const_4) + 1/2\ln c - \ln\eta$$ [9.39]

where:

c	concentration, mol l^{-1}
consts	calculated from the equations[11] based on crystallographic radii of the ions, dipole moments of molecules of mixed solution, and ε of mixture components

From equations [9.38] and [9.39], it follows that isotherms of the logarithm of conductivity corrected for viscosity and concentration $\ln\kappa\eta c^{-1/2}$ have to be a linear function of reciprocal ε. Validity of this assumption is confirmed in Figure 9.1. Control of properties of multi-component mixture of solvents is achieved by methods of optimization based on analytical dependencies of their properties in composition:

$$y^I = f\left(y_1^I, y_2^I, \cdots c_1, c_2, \cdots c_{i-1}\right), \quad y^{II} = f\left(y_1^{II}, y_2^{II}, \cdots c_1, c_2 \cdots c_{i-1}\right)$$ [9.40]

where:

y^I, y^{II}	any property of solvent
y_1^I, y_2^{II}	initial property of solvent

Concentration dependencies of permittivity, viscosity, density (molar volume) and conductivity described here permit to select with certainty the composition of mixed solvent, characterized by any value of mentioned properties.
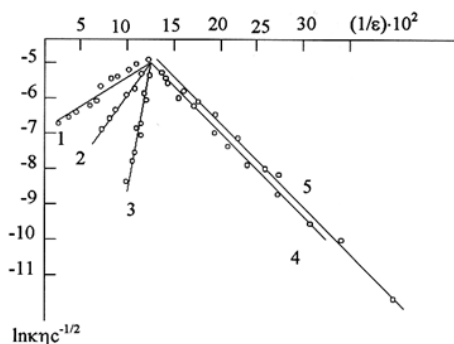

Figure 9.1. Dependencies $\ln\kappa\eta c^{-1/2}$ on $1/\varepsilon$ at 393.15K for systems containing tetrabutylammoniumbromide and aprotic solvent (1-nitromethane, 2-acetonitrile, 3-pyridine, 4-chlorobenzene, 5-benzene).

9.3.2 PHYSICAL CHARACTERISTICS OF THE MIXED SOLVENTS WITH CHEMICAL INTERACTION BETWEEN COMPONENTS

In this section, we discuss physical characteristic change due to the changes of binary mixed solvent composition in the systems with chemical interactions between components (these systems are the most commonly used in science and technology). Comprehensive discussion of the physical and chemical analysis of such systems, including stoichiometry and stability constants, determination of the formation of heteromolecular
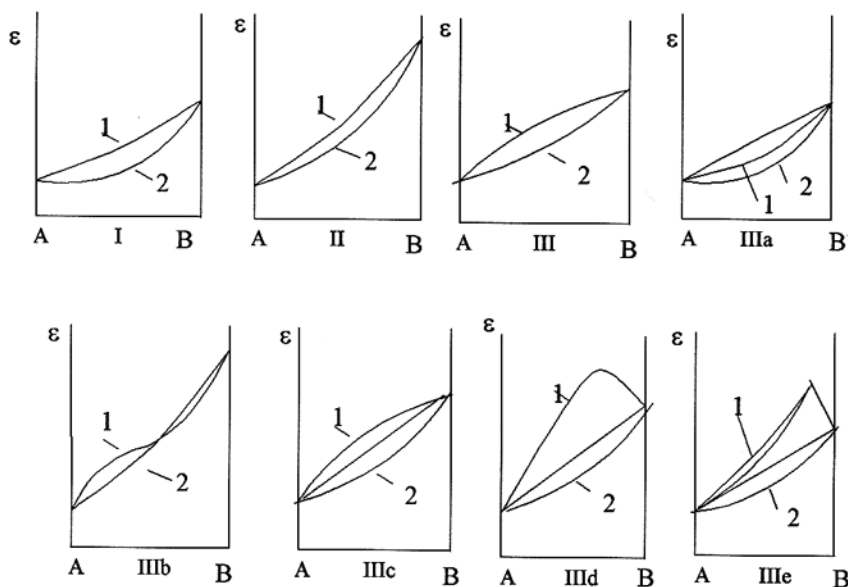
Figure 9.2. Classification of permittivity isotherms for binary solvents: 1 and 2 - isotherms for systems with interaction and without interaction, respectively.

associates can be found in a specialized monograph.[3]

In theory, if composition of the mixture is known, then calculation of any characteristic property of the multi-component mixture can be performed by the classical physical and chemical analysis methods.[3] For binary liquid system, it is possible only if all chemical forms (including all possible associates), their stoichiometry, stability constants, and their individual physical and chemical properties are well determined. A large volume of correct quantitative thermodynamic data required for these calculations is not available. Due to these obstacles, data on permittivity, viscosity and other macro-properties of mixed solvents with interacting components are obtained by empirical means. Data on empirical physical properties of liquid systems can be found in published handbooks.[1,2,10] Principles of characteristic changes due to the compositional change of liquid mixtures with interacting components are discussed here. Assessment of nature of such interactions can only be made after evaluation of the equilibrium constant (energy) of such interactions between solvents.

9.3.2.1 Permittivity

Permittivity, ε, is the only property of the mixed liquid systems with chemical interaction between components that has not been studied as extensively as for systems without chemical interaction.[10] When interaction between components is similar to a given in equation [9.8], formation of conductive solutions occurs. Determination of ε for these solutions is difficult, and sometimes impossible. Although, more or less successful attempts to develop such methods of permittivity determination are published from time to time, the problem until now has not been solved.

Classification of the isotherms ε vs. composition of liquid systems[3] is based on deviations of the experimental isotherms, which are then compared with isotherms of the system

without chemical interaction between components. The latter isotherms are calculated from equations [9.24] - [9.26], (Figure 9.2).

Type I isotherm corresponds to the experimental isotherm with isotherms [9.24] or [9.26] of the liquid systems without interaction. The additive ε increase is compensated by ε decrease, due to homomolecular association process. The system diethyl ether - m-cresol illustrates this type of isotherm.

Type II is determined by the negative deviations from isotherm [9.26]. This type corresponds to systems with weak heteromolecular interactions between components, but with strong homomolecular association of one of the components. The system formic acid-anisole is an example of this kind of isotherm. Furthermore, these isotherms are characteristic when non-associating components in pure state form heteromolecular associates with lower dipole moment, DM, then DM of both components. The average DM for such kind of interaction in mixed systems is lower than correspondent additive value for non-interacting system. The system 1,2-dichloroethane - n-butylbromide can be referenced as an example of this kind of mixed binary solvent.

Type III combines ε isotherms, which are above the isotherm calculated from equation [9.26]. This kind of isotherm suggests interaction between components of mixed solvent. The variety of such systems allows us to distinguish between five isotherm subtypes.

Subtype IIIa is represented by isotherms lying between the curve obtained from eq. [9.26] and the additive line. This isotherm subtype occurs in systems with low value of heteromolecular association constant. The system n-butyric acid - water can be mentioned as a typical example of the subtype.

Subtype IIIb combines S-shaped ε isotherms. This shape is the result of coexistence of homo- and heteromolecular association processes. System pyridine-water is a typical example of this subtype.

Subtype IIIc combines most common case of ε isotherms - curves monotonically convex from the composition axis ($\partial\varepsilon / \partial V \neq 0, \partial^2\varepsilon / \partial V^2 < 0$). The system water-glycerol can serve as typical example of the subtype.

Subtype IIId is represented by ε isotherms with a maximum. Typically, this kind of isotherm corresponds to systems with high heteromolecular association constant. Component interaction results in associates with greater values of DM than expected from individual components. Carboxylic acids-amines have this type of isotherms.

Finally, subtype IIIe includes rare kind of ε isotherms with a singular maximum, which indicates equilibrium constant with high heteromolecular association. This kind of isotherm is represented by system $SnCl_4$-ethyl acetate.

9.3.2.2 Viscosity

Shapes of binary liquid system viscosity - composition isotherms vary significantly. The basic types of viscosity - composition isotherms for systems with interacting components are given in Figure 9.3.

Type I - viscosity isotherms are monotonically convex in direction to the composition axis ($\partial\eta / \partial x \neq 0, \partial^2\eta / \partial x^2 > 0$). Chemical interaction influences the shape of viscosity isotherm that is typical when experimental isotherm is situated above the curve calculated under assumption of absence of any interaction (i.e., from equation [9.31a]). The means of increasing heteromolecular association and determination of stoichiometry of associates for this type of isotherms was discussed elsewhere.[3] Piperidine-aniline system is an example of this kind of interacting system.
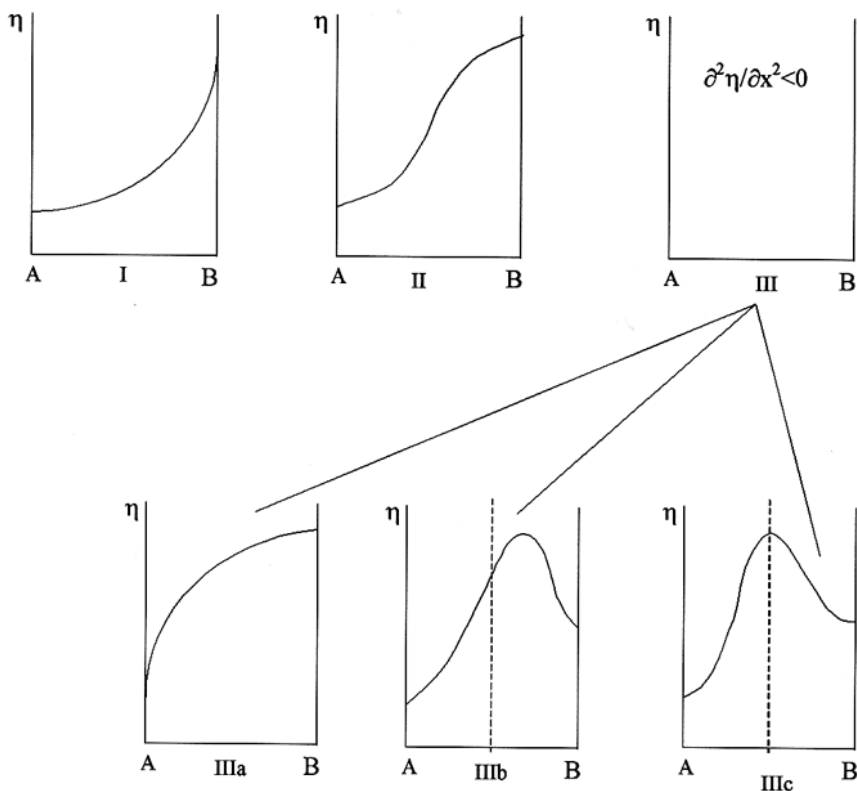
Figure 9.3. Classification of viscosity isotherms for binary solvents.

Type II - S-shaped viscosity curves ($\partial\eta / \partial x \neq 0, \partial^2\eta / \partial x^2 = 0$ at the inflection point). This type of isotherm is attributed to systems which have components differing substantially in viscosity, but have low yield of heteromolecular associates to form local maximum in isotherms. Systems such as sulfuric acid-pyrosulfuric acid and diphenylamine - pyridine are examples of this kind of viscosity isotherm.

Type III combines viscosity isotherms, which are convex-shaped from composition axis as its common attribute, i.e., $\partial^2\eta / \partial x^2 < 0$. In the whole concentration range, we have positive values of excessive viscosity $\eta^E = \eta_{exp} - [(\eta_1 - \eta_2)x + \eta_2]$, where η_{exp} is experimental value of viscosity. It shall be mentioned that, although the term η^E is used in literature, unlike the excessive logarithm of viscosity $(ln\eta)^E = ln\eta_{exp} - (ln\eta_1/\eta_2 + ln\eta_2)$, it has no physical meaning. Viscosity isotherms of this type for interacting liquid systems are most commonly encountered and have shape diversity, which can be divided into three subtypes.

Subtype IIIa - isotherms monotonically convex shaped from composition axis, but without maximum (in the whole composition range $\partial\eta / \partial x \neq 0$). Dependence viscosity-composition of water-monochloroacetic acid can serve as an example.

Subtype IIIb - isotherms with "irrational" maximum (i.e., with maximum which does not correspond to any rational stoichiometric correlation of components in mixed solvent). This subtype is the most common case of binary mixed solvents with interacting compo-

nents. System trifluoroacetic acid-acetic acid is common example. The true stoichiometry determination method for this case was described elsewhere.[3]

Subtype IIIc - isotherms with maximum at rational stoichiometry, which corresponds to composition of heteromolecular associate. This case can be exhibited by the system pyrosulfuric acid-monochloracetic acid.

Occasionally, isotherms with singular maximum can also occur. This behavior is characteristic of the system mustard oil-amine.

This classification covers all basic types of viscosity isotherms for binary mixed systems. Although the classification is based on geometrical properties of isotherm, heteromolecular associations determine specific isotherm shape and its extent. The relative level of interactions in binary mixed systems increases from systems with isotherms of type I to systems with type III isotherms.

9.3.2.3 Density, molar volume

Unlike the dependencies of density deviation (from additive values) on system composition, correspondent dependencies of specific (molar) volume deviation from the additive values:

$$\Delta\theta = \theta_{exp} - \left[(\theta_1 - \theta_2)x + \theta_2\right] \qquad\qquad [9.41]$$

where:

$\Delta\theta$ departure from of molar volume
θ_{exp} experimental value of molar volume
θ_i molar volumes of components
x   molar fraction of the second component

allow us to make a meaningful assessment of the heteromolecular association stoichiometry.[3] Classification of volume-dependent properties of binary mixed solvents are based on dependencies of $\Delta\theta$ value (often called "excessive molar volume", θ^E).

It is evident both from "ideal system" definition and from equation [9.36], that for non-interacting systems $\Delta\theta \approx 0$.

Interaction is accompanied by formation of the heteromolecular associates. It can be demonstrated by analysis of volumetric equations for the liquid mixed systems, data on volume compression, i.e., positive density deviation from additivity rule, and hence negative deviations of experimental specific molar volume from partial molar volume additivity rule.

There are three basic geometrical types of $\Delta\theta$ isotherms for binary liquid systems with chemically interacting components[12] (Figure 9.4.).

Type I - rational $\Delta\theta$ isotherms indicating that only one association product is formed in the system (or that stability constants for other complexes in system are substantially lower than for main adduct). Most often, adduct of equimolecular composition is formed, and the maximum on $\Delta\theta$ isotherm occurs at $x = 0.5$. Fluorosulfonic acid-trifluoroacetic acid system is an example of the type.

Type II - irrational $\Delta\theta$ isotherms with maximum not corresponding to the stoichiometry of the forming associate. This irrationality of $\Delta\theta$ isotherms indicates formation of more than one adduct in the system. In the case of formation of two stable adducts in the system, the $\Delta\theta$ maximum position is between two compositions which are stoichiometric for each associate. If in the system, two adducts AB and AB_2 are formed,
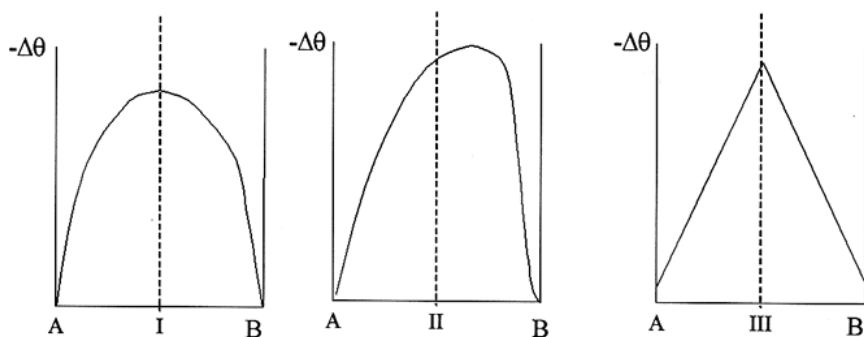
Figure 9.4. Classification of isotherms of molar volume deviation from additivity for binary solvents.

then $\Delta\theta$ position of maximum is between x_A values of 0.5 and 0.33 molar fractions. This type of $\Delta\theta$ isotherm is most common for interacting binary liquid systems, for example, di-ethyl aniline-halogen acetic acids.

Type III includes $\Delta\theta$ isotherms with a singular maximum. According to metrical analysis,[3] dependencies of this type are typical of systems where adduct formation constant, $K_f \to \infty$. Mustard oil-amine is an example of this behavior.

Relative extent of the interaction increases from systems with $\Delta\theta$ isotherms of type I to systems of type III isotherms. This conclusion comes from analysis of metrical molar volume equations and comparison of binary systems composed of one fixed component and a number of components, having reactivity towards fixed component changing in well-defined direction.

9.3.2.4 Conductivity

The shape of specific conductivity relation on composition of the binary mixed solvent depends on conductivity of the components and some other parameters discussed below. Because of molar conductivity calculation of binary mixed solvent system, the ion associate concentration should be taken into account (eq. [9.7]). This quantity is known in very rare instances,[13,14] therefore, the conductivity of interacting mixed solvent is most often expressed in specific conductivity terms.

Classification of conductivity shapes for binary liquid systems may be based on the initial conductivity of components. Principal geometrical types of the conductivity isotherms are presented in Figure 9.5.

The type I isotherm includes the concentration dependence of conductivity of the systems (Figure 9.5).

These systems are not often encountered in research and technology practice. The type I can be subdivided into subtype Ia - isotherms with a minimum (for example, selenic acid-orthophosphoric acid) and subtype Ib - isotherms with a maximum (for instance, orthophosphoric acid-nitric acid).

The type II isotherms describe the concentration dependence of conductivity for binary systems containing only one conductive component. In this case also, two geometric subtypes may be distinguished. Subtype IIa - has monotonically convex shape (i.e., without extreme) in the direction of the composition axis. The binary system, selenic acid-acetic acid, can serve as an example of this kind of dependency. Subtype IIb includes isotherms with a maximum (minimum) - most widespread kind of isotherms (for example: perchloric
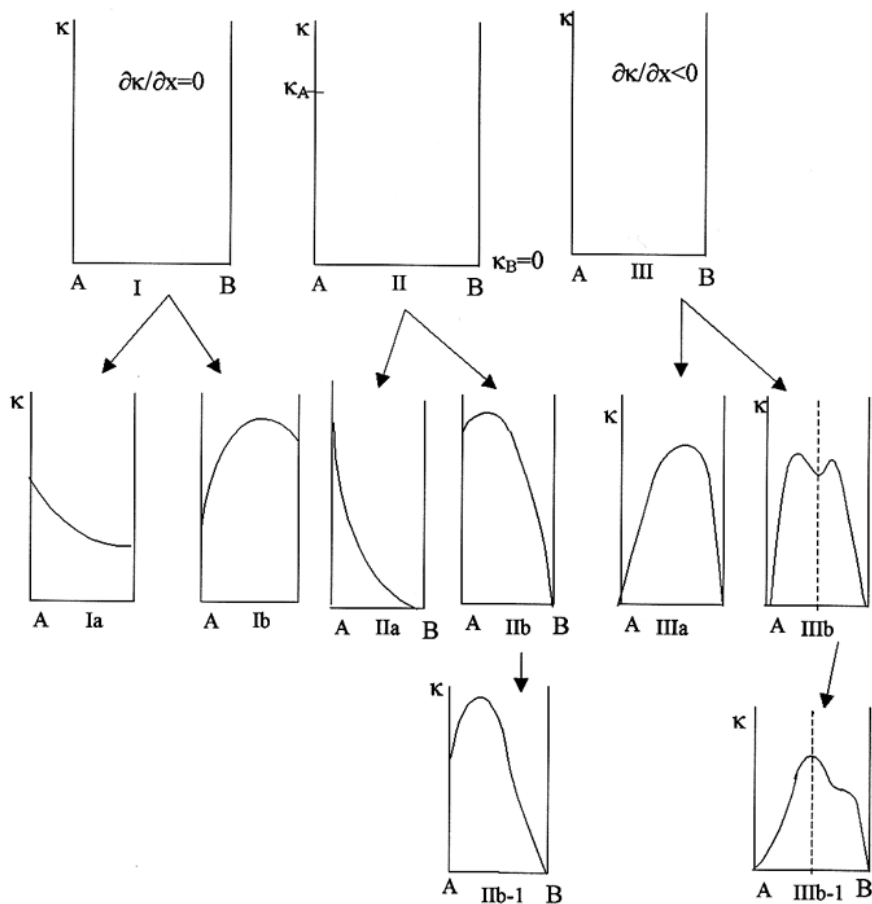
Figure 9.5.Classification of specific conductivity isotherms for binary solvents.

acid-trifluoroacetic acid). The next frequently observed case is separated as subtype IIb-1; these are isotherms with $\chi=0$ in the middle of concentration range. The system sulfuric acid-ethyl acetate illustrates the subtype IIb-1.

Geometrically, the conductivity isotherms of I and II types are similar to the χ isotherms for binary liquid systems without interaction (Section 9.3.1.4). But conductivity dependencies corrected for viscosity vs. the concentration of interacted system differ from the corresponding dependencies for non-interacting systems by the presence of maximum. Also, interacting and non-interacting systems differ based on analysis of effect of the absolute and relative temperature conductivity coefficients on concentration.[3] The relative temperature electric conductivity coefficient, β_{χ}, differs from the electric conductivity activation energy, E_{act}, by a constant multiplier.[15]

Systems formed by non-electrolyte components are the most common types of electrolyte systems.

Conductivity of the systems results from the interaction between components. This interaction proceeds according to the steps outlined in the scheme [9.8]. Conductivity of the mixed electrolyte solution confirms the interaction between components.

Subtype IIIa isotherms are the most widespread. Such isotherms have one maximum and bring the conductivity to the origin for pure components.

Subtype IIIb isotherms have a minimum situated between two maxima. The maximum appears because of the significant increase of the solution viscosity due to the heteromolecular association process. When the conductivity is corrected for viscosity, the maximum disappears. Conductivity of the mixed solvent pyrosulfuric acid-acetic acid is an example of the system.

Subtype IIIb-1 isotherms with a curve is a special case of subtype IIIb isotherms. The curve is caused by viscosity influence. Isotherm IIIb turns to subtype IIIb-1 at higher temperatures. A concentration dependence of conductivity for stybium (III) chloride-methanol is an example of the systems.

Determination of stoichiometry of interaction between the components of the mixed solvent is discussed elsewhere.[3,12]

9.3.3 CHEMICAL PROPERTIES OF MIXED SOLVENTS

Solvating ability of mixed solvent differs from solvating ability of individual components. In addition to the permittivity change and the correspondent electrostatic interaction energy change, this is also caused by a number of reasons, the most important of which are discussed in the chapter.

9.3.3.1 Autoprotolysis constants

Let both components of mixed solvent, AH-BH, to be capable of autoprotolysis process.

$$2HA \leftrightarrow H_2A^+ + A^- \qquad\qquad\qquad\qquad [9.42a]$$

$$2BH \leftrightarrow H_2B^+ + B^- \qquad\qquad\qquad\qquad [9.42b]$$

As Aleksandrov demonstrated,[15] the product of the activities of lionium ions sum $(a_{H_2A^+} + a_{H_2B^+})$ on the liate activities sum $(a_{A^-} + a_{B^-})$ is a constant value in the whole concentration range for a chosen pair of cosolvents. This value is named as ion product of binary mixed solvent.

$$K_{ap}^{HA-HB} = \left(a_{H_2A^+} + a_{H_2B^+}\right)\left(a_{A^-} + a_{B^-}\right) \qquad\qquad [9.43]$$

If components of binary mixed solvent are chemically interacting, then the equilibrium of protolysis processes [9.42] is significantly shifting to one or another side. In most such instances, concentrations of lionium ions for one of components and liate ions for another become so low that correspondent activities can be neglected, that is autoprotolysis constant can be expressed as:

$$K_{ap}^{HA-HB} = a_{H_2A^+} + a_{B^-} \qquad\qquad\qquad [9.44a]$$

$$K_{ap}^{HA-HB} = a_{H_2B^+} + a_{A^-} \qquad\qquad\qquad [9.44b]$$

As an example, let us consider mixed solvent water-formic acid. Both components of the system are subject to autoprotolysis:

$$2H_2O \leftrightarrow H_3O^+ + OH^- \quad \text{and} \quad 2HCOOH \leftrightarrow HCOOH_2^+ + HCOO^-$$
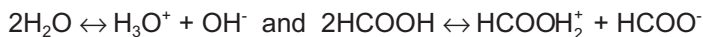
It is obvious, that in the mixed solvent, concentrations of the $HCOOH_2^+$ ions (strongest acid from possible lionium ions in the system) and the OH^- ions (strongest base from two possible liate ions) are neglected, because these two ions are mutually neutralized. Equilibrium constant of the direct reaction is very high:

$$HCOOH_2^+ + OH^- \leftrightarrow HCOOH + H_2O$$
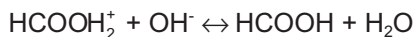
Therefore, in accordance with [9.44a] autoprotolysis constant for this mixed solvent can be expressed as:

$$K_{ap}^{HA-HB} = a_{H_3A^+} + a_{HCOO^-}$$

Because of lionium and liate ions activities, both mixed solvent components depend on solvent composition, as does autoprotolysis constant value for mixed solvent.

Figure 9.6 demonstrates dependencies of pK_{ap} values on composition for some mixed solvents. Using the dependencies, one can change the mixed solvent neutrality condition in a wide range. That is, for mixed solvent composed of DMSO and formic acid, neutrality condition corresponds to concentration of H^+ (naturally solvated) of about 3×10^{-2} g-ion*l^{-1} at 80 mol% formic acid, but only 10^{-4} g-ion*l^{-1} at 10 mol% acid component.

Figure 9.6. Dependence of pK_{ap} ($-logK_{ap}$) on the mixed solvent composition: 1-DMSO-formic acid; 2-DMSO-acetic acid; 3- formic acid-acetic acid.

The method of autoprotolysis constant value determination based on electromotive force measurement in galvanic element composed from Pt,H_2(1 atm)|KOH(m), KBr(m), solvent|AgBr,Ag was proposed elsewhere.[15a] The method was used for polythermal study of autoprotolysis constant of binary mixed solvent 2-methoxyetanol - water. On the basis of ionization constants, polytherms data, and the autoprotolysis process, thermodynamic data were calculated.

A large data set on the electrophility parameter E_T (Reichardt parameter[65]) for binary water-non-water mixed solvents was compiled.[66]
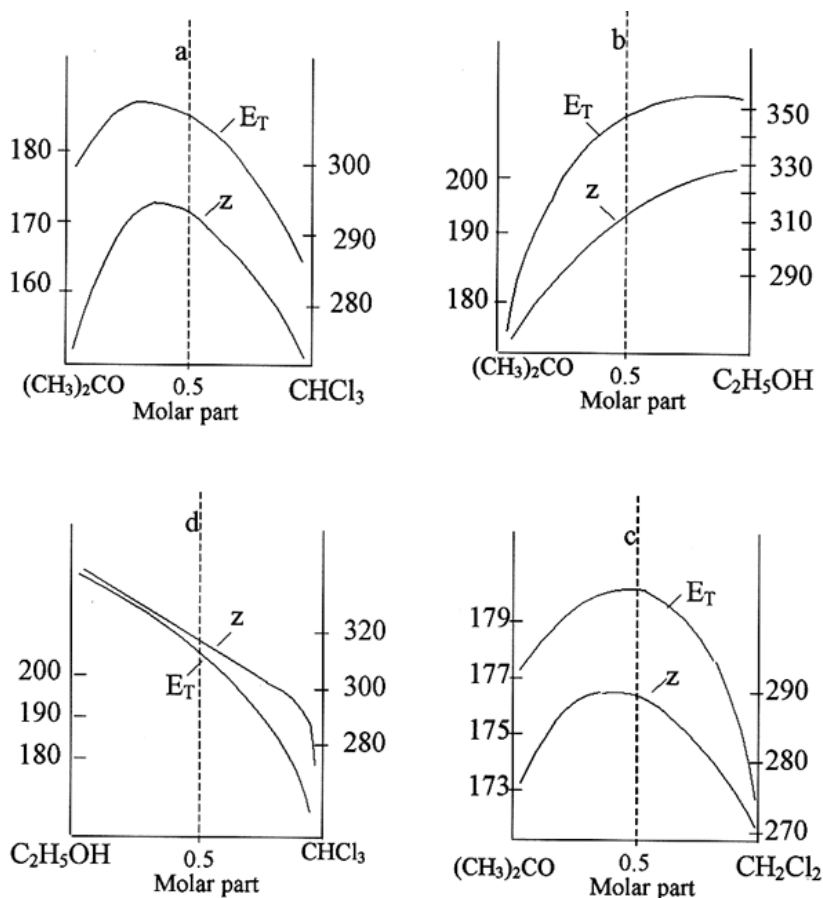
Figure 9.7. E_T and Z parameters for some mixed solvents.

9.3.3.2 Solvating ability

Applying the widely-used chemical thermodynamics concept of free energy linearity, it is easy to demonstrate that any characteristic y which linearly depends on free energy or on free activation energy of process in the mixed solvent composed of specifically non-interacting components, shall be linear function of the components with partial molar concentration x.

$$y = \sum_{1}^{i} y_i x_i \qquad\qquad [9.44]$$

The formula was developed analytically by Palm.[16] In the mixed solvents with chemically interacting components, the function y=f(x) can substantially deflect from the linear form including appearance of extrema.

Selection of the mixed solvent components allows us in most cases to provide controlled solvation of all substances, participating in the chemical process performed in solu-

tion. Often, it can be achieved by combination of solvate active and solvate inert components. For example, it is obvious that in all compositional range of mixture DMSO-CCl_4 (except 100% CCl_4) specific solvation of acid dissolved in this mixture is realized by DMSO. Similarly in mixed solvent formic acid-chlorobenzene, solvation of the dissolved donor substance is performed exclusively by formic acid.

Selection of the second (indifferent) component's ε also provides means to control the universal solvation ability of mixed solvent. In the above mentioned examples, increasing the solvate inert component concentration results in the decrease of mixed solvent ε. On the contrary, addition of indifferent component (propylene carbonate) into the systems such as acetic acid-propylene carbonate or propylene carbonate-aniline causes ε to rise. Because in the last two systems acetic acid and aniline were chosen as solvate active components, it was obviously intended to use these mixtures for specific solvation of the dissolved donor and acceptor compounds respectively.

9.3.3.3 Donor-acceptor properties

As was demonstrated,[17] the parameters E_T and Z of the binary mixed solvent 1,2-dibromoethane - 1,2-dibromopropane are strictly additive function of molar composition. For the mixed solvents, having components engaged into specific interaction, dependencies $E_T = f(x)$ and $Z = F(x)$ are non-linear and even extremal, as can be seen from the examples in Figure 9.7.

The method was proposed[18] to linearize polarity index of mixed solvent by introducing a parameter, which connects the E_T and Z values with fractional concentrations of components.

9.4 MIXED SOLVENT INFLUENCE ON THE CHEMICAL EQUILIBRIUM

9.4.1 GENERAL CONSIDERATIONS[7]

The chemical process established in a solvent can be represented in a general form:

$$E \leftrightarrow F \qquad [9.45]$$

where:

E	all chemical forms of reaction reagents
F	all chemical forms of reaction products

Considering the traditional thermodynamic cycle, we can use the general equation of Gibbs' energy variation because of the process [9.45]:

$$\Delta G = \Delta G_{solv,E} - \Delta G_{solv,F} - \Delta G^{(v)} \qquad [9.46]$$

where:

$\Delta G_{solv,E}, \Delta G_{solv,F}$	Gibbs' solvation energy of [9.45] equilibrium members
$\Delta G^{(v)}$	Gibbs' energy of process [9.45] in vacuum

The process [9.45] takes place in mixed solvent A-B. Solvation energies of equilibrium members are the algebraic sum of those for each of the mixed solvent components (this sum also takes into account the energy of mixed solvates such as EA_xB_y and FA_zB_t):

$$\Delta G_{solv,i} = \Delta G_{solv,A} + \Delta G_{solv,B} = \sigma_{solv,i} \qquad [9.47]$$

Therefore the equation [9.46] can be represented in the form

$$\Delta G = \sigma_{solv,E} - \sigma_{solv,F} - \Delta G^{(v)} \tag{9.48}$$

The variation of free energy due to any chemical process consists of both covalent and electrostatic components:

$$\Delta G = \Delta G^{(cov)} - \Delta G^{(el)} \tag{9.49}$$

Substituting [9.49] in [9.48], we come to an equation that in general describes the mixed solvent effect on the equilibrium chemical process:

$$\Delta G = -\Delta G^{(v)} + \left(\sigma_{solv,E}^{(cov)} - \sigma_{solv,F}^{(cov)} \right) + \left(\sigma_{solv,E}^{(el)} - \sigma_{solv,F}^{(el)} \right) \tag{9.50}$$

For universal (chemically indifferent) solvents where $\sigma^{(el)} >> \sigma^{(cov)}$, it may by assumed that

$$\Delta G = -\Delta G^{(v)} + \sigma_{solv,E}^{(el)} - \sigma_{solv,F}^{(el)} \tag{9.51}$$

Thus the mixed solvent effect on the equilibrium of the chemical process [9.45] is determined not only by the vacuum component but also by the solvation energy of each of the chemical forms of equilibrium members.

From free energy to equilibrium constants, one can obtain the equation describing mixed solvent effect on the equilibrium constant of the [9.45] process:

$$\ln K = \left[\Delta G^{(v)} + \left(\sigma_{solv,F}^{(cov)} - \sigma_{solv,E}^{(cov)} \right) + \left(\sigma_{solv,F}^{(el)} - \sigma_{solv,E}^{(el)} \right) \right] / RT \tag{9.52}$$

In the special case of universal media, i.e., mixed solvent formed by both solvation-inert components, this equation can be presented as:

$$\ln K^{(univ)} = \left[\Delta G^{(v)} + \sigma_{solv,f}^{(el)} - \sigma_{solv,E}^{(el)} \right] / RT \tag{9.53}$$

Because the energy of all types of electrostatic interaction is inversely proportional to permittivity, these equations can be rewritten in the form:

$$\ln K = \left[\Delta G^{(v)} + \left(\sigma_{solv,F}^{(cov)} - \sigma_{solv,E}^{(cov)} \right) + \left(\beta_{solv,F} - \beta_{solv,E} \right) / \varepsilon \right] / RT \tag{9.52a}$$

and

$$\ln K^{(univ)} = \left[\Delta G^{(v)} + \left(\beta_{solv,F} - \beta_{solv,E} \right) / \varepsilon \right] / RT \tag{9.53a}$$

where:

β	the multipliers of the magnitudes of reciprocal permittivity in equations of energy of the main types of electrostatic interactions such as dipole-dipole, ion-dipole, and ion-ion interactions

As follows from [9.52a], in binary mixed solvents formed from solvation-indifferent components (i.e., universal media), equilibrium constants of the [9.45] process are expo-

nent dependent on the $1/\varepsilon$ values (i.e., it is a linear correlation between $\ln K^{(univ)}$ and $1/\varepsilon$ magnitudes).

The vacuum component of energy of the [9.45] process can be obtained by the assumption of hypothetical media with $\varepsilon \to \infty$ and $1/\varepsilon \to 0$:

$$\Delta G^{(v)} = RT \ln K^{(univ)}_{1/\varepsilon \to 0} \qquad [9.54]$$

For binary solvents formed by solvation (active component A and indifferent component B) analysis of equation [9.52a] demonstrates that there is also a linear correlation between $\ln K$ and $1/\varepsilon$. Such mixed solvents are proposed to be called as conventionally universal.

To analyze the solvent effect on the process [9.45], it is often convenient to represent the temperature and permittivity dependencies of $\ln K$ in approximated form:

$$\ln K = a_{00} + a_{01}/T + a_{02}/T^2 + \cdots + \left(a_{10} + a_{11}/T + a_{12}/T^2 + \cdots\right)/\varepsilon +$$
$$+ \left(a_{20} + a_{21}/T + a_{22}/T^2 + \cdots\right)/\varepsilon^2 + \cdots = \sum_{\substack{i=0 \\ j=o}}^{\substack{i=m \\ j=n}} \frac{a_{ij}}{\varepsilon^j T^i} \qquad [9.55]$$

For the universal and conventionally-universal media, this dependence described by the equation can be represented in the form

$$\ln K^{(univ)} = a_{00} + a_{01}/T + a_{10}/\varepsilon + a_{11}/\varepsilon T \qquad [9.56]$$

9.4.2 MIXED SOLVENT EFFECT ON THE POSITION OF EQUILIBRIUM OF HOMOMOLECULAR ASSOCIATION PROCESS

All questions this part deals with are considered based on the example of a special and wide-studied type of homomolecular association process, namely, monomer-dimer equilibrium:

$$2E \leftrightarrow E_2 \qquad [9.57]$$

For this process, equation [9.52] can be presented in the form:

$$\ln K_{dim} = \left[\Delta G_{dim} + \Delta G^{(cov)}_{solv,E_2} - 2\Delta G^{(cov)}_{solv,E} + \left(\beta_{solv,E_2} - 2\beta_{solv,E}\right)/\varepsilon\right]/RT \qquad [9.58]$$

where:

β value at the $1/\varepsilon$ is calculated in accordance with the following equation
$\Delta G^{el}_{d-d} = -120.6\mu^2/r^3_{d-d}$ kJ/mol
μ dipole moment

Because of the electrostatic component of process [9.57], the free energy is conditioned by dipole-dipole interactions such as dimer-solvent and monomer-solvent.

In mixed solvent, CCl_4-C_6H_5Cl, universal relation to acetic acid (because the mixed solvent components do not enter into specific solvation with the acid), the dimerization constant dependence on the temperature and permittivity in accordance with [9.52.a] and [9.56] is described by equation:[19]

$\ln K_{dim} = -1.72 + 1817.1/T + 0.92/\varepsilon + 1553.4/\varepsilon T$

The dimer form concentration, c_M (mol/l), is related to initial analytical concentration of dissolved compound and dimerization constant in equation:

$$c_M = \left[4K_{dim} c_M^o + 1 - \left(8K_{dim} c_M^o + 1 \right)^{1/2} \right] / 8K_{dim} \qquad [9.59]$$

One can calculate, with the help of this equation, that in hexane at $c_M^o = 0.1$, half of the dissolved acetic acid is in dimer form ($K_{dim} \approx 1.5 \times 10^3$). In nitrobenzene solution ($K_{dim} \approx 10^2$), only a third of analytical concentration of acid is in dimer form. For phenol these values are 12% and 2%, respectively. Therefore the composition variation of universal mixed solvents, for instance, using hexane-nitrobenzene binary solvent, is an effective method to control the molecular composition of dissolved compounds able to undergo homomolecular association, in particular, through H-bonding.

Typically, in specific solvents, the process of monomer formation [9.57] is characterized by considerably lower dimerization constants, as compared with those in universal media. In fact, acetic acid dimerization constant in water-dioxane binary solvent, the components of which are solvation-active in respect to the acid, vary in the 0.05-1.2 range. Replacing the solvent is often the only method to vary the molecular association state of dissolved compound. To achieve dimer concentration in 0.1 M solution of phenol in n-hexane equal to dimer concentration in nitrobenzene solution (50% at 25°C), it would be necessary to heat the solution to 480°C, but it is impossible under ordinary experimental conditions.

9.4.3 MIXED SOLVENT INFLUENCE ON THE CONFORMER EQUILIBRIUM

Equilibrium took place in solutions

Conformer I ↔ Conformer II   [9.60]

and the special case, such as

Cis-isomer ↔ Trans-isomer   [9.61]

when investigated in detail. But the concentration-determining methods of equilibrium [9.60, 9.61] members are often not very precise. Dielcometry, or in our measurement the mean dipole moment, can be used only in the low-polar solvents. The NMR methods allowed us to obtain the equilibrium constants of processes by the measurement of chemical dislocation and constants of spin-spin interactions of nucleuses, which are quite precise but only at low temperatures (that is why the numerous data, on conformer and isomerization equilibrium, in comparison with other types of equilibria, are in solutions at low temperatures).

It is evident that the accuracy of the experimental definition of equilibrium constants of the investigated process is insufficient. Thus, the summarization of experimental data on solvent effect on [9.60, 9.61] equilibrium encounters several difficulties.

As a rule, the differences in conformer energies are not very high and change from one tenth to 10-12 kJ/mol. This is one order value with dipole-dipole interaction and specific solvation energies, even in low-active solvents. Moreover, the dipole moments of con-

former highly differ one from another, so ε is one of the main factors which affects equilibrium, such as in equations [9.60, 9.61].

If equations of processes are identical to that of scheme [9.45] in the form and maintenance, it is possible to apply the equations from Section 9.4.1 to calculate the equilibrium constants of the investigated process.

Abrahem[20] worked out details of the solvent effect theory on changing equilibrium. This theory also accounts for the quadruple interactions with media dipoles. It demonstrates that the accuracy of this theory equations is not better than that obtained from an ordinary electrostatic model.

Because of low energy of [9.60, 9.61] processes, it is not possible to assign any solvents strictly to a universal or specific group. That is why only a limited number of binary solvents can be used for the analysis of universal media influence on conformer equilibrium constants. It is interesting to note that over the years, the real benzene basicity in liquid phase has not been sufficiently investigated. There were available conformer equilibrium constants in benzene, toluene, etc., highly differing from those in other low-polar media. Such phenomenon is proposed to be called the "benzene effect".[21]

Sometimes rather than equilibrium constants, the differences in rotamer energies - for example, gosh- and trans-isomers - were calculated from the experiment. It is evident that these values are linearly proportional to the equilibrium constant logarithm.

Different conformers or different intermediate states are characterized by highly distinguished values of dipole moments.[22] Indeed, the media permittivity, ε, change highly influences the energy of dipole-dipole interaction. Therefore, according to [9.53a], it is expected that conformer transformation energies and energies of intermediate processes in universal solvents are inversely proportional to permittivity. But equilibrium constants of reactive processes are exponent dependent on $1/\varepsilon$ value, i.e., there is a linear correlation between $\ln K_{conf}$ and reciprocal permittivity:

$$E_{conf\,(turning)} = A + B / \varepsilon \qquad\qquad [9.62]$$

$$\ln K_{conf\,(turning)} = a + b / \varepsilon \qquad\qquad [9.63]$$

The analysis of experimental data on conformer and intermediate equilibrium in universal media demonstrates that they can be described by these equations with sufficient accuracy not worse than the accuracy of experiment.

The differences in rotamer energies of 1-fluoro-2-chloroetane in mixed solvents such as alkane-chloroalkane can be described by equation:[20]

$$\Delta E = E_{gosh} - E_{trans} = -2.86 + 8.69/\varepsilon, \text{ kJ/mol}$$

According to equation [9.51], the permittivity increase leads to decreasing absolute value of electrostatic components of conformer transformations free energies in universal solvents. For instance, conformer transformation free energy of α-bromocyclohexanone in cyclohexane ($\varepsilon=2$) is 5.2 kJ/mol, but in acetonitrile ($\varepsilon=36$) it is -0.3 kJ/mol.

Specific solvation is the effective factor which controls conformer stability. The correlation between equilibrium constants of the investigated processes [9.60] and [9.61] and polarity of solvation-inert solvents is very indefinite. For instance, diaxial conformer of 4-methoxycyclohexanone in acetone (as solvent) ($\varepsilon=20.7$) is sufficiently more stable than in

methanol (ε=32.6). But the maximum stability of that isomer is reached in low-polar trifluoroacetic acid as solvent (ε=8.3).

Formation of the internal-molecular H-bonding is the cause of the increasing conformer stability, often of gosh-type. Therefore solvents able to form sufficiently strong external H-bonds destroy the internal-molecular H-bonding. It leads to change of conformer occupation and also to decrease of the internal rotation barrier.

Due to sufficiently high donority, the benzene has a comparatively high degree of conformer specific solvation ("benzene effect"). This leads to often stronger stabilization of conformer with higher dipole moment in benzene than in substantially more polar acetonitrile.

In a number of cases, the well-fulfilled linear correlation between conformer transformation constants and the parameter E_T of mixed solvent exists (see Section 9.3.4.3).

It is often the solvent effect that is the only method of radical change of relative contents of different conformer forms. Thus, with the help of the isochore equation of chemical reaction, the data on equilibrium constants and enthalpies of dichloroacetaldehyde conformer transformation allow us to calculate that, to reach the equilibrium constant of axial rotamer formation in cyclohexane as solvent (it is equal to 0.79) to magnitude K=0.075 (as it is reached in DMSO as solvent), it is necessary to cool the cyclohexane solution to 64K (-209°C). At the same time, it is not possible because cyclohexane freezing point is +6.5°C. By analogy, to reach the "dimethylsulfoxide" constant to value of "cyclohexane", DMSO solution must be heated to 435K (162°C).

9.4.4 SOLVENT EFFECT ON THE PROCESS OF HETEROMOLECULAR ASSOCIATION

Solvent effect on the process of heteromolecular association

$$mE + nF \leftrightarrow E_m F_n \qquad [9.64]$$

has been studied in detail.[22,23] In spite of this, monographs are mainly devoted to individual solvents.

In universal media formed by two solvate-inert solvents according to equation [9.53a], equilibrium constants of the process of heteromolecular adduct formation depend exponentially on reciprocal permittivity; thus

$$\ln K_{add} = a + b / \varepsilon \qquad [9.65]$$

The process of adduct formation of acetic acid (HAc) with tributyl phosphate (TBP) nHAc•TBP in the mixed solvent n-hexane-nitrobenzene[7] can serve as an example of the [9.65] dependence validity. Equilibrium constants of the mentioned above adducts in individual and some binary mixed solvents are presented in Table 9.2.

The concentration of adduct EF c_M is related to constant K_{add} and initial concentration of the components c_M^o by equation

$$c_M = \left[2K_{add}c_M^o + 1 - \left(4K_{add}c_M^o + 1\right)^{1/2} \right] / 2K_{add} \qquad [9.66]$$

Table 9.2. Equilibrium constants of adduct (nHAc•TBP) formation in the mixed solvent n-hexane - nitrobenzene (298.15K) and coefficients of equation [9.65]

Solvent	K_{add}			
	HAc•TBP	2HAc•TBP	3HAc•TBP	4HAc•TBP
Hexane (ε=2.23)	327	8002	6.19×10^5	1.46×10^{-7}
H+NB (ε=9.0)	28.1	87.5	275	1935
H+NB (ε=20.4)	19.6	45.0	88.1	518
Nitrobenzene (ε=34.8)	17.4	36.2	60.8	337
Coefficients of equation [9.65]:				
a	2.69	3.28	3.58	5.21
b	5.82	10.73	18.34	21.22

When stoichiometric coefficients are equal to m and n (equation [9.64]), K_{add} expression is an equation of higher degree relative to c_M

$$K_{E_m F_n} = c_M / \left(c_{M,E}^o - n c_M \right)^n \left(c_{M,F}^o - m c_M \right)^m \qquad [9.67]$$

Let us consider an example of the interaction between acetic acid and tributyl phosphate (the change of permittivity of universal solvent permits us to change essentially the output of the reaction product). When initial concentration of the components equals to c_M^o=0.1 mol/l, the output (in %) of complexes of different composition is listed in table below:

|	1:1	2:1	3:1	4:1
In hexane	84	46	32	22
In nitrobenzene	43	13	4.5	2

Relative concentration changes the more essentially, the larger the value of electrostatic component of the process free energy, $\Delta G_{\varepsilon=0}^{el}$.

Just as in the previous cases, the solvent use in this case is an effective means of process adjustment. To reduce the output of adduct HAc•TBF in nitrobenzene to the same value as in hexane solution, nitrobenzene solution must be cooled down to -78°C (taking into account that enthalpy of adduct formation equals 15 kJ/mol).[24] Naturally, the process is not possible because the nitrobenzene melting point is +5.8°C.

Let us consider the effect of specific solvation on equilibrium constant of the heteromolecular association process as an example of associate formation with a simplest stoichiometry:

$$E + F \leftrightarrow EF \qquad [9.68]$$

Only when A is a solvate-active component in the mixed solvent A-B, in the general case, both A and B initial components undergo specific solvation:

$$E + A \leftrightarrow EA \qquad\qquad\qquad [9.69]$$

$$F + A \leftrightarrow FA \qquad\qquad\qquad [9.70]$$
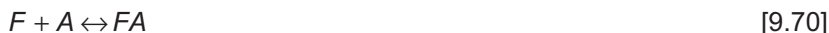
where:

      EA, FA   solvated molecules by the solvent (it is not necessary to take into account solvation number for further reasoning)

Since specific solvation of the adduct EF is negligible in comparison with specific solvation of initial components, A-B interaction in the solvent can be presented by the scheme:

$$EA + FA \leftrightarrow EF + 2A \qquad\qquad\qquad [9.71]$$

i.e., the heteromolecular association process in the specific medium is a resolution process, since both initial components change their solvative surrounding. That is why equilibrium constants of the heteromolecular association process, calculated without consideration of this circumstance, belong indeed to the [9.71] process but not to the process [9.68].

Let us develop a quantitative relation between equilibrium constants for the process [9.68]

$$K_{EF} = [EF] / [E][F] \qquad\qquad\qquad [9.72]$$

and for the resolution process [9.71]

$$K_{us} = [EF] / [EA][FA] \qquad\qquad\qquad [9.73]$$

Concentration of the solvate active solvent or the solvate active component A of mixed solvent in dilute solution is higher than the initial concentration of equilibrium components $[E]_0$ and $[F]_0$. Then activity of equilibrium components is equal to their concentrations. Then equations of material balance for components A and B can be set down as

$$[E]_0 = [E] + [EF] + [EA] \qquad\qquad\qquad [9.74]$$

$$[F]_0 = [F] + [EF] + [FA] \qquad\qquad\qquad [9.75]$$

Hence equilibrium constants of the process [9.69, 9.70] are presented by expressions

$$K_{EA} = [EA] / [E] = [EA] / \left([E]_0 - [EF] - [EA] \right) \qquad\qquad [9.76]$$

$$K_{FA} = [FA] / [F] = [FA] / \left([F]_0 - [EF] - [FA] \right) \qquad\qquad [9.77]$$

Definition [9.72] is presented in the form

$$K_{EF} = [EF] / \left([E]_0 - [EF] - [EA] \right) \left([F]_0 - [EF] - [FA] \right) \qquad [9.78]$$

and re-solvation constant

$$K_{us} = [EF] / \left([E]_0 - [EF]\right)\left([F]_0 - [EF]\right)$$ [9.79]

Inserting [9.76] in [9.77] and [9.79] in [9.78], we come to the equation relating the equilibrium constants of all considered processes:

$$K_{EF} = K_{us}\left(1 + E_A\right)\left(1 + F_A\right)$$ [9.80]

A similar form of equation [9.80] has been proposed elsewhere.[25]

If it is impossible to neglect the solvent concentration (or the concentration of solvate component of the mixed solvent) in comparison with $[E]_0$ and $[F]_0$, equation [9.80] is written in the form:

$$K_{EF} = K_{us}\left(1 + K_{EA}^A\right)\left(1 + K_{FA}^S\right)$$ [9.81]

Let E be acidic (acceptor) reagent in reaction [9.68], F basic (donor) reagent. Then, if A is acidic solvent, one can neglect specific solvation of the reagent E. Thus equations for equilibrium constant of the process [9.68] can be written in the form

$$K_{EF} = K_{us}\left(1 + K_{FS}\right) \quad K_{EF} = K_{us}\left(1 + K_{FS}^A\right)$$ [9.82]

If A is a basic component, equation [9.82] can be re-written to the form

$$K_{EF} = K_{us}\left(1 + K_{EA}\right) \quad K_{EF} = K_{us}\left(1 + K_{EA}^A\right)$$ [9.83]

Equations [9.82] and [9.83] were developed[26-28] for the case of specific solvation.

Thus for K_{EF} calculation one must obtain the equilibrium constant of processes: [9.71] - K_{us}, [9.69] - K_{EA} and [9.70] - K_{FS} from conductance measurements. The constant K_{EF} is identified in literature as "calculated by taking into account the specific solvation".[29] The value K_{EF} characterizes only the universal solvation effect on the process of heteromolecular associate formation. The approach cited above can be illustrated by equilibrium:

$$(CH_3)_2SO + o\text{-}CH_3C_6H_4OH \leftrightarrow (CH_3)_2SO \bullet CH_3C_6H_4OH$$ [9.84]
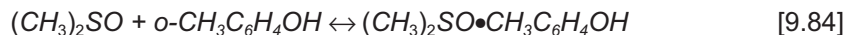
studied in binary mixed solvents:

A) CCl_4 - hepthylchloride[30] formed by two solvate inert components [9.84]
B) CCl_4 - nitromethane[31] formed by solvate inert component (CCl_4) and acceptor (nitromethane) component
C) CCl_4 - ethyl acetate[32] formed by solvate inert component (CCl_4) and donor (ester) component;

The isotherms $\ln K$ vs. $1/\varepsilon$ (298.15K) are presented in Figure 9.8. These dependencies (right lines 1,2,4,5) are required for calculation of equilibrium constants of the heteromolecular association process free from specific solvation effect. It can be seen from Figure 9.8 that the values $\ln K$, regardless of solvent nature, lie on the same line 3, which describes the change of equilibrium constants of the process [9.84] in the universal solution CCl_4-heptylchloride.
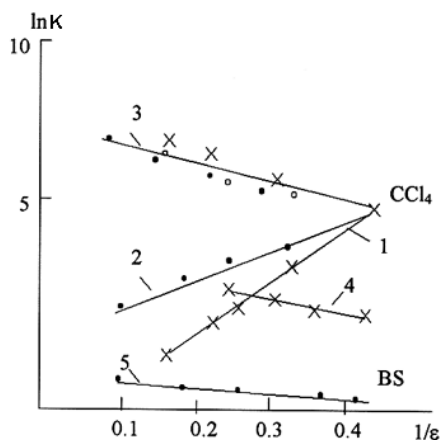
Figure 9.8. Dependence of equilibrium constant for the formation process of addition product DMSO to o-cresol on permittivity in solution based on heptylchloride (o), ethyl acetate (x) and nitromethane (•):1 - resolution of o-cresol solvated in ethyl acetate in DMSO in mixed solvent CCl$_4$-ethyl acetate; 2 - resolution of DMSO solvated in nitromethane in o-cresol in mixed solvent CCl$_4$-nitromethane; 3 - process [9.84] in mixed solvent CCl$_4$-heptylchloride; 4 - solvation of o-cresol in ethyl acetate; 5 - solvation of DMSO in nitromethane.

The data obtained for equilibrium [9.84] in binary mixed solvents of different physical and chemical nature are in need of some explanatory notes.

First of all, if solvents are universal or conditionally universal ones, in accordance with general rules of equilibrium constants, the dependence on permittivity and the dependence of K= f(1/ε) in all cases is rectilinear.

As appears from the above, specific solvation of one component decreases equilibrium constants in comparison with equilibrium constants in isodielectric universal solvent.

The increase of K$_{EF}$ with permittivity increase in DMSO - o-cresol system required supplementary study.[33]

The method of study of specific solvation effect on the process of heteromolecular association has been described in work,[34] devoted to study of the following interaction:

$$C_6H_3(NO_2)_3 + C_6H_5N(CH_3)_2 \leftrightarrow C_6H_3(NO_2)_3 \bullet C_6H_5N(CH_3)_2 \qquad [9.85]$$
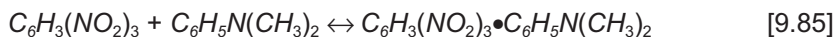
in the binary liquid solvent formed from a solvate-inert component (heptane) and one of the following solvate-active component: trifluoromethylbenzene, acetophenone or p-chlorotoluene.

Therefore trinitrobenzene, TNB, is solvated in initial mixed solvents, so its interaction with donor represents the resolution process.

$$C_6H_3(NO_2)_3 \bullet A + C_6H_5N(CH_3)_2 \leftrightarrow C_6H_3(NO_2)_3 \bullet C_6H_5N(CH_3)_2 + (A) \qquad [9.85a]$$
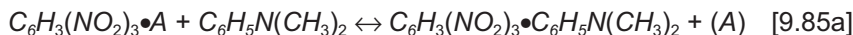
Equation [9.62] applied to process of the heteromolecular association is written in the form:

$$\ln K = \left[\Delta G^{(v)} + \left(\sigma G_{solv,EF}^{(cov)} - \sigma G_{solv,E}^{(cov)} - \sigma G_{solv,F}^{(cov)} \right) + \sigma \beta_{solv} / \varepsilon \right] / RT \qquad [9.86]$$

But for equilibrium [9.85a] in mixed solvents one can assume $\sigma G_{solv,EF}^{(cov)} \approx 0$. That is why equation [9.52] can be converted for the process in conditionally universal media:

$$\ln K_{us} = \left[\Delta G^{(v)} - \sigma G_{solv,E}^{(cov)} + \sigma \beta_{solv} / \varepsilon \right] / RT \qquad [9.86a]$$

It follows from equation [9.86a] that dependence of $\ln K_{us}$ vs. $1/\varepsilon$ will be rectilinear. Experimental data of equilibrium constants for process [9.85a] are in agreement with the conclusion. Approximation of data by equation [9.65] is presented in Table 9.3.

It also follows from equation [9.86a] that RT, unlike in the cases of chemical equilibrium in universal solvents, describes, not the vacuum component of the process free energy, but the remainder $\Delta G^{(v)} - \sigma G^{(cov)}_{solv,TNB}$ and $\sigma G^{(el)}_{solv,TNB}$. The values of the remainder as well as electrostatic component of the free energy for the described chemical equilibrium are summarized in Table 9.4.

Although the solvate-active components are weak bases, their differences influence the values $\Delta G^{(v)} - \sigma G^{(cov)}_{solv,TNB}$ and $\sigma G^{(el)}_{\varepsilon=1}$. The first value characterizes the difference between the covalent components of solvation energy for trinitrobenzene in any solvate-active solvent. It follows from the table, that contributions of the covalent and electrostatic components are comparable in the whole concentration range of the mixed solvents. This indicates the same influence of both donor property and permittivity of the solvent on the [9.85a] process equilibrium.

Table 9.3. Coefficients of equation [9.65] equilibrium constants of the [9.85a] process at 298.15K (r-correlation coefficient)

Solvent	a	b	r
Heptane-trifluoromethylbenzene	-0.80	5.50	0.997
Heptane-acetophenone	-1.49	6.74	0.998
Heptane-chlorotoluene	-2.14	7.93	0.998

Table 9.4. Free energy components (kJ/mol) of resolution process [9.85a] in mixed solvents at 298.15K

ε	-ΔG in system heptane - S, where S:		
	trifluoromethylbenzene	acetophenone	chlorotoluene
2	6.8	8.3	9.8
4	3.4	4.1	4.9
6	2.3	2.8	3.3
8	1.7	2.1	-
$\Delta G^{(v)} - \sigma G^{(cov)}_{solv,TNB}$	-2.0	-3.7	-5.3
$\sigma G^{(el)}_{\varepsilon=1}$	13.6	16.7	19.6

According to the above energy characteristics of the heteromolecular association process (resolution) in specific media, the solvent exchange affects the products' output (the relationship of output c_M and K_{us} is estimated from the equation [9.66]). This shows that the product output (with initial concentration of reagents 0.1M) can be changed from 34% (pure heptane) to 4 % (pure n-chlorotoluene) by changing the binary mixed solvent composition. The processes [9.85a] and [9.85] can be eliminated completely when the solvate active component (more basic then chlorotoluene) is used.

Possibility of management of the products` output may by illustrated by the data from reaction equilibrium [9.84]. As follows from Figure 9.8, maximum equilibrium constant (in investigated solvents) is for pure chloroheptane; the adducts output in this solvent equals to 86% (at initial concentration of reagent 0.1 M). Minimum equilibrium constant of the process is in pure ethyl acetate, where the products` output equals to 18 % (at initial concentration of reagent 0.1 M). Thus the products` output of the reaction [9.84] can be changed directionally in the range 90 up to 20% by means of choice of corresponding binary or individual solvent. If selected solvent is more basic than ethyl acetate or more acidic than nitromethane, the process is not possible.

Heteromolecular association process of o-nitrophenol and triethylamine can be an example of the management of products` output. Association constant of this process has been determined for some solvents.[35] Use of hexane instead of 1,2-dichloroethane, DHLE, increases products' output from 6% to 93%.

When both components of the mixed solvent are solvate-active towards the reagents of equilibrium [9.64], the following interactions take place:

$$E + A \leftrightarrow EA; \quad F + A \leftrightarrow FA; \quad E + B \leftrightarrow EB; \quad F + B \leftrightarrow FB \qquad [9.87]$$

The process of heteromolecular association [9.64] is due to displacement of the solvent components and formation of completely or partially desolvated adduct:

$$xEA + yFA + (m - x)EB \leftrightarrow E_m F_n + (A) + (B) \qquad [9.88]$$
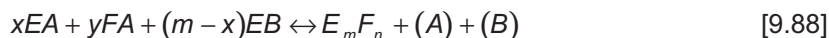
It is easy to develop the equation for binary solvent formed from two solvate-active components similar to [9.90] by using the above scheme for the binary solvent with one solvate active component (equations [9.76 - 9.80]) and introducing equilibrium constant of the process [9.88] such as K_{us}:

$$K_{EF} = K_{us} (1 + K_{EA})(1 + K_{FA})(1 + K_{EB})(1 + K_{FB}) \qquad [9.89]$$

where:
$\quad K_i \qquad$ equilibrium constant of the processes [9.87]

9.4.4.1 Selective solvation. Resolution

When component B is added to solution E in solvent A (E is neutral molecule or ion), resolution process takes place:

$$EA_p + qB = EB_q + pA \qquad [9.90]$$

Equilibrium constant of this process in ideal solution (in molar parts of the components) equals to:

$$K_{us} = m_{EB_q} m_A^p / m_{EA_p} m_B^q \qquad [9.91]$$

where:
$\quad m_i \qquad$ a number of moles
$\quad p, q \qquad$ stoichiometric coefficients of reaction

On the other hand, resolution constant K_{us} equals to the ratio of equilibrium constants of solvation processes $E + pA \leftrightarrow EA_p(I); E + qB \leftrightarrow EB_q(II)$:

$$K_{us} = K_{II} / K_{I} \qquad\qquad [9.92]$$

The method of K_{us} determination, based on the differences between free energy values of electrolyte transfer from some standard solvent to A and B, respectively, leads to a high error.

If the concentration ratio of different solvative forms is expressed as α, the concentrations A and B are expressed as $1-x_B$ and x_B, respectively, (x_B - molar part B), equation [9.91] may be presented in the form:

$$K_{us} = \alpha x_B^p / (1 - x_B)^q \qquad\qquad [9.91a]$$

or

$$\ln K_{us} = \ln a + p \ln x_B - q \ln(1 - x_B) \qquad\qquad [9.93]$$

The last equation permits to calculate value for the solvent of fixed composition and x_B determination at certain composition of the solvate complexes p and q and resolution constant K_{us}.

It follows from the equations [9.91] and [9.91a]

$$K_{us} = \left[m_E^{(q)} q / \left(m_E^o - m_E^{(q)} \right) p \right] \left[x_0^{(q)} \left(1 - x_B^{(q)} \right)^q \right] \qquad\qquad [9.91b]$$

where:

m_E^o a number of moles E in solution
$m_E^{(q)}$ a number of moles E solvated by the solvent A

Hence

$$K_{us} = x_B' x_B^p / \left[(1 - x_B')(1 - x_B)^q \right] \qquad\qquad [9.91c]$$

where:

x_B' molar fraction of B in solvate shell

Equation [9.91c] developed for the ideal solution E-A-B permits us to establish the relationship between the composition of mixed solvent x_B and the solvate shell composition x_B'. For the special case of equimolar solvates, the expression of resolution constant is written in the form:

$$K_{us} = \alpha x_B / (1 - x_B) \qquad\qquad [9.91d]$$

It follows that even in ideal solution of the simplest stoichiometry, α is not a linear function of the mixed solvent composition x_B. Dependence of isotherm α on the solvent composition at $K_{us} = 1$ is presented in Figure 9.9a.

Analytical correlation between the composition of solvate shell x_B' and the mixed solvent composition can be developed:

$$K_{us} = \left[x_B' / (1 - x_B') \right] \left[x_B^p / (1 - x_B)^q \right] \qquad\qquad [9.94]$$
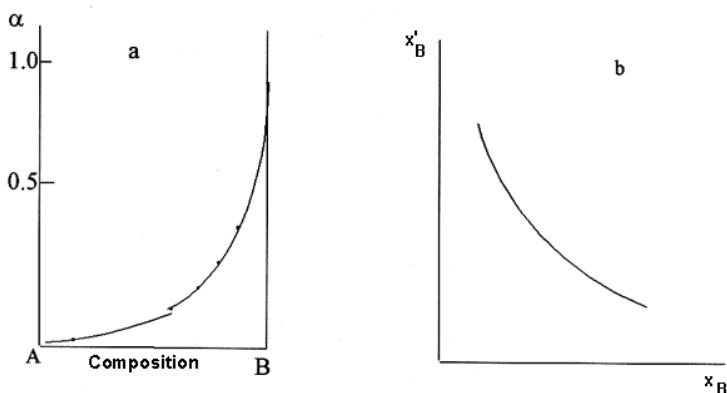
Figure 9.9. Characteristics of solvate shells in the mixed solvent A-B: a - dependence $\alpha = EA/EB$ on composition of the mixed solvent; b - dependence of the solvate shell composition, x'_B, on composition x_B of the mixed solvent E-A-B.
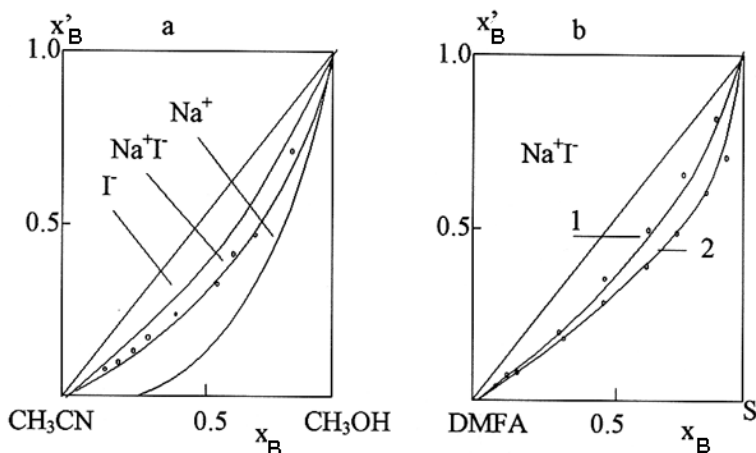

Figure 9.10. Selective solvation of NaI in mixed solvent cyanomethane-methanol (a) and DMFA-methanol (b, curve1), DMFA - cyanomethane (b, curve 2): x_B - composition of mixed solvent; x'_B - composition of solvate shell in molar parts of the second component.

The dependence for $K_{us} = 1$ is given in Figure 9.9b. As it follows from the analysis of equation [9.94] and Figure 9.9, the compositions of solvate shell and mixed solvent are different.

A similar approach has been developed for calculation of solvate shell composition Na^+ and I^- in the mixed solvent formed by the components with close values of permittivity. Such solvent selection permits us to eliminate the permittivity effect on solvation equilibrium. Resolvation constants have been determined from the calorimetric study. The composition of anions solvate complex has been determined from experimental data of electrolyte Bu_4NI assuming lack of the cation specific solvation. Experimental data are presented in Figure 9.10.

Padova[36] has developed this approach to non-ideal solutions. He has proposed an equation based on electrostatic interaction which relates molar fractions of the components (x_B - in the mixed solvent and x'_B - in the solvate shell) to the activity coefficient of components of the binary solvent:

$$\alpha = \ln\left[(1-x'_B)/(1-x_B)\right] = \ln\gamma_B^2 \qquad [9.95]$$

Strengthening or weakening interaction (ion-dipole interaction or dipole-dipole interaction) of universal solvation leads to re-distribution of molecules in the mixed solvate and to the change of the composition of solvate shell in contrast to the composition of mixed solvent.

The method for determination of average filling of molecules` coordination sphere of dissolved substance by molecules of the mixed solvent (with one solvate-inert component) has been proposed.[37] The local permittivity is related to average filling of molecules' coordination sphere expressed by the equation:

$$\bar{\varepsilon}_p = \varepsilon_A x'_A + \varepsilon_B x'_B \qquad [9.96]$$

where:

$$x'_A = z_A/(z_a + z_B); \quad x'_B = z_B/(z_A + z_B) \qquad [9.97]$$

where:

z_A, z_B average numbers of A and B molecules in the first solvate shell

The last equations can be used for development of the next expression permitting to calculate the relative content of B molecules in the solvate shell

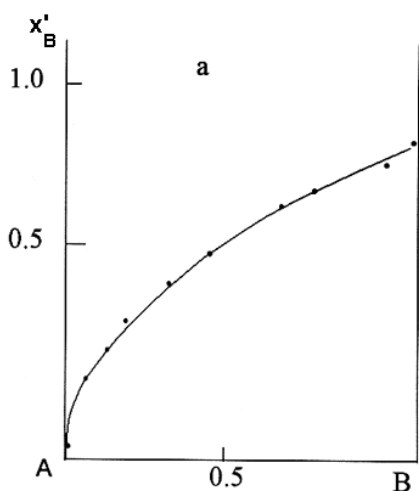$$x'_B = (\varepsilon_p - \varepsilon_A)/(\varepsilon_B - \varepsilon_A) \qquad [9.98]$$

where:

ε_p permittivity of binary solvent
$\varepsilon_A, \varepsilon_B$ permittivities of components

Value x'_B can be found from the equation linking the location of maximum of absorption band of IR spectrum with refraction index and ε of the solution.

The data on selective solvation of 3-aminophthalimid by butanol from butanol-hexane mixture are presented in Figure 9.11. The data have been calculated from the equations presented above. Alcohol content in solvate shell has higher concentration than in solvent composition even at low concentration of alcohol in the solvent. For example, when molar fraction of n-butanol in the mixture was 7%, the relative molar fraction of n-butanol in the solvate shell of
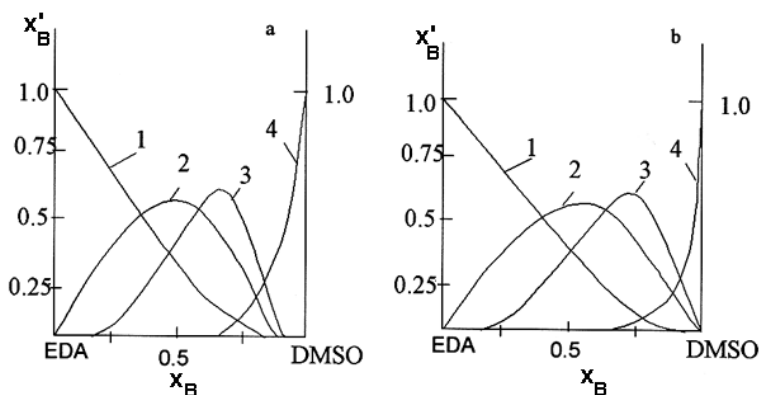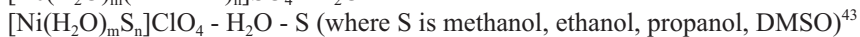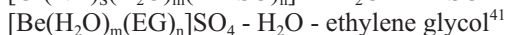

Figure 9.11. Selective solvation of 3-aminophthalimid (A) by n-butanol (B) from the mixed solvent hexane-n-butanol.

Figure 9.12. Dependence of concentration (in molar parts) of solvate forms Li(EDA)$_m$S$_n$ on molar fraction, x_B, of the second component in the binary solvents ethylenediamine-DMSO (a) and ethylenediamine-DMFA (b): 1-m=4, n=0;2- m=n=2;4-m=0, n=4.

aminophthalimide was 30%. Resolution process completes at n-butanol concentration in solution ≈90%.

Mishustin[37] proposed a strict and accurate method for selective solvation study. The method is based on data of free energy transfer of electrolyte from individual solvent A to mixed solvent A - B. The method takes into account non-ideality of the system, and allows calculation of the concentration of different solvate forms and their dependence on the mixed solvent composition.

An example of application of this method is in the work.[39] Authors have calculated relative concentration of different solvate forms of Li$^+$ in the mixed solvent ethylenediamine - DMSO and ethylenediamine-DMFA (Figure 9.12). Free energy of lithium transfer from DMSO (DMFA) in the mixed solvent has been calculated from the time of spin-lattice relaxation of kernel ^{7}Li. The curves presented in Figure 9.12 depict quantitatively the selectivity of Li$^+$ relative to ethylenediamine, which is more basic component in contrast to the second components of the mixed solvent, namely DMSO and DMFA.

The following systems can serve as examples of the effect of composition of the mixed solvent on the solvate shell composition:

[Cr(NH)$_S$(H$_2$O)$_m$(DMSO)$_n$]$^{3+}$ - H$_2$O - DMSO[40]

[Be(H$_2$O)$_m$(EG)$_n$]SO$_4$ - H$_2$O - ethylene glycol[41]

[Be(H$_2$O)$_m$(HMPTA)$_n$]SO$_4$ - H$_2$O - HMPTA[42]

[Ni(H$_2$O)$_m$S$_n$]ClO$_4$ - H$_2$O - S (where S is methanol, ethanol, propanol, DMSO)[43]

Data presented in Figure 9.13 contain information on the composition of solvate shell as a function of molar fraction of water in the mixed solvent H$_2$O-other solvents.[43] Monograph[44] contains collection of data on resolution constants of the ions in the mixed solvents.

The above presented dependencies of the composition of solvate shell on the mixed solvent composition as well as resolution constants permit calculation of the solvate composition by varying solvent composition. The dependence of resolution constants on the permittivity of the solvent is discussed in the example of the proton resolution process.
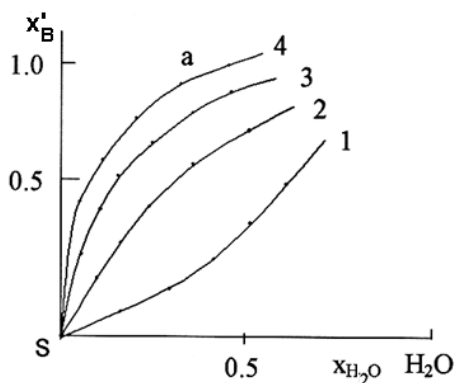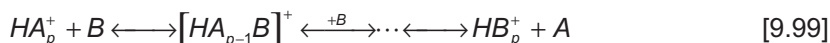
Figure 9.13. The composition of solvate shell Ni^{2+} (in molar parts of water) in the mixtures of solvents formed from water and propanol (1), ethanol (2), methanol (3) and DMSO (4). Data from Ref. 43.

In the mixed solvents water - non-aqueous solvent, in spite of its donor and polar properties, water is a preferred solvating agent. This generalization has some exceptions (solvation in systems Ag^+ - H_2O - acetonitrile, Cr^{3+} - H_2O - DMSO, F- H_2O-ethylene glycol).[45]

Solvation energy of proton by donor solvents is very high. The regularities of the proton selective solvation and re-solvation processes were studied in more detail in comparison with other ions.

Let us consider the changes in the system, when donor component is added to protic acid HA in solvent A. Anion solvation can be neglected, if both solvents have donor character. The interaction influences the proton re-solvation process.

$$HA_p^+ + B \longleftrightarrow \left[HA_{p-1}B\right]^+ \xrightarrow{+B} \cdots \longleftrightarrow HB_p^+ + A \qquad [9.99]$$

or

$$HA_p^+ + qB \longleftrightarrow \cdots \longleftrightarrow HB_q^+ + pA \qquad [9.99a]$$

The model related to eq. [9.99a] was evaluated,[46] resulting in the supposition that the equilibrium of two forms of solvated proton: HA_p^+ and HB_q^+ is important. Solvation stoichiometry was not considered. Both proton solvated forms are denoted as HA^+ and HB^+.

If B is the better donor component (it is a necessary requirement for equilibrium [9.99] shift to the right hand side of equation), the equation from work[46] can be simplified to the form:[47]

$$K_a = K_a^A + \left(K_a^B - K_a^A\right)\left\{\left[K_{us}x_B / (1-x_B)\right] / \left[1 + K_{us}x_B / (1-x_B)\right]\right\} \qquad [9.100]$$

where:

K_a	ionic association constant
K_a^A, K_a^B	the ionic association constants of acid in individual solvents A and B
K_{us}	a constant of resolution process
x_B	molar fraction of B

For the calculation of resolution constant, one must determine the experimental constant of HA association in the mixed solvent and determine independently K_a^A and K_a^B.

When the resolution process is completed at low concentration of the second component, the change of permittivity of mixed solvent A-B may be ignored. Thus, one may assume that K_a^A and K_a^B are constant and calculate K_{us} from the equation [9.100] in the form:

$$1/\left(K_a - K_a^A\right) = 1/\left(K_a^B - K_a^A\right) + \left\{\left[(1-x_B)/x_B\right]\left[1/K_{us}\left(K_a^B - K_a^A\right)\right]\right\} \qquad [9.101]$$
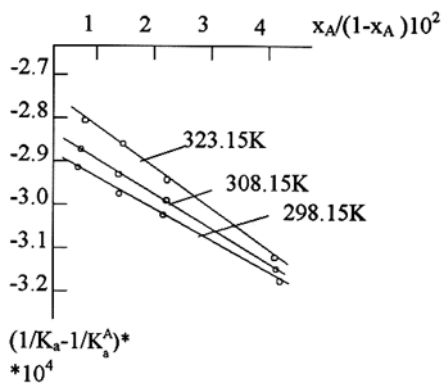
Figure 9.14. Dependence of $1/(K_a - K_a^A)$ for CF_3COOH on the mixed solvent composition DMSO (A) - dimethylalanine at different temperatures.

Thus K_{us} is calculated as a slope ratio of coordinates: $1/(K_a - K_a^A) = (1-x_B)/x_B$ and $(K_a - K_a^A)$ remainder is obtained as Y-intercept. Dependence of eq. [9.101] is presented in Figure 9.14.

K_{us} for proton was calculated in a series of mixed solvents. It was shown[47] that, when pyridine, dimethylalanine or diphenylamine (resolvating agents with decreasing donor numbers) are added to the solution of trifluoroacetic acid in DMSO, proton decreases consecutively and its values are equal to 2.7×10^4; 4.2×10^3 and 35.4, respectively.

Consideration of permittivity of the mixed solvent has allowed calculation of proton in whole concentration range of the mixed solvent DMSO - diphenylamine. The data have been approximated using equation [9.55].

$$\ln K_{us} = -12.2 + 3400/T + 453.7/\varepsilon - 75043/\varepsilon T$$

Equilibrium constants for exchange process of alcohol shell of solvates to water shell were calculated:[48]

$$ROH_2^+ + H_2O \leftrightarrow H_3O^+ + ROH \qquad [9.102]$$

The solutions of HCl and $HOSO_3CH_3$ in aliphatic alcohol (i.e., $C_nH_{2n+1}OH$) - normal alcohol C_1-C_5 and isomeric alcohol C_3-C_5 have been studied. If the components taking part in resolution process are capable of H-bonding, the anion solvation by these components cannot be neglected. The differences in K_{us} values for both acids in different solvents may be explained as follows.

The dependence of K_{us} on permittivity and temperate is described by the equation:

$$\ln K = a_{00} + a_{01}/T + a_{02}/T^2 + (a_{10} + a_{11}/T)/\varepsilon \qquad [9.103]$$

The coefficients of equation [9.103] are presented in Table 9.5.

Table 9.5. Coefficients of the equation [9.103] for constants of resolution process

System	a_{00}	$a_{01} \times 10^{-2}$	$a_{02} \times 10^{-4}$	a_{10}	$a_{11} \times 10^{-3}$	$\pm \delta$
HCl - n-alcohol	12.4	46.0	56.3	186.8	71.1	0.3
HCl - isomeric alcohol	13.1	5.9	-36.9	318.4	94.7	0.2
$HOSO_3CH_3$ - n-alcohol	6.3	4.4	-5.4	177.7	60.9	0.3

The solvent effect in the following resolution process was studied:[49]

$$ROH_2^+ + Py \leftrightarrow HPy^+ + ROH \qquad [9.104]$$

The solutions of trifluoroacetic acid in ethanol and methanol in the temperature range 273.15-323.15K were investigated. The dependence of K_{us} on permittivity and temperature is described by the equation:

$$\ln K_{us} = 9.44 + 1768/T + 77.8/\varepsilon - 11076/\varepsilon T$$

Unlike the processes considered above, in the case of process [9.104] permittivity decrease leads to decreasing K_{us}. The explanation of the results based on covalent and electrostatic components of resolution process enthalpy is given.[50]

The reaction [9.104] also has been studied for isodielectric mixtures of alcohol-chlorobenzene with $\varepsilon=20,2$ (permittivity of pure n-propanol) and $\varepsilon=17.1$ (permittivity of pure n-butanol) to investigate the relative effect of universal and specific solvation on the resolution process. The mixtures were prepared by adding chlorobenzene to methanol, ethanol, and C_1-C_3 alcohol. Alcohol is a solvate-active component in these isodielectric solvents. K_{us} data are given in Table 9.6.

Table 9.6. Equilibrium constants of the process [9.104] in isodielectric solvents

Solvents with $\varepsilon=20.2$	$K_{us}\times 10^{-5}$	Solvents with $\varepsilon=17.1$	$K_{us}\times 10^{-5}$
Methanol +23.5% chlorobenzene	3.9	Methanol + 32.8% chlorobenzene	1.4
Ethanol + 13% chlorobenzene	4.9	Ethanol + 24% chlorobenzene	2.0
n-Propanol	7.3	n-Butanol	4.9

Insignificant increase of K_{us} in n-butanol (or n-propanol) solution in comparison to methanol is due to relaxation of the proton-alcohol bond, when the distance of ion-dipole interaction increases.

The change of donor property of the solvate-active component is not significant. The equations relating K_{us} to ε permit to divide free energy of resolution process into the components. Corresponding data are presented in Table 9.7.

Table 9.7. The components of free energy (kJ mol^{-1}) of proton resolution process at 298.15K

Solvent	ε	$\sigma\Delta G^{el}$ in process		
		[9.102]		[9.104]
		HCl	$HOSO_3CH_3$	CF_3COOH
Methanol	32.6	3.9	2.0	-3.1
Ethanol	24.3	5.3	2.7	-4.1
n-Propanol	20.1	6.4	3.3	-5.0
n-Butanol	17.1	7.5	3.9	-5.9
n-Pentanol	14.4	8.9	4.6	-

Solvent	ε	$\sigma\Delta G^{el}$ in process		
		[9.102]		[9.104]
		HCl	$HOSO_3CH_3$	CF_3COOH
$-\delta\Delta G^{cov}$		8.2	17.7	-38.1
$-\delta\Delta G^{el}_{\varepsilon=1}$		128	66.0	-100.6

In contrast to the processes considered earlier, the vacuum electrostatic component of resolution process has high value whereas $-\delta\Delta G^{el}$ values are comparable with the covalent component, $\delta\Delta G^{cov}$.

$\delta\Delta G$ values according to [9.51] are equal to:

$$\delta\Delta G = \left(\Delta G_{HB^+} + \Delta G_A - \Delta G_{HA^+} + \Delta G_B\right)_{sol}$$

For small additions of B (to component A), $(\Delta G_A)_{sol}=0$ and $(\Delta G_{HA})_{sol}=0$, then

$$\delta\Delta G = (\Delta G_{HB+} + \Delta G_B)_{sol}$$

Solvation energy of complex HB^+ by solvent A is small because coordination vacancies of the proton are saturated to a considerable extent. Therefore the interaction energy between A and B influences significantly the value of $\sigma\Delta G$. That is why, the mixed solvents (alcohol-water and alcohol-pyridine, for instance) are different because of the proton resolution process. This can be explained in terms of higher energy of heteromolecular association for the alcohol-water in comparison with alcohol pyridine.

The concept of solvent effect on the proton resolution process was confirmed by quantum chemical calculations.[51] Above phenomena determine the dependence of resolution constant on physical and chemical properties.

Let the resolution process proceeds at substantial abundance of the component A in mixed solvent and initial concentrations HA (HA^+) and B to be equal. The output of the process can be calculated from the equation similar to equation [9.66]. The large value of K_{us} in all considered processes of proton resolution indicates the effect of permittivity change on the yield of complex HB^+ formation. The output of resolvated proton in process [9.104] proceeding in methanol equals 100%, whereas in the same process in low polarity solvent (e.g., methanol-hexane), with abundance of the second component, the equilibrium is shifted to the left, resulting in solvate output of less than 0.1%. K_{us} values in single alcohol solvents are large, thus the output of reaction does not depend on solvent exchange.
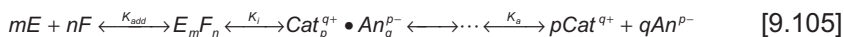
The process $H{\bullet}DMSO^+ + B \leftrightarrow HB^+ + DMSO$ may be considered as an example of the effect of chemical properties of B on the output of the reaction [9.99]. The output of HB^+ equals to 98%, if pyridine is included in the process at initial concentration of 0.1M. Use of diphenylamine, having lower donor properties, decreases the output to 60%. The output differs even more at smaller concentrations of component, such as 10^{-3} M, which gives yields of 83 and 33%, respectively.

9.4.5 MIXED SOLVENT EFFECT ON THE ION ASSOCIATION PROCESS

The ion association process (or opposite to it - ion dissociation process) has been studied in detail in comparison with other types of chemical equilibrium in solutions. The modern

state of the theory of individual solvent effects on equilibrium constant of ion association process (K_a) is described in monographs by Izmailov[53] and Barthel.[54]

The formation of free (preferably solvated) ions is due to a successive equilibrium states proceeding in solution:

$$mE + nF \xleftrightarrow{K_{add}} E_mF_n \xleftrightarrow{K_i} Cat_p^{q+} \bullet An_q^{p-} \longleftrightarrow \cdots \xleftrightarrow{K_a} pCat^{q+} + qAn^{p-} \qquad [9.105]$$

where:

K_{add}	a constant of adduct formation
K_i	ionization constant
K_a	association constant

The true constant of ion association is a ratio of ionic associate concentration $Cat_p^{q+} \bullet An_q^{p-}$ to ion concentration product. If ionic associate concentration is unknown (as is true in many cases), ion association constant is calculated from the analytical concentration of dissolved substance:

$$K_a = \left\{ c_0 - p\left[Cat^{q+} \right] - q\left[An^{p-} \right] \right\} / \left[Cat^{q+} \right]^p \left[An^{p-} \right]^q$$

where:

c_0	initial concentration of electrolyte

The general theory of ionic equilibrium[53,54] leads to the conclusion that ion association constant in universal or conditionally universal media, in accordance to the equation [9.53a], depends exponentially on reciprocal value of permittivity:

$$\ln K_a = a_{00} + a_{01} / \varepsilon \qquad [9.106]$$

where:

a_{00}, a_{01}	approximation coefficients

If ion association process has high energy, the solvents are solvate-inert because of large ions, such as $(C_nH_{2n+1})_4N^+$, $(C_nH_{2n+1})_4P^+$, etc. Solution of $(C_2H_5)_4NBr$ in mixed solvents propylene carbonate - o-dichlorobenzene and propylene carbonate - pyridine[55] serve as an example. The components of these binary solvents (with the exception of inert dichlorobenzene) possess donor properties, though they do not solvate the large anion R_4N^+ because it is solvate-inert component in relation to anion. That is why $\ln K_a$ - $1/\varepsilon$ isotherms follow the same line (see Figure 9.15). But the $\ln K_a$ - $1/\varepsilon$ isotherm for solution of propylene carbonate - acetic acid differs from the other two because acetic acid is a solvate-active component in relation to anion Br^-.

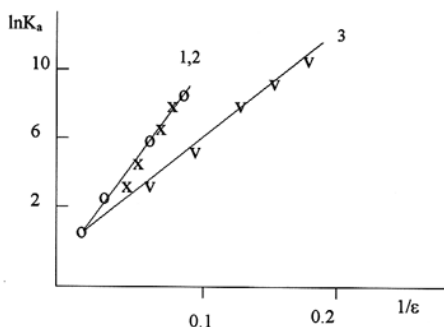Figure 9.15. Dependence K_a of $(C_2H_5)_4NBr$ on permittivity in mixed solvents formed by propylene carbonate with o-dichlorobenzene (1,2-o), pyridine (1,2-x) and acetic acid (3) at 298.15K.

Coefficients of equation 9.56 for the various systems are presented in Table 9.8.

Table 9.8. Coefficients of equation [9.56] for ionic association of tetraethyl ammonium bromide at 298-323K

Solvent	$-a_{00}$	a_{10}	a_{01}	a_{11}
Propylene carbonate - o-dichlorobenzene	5.2	1440	78.8	9523
Propylene carbonate - pyridine	6.3	1850	114	0
Propylene carbonate - acetic acid	7.7	2400	110.5	-11500

The $\ln K_a$ - $1/\varepsilon$ dependence for universal media is linear in full range of permittivity.

Validity of the following equation was evaluated[7] for the mixed solvent propylene carbonate - 1,4-dioxane in the range of permittivity $\varepsilon=65\pm3$ for the solutions Et_4NBr

$$\ln K_a = 1.32 + 80.05/\varepsilon$$

Table 9.9. Components of free energy (kJ mol^{-1}) of ion association of methyl octyl ammonium methyl sulfate in universal solvents at 298.15K

Solvent	ε	σ_{solv}^{el}
Pyridine-DMFA	25.0	7.6
Pyridine-acetonitrile	19.2	9.9
Pyridine-propylene carbonate	16.0	11.9
Nitrobenzene-acetic acid	11.9	16.0
Propylene carbonate-acetic acid	10.6	17.9

Comparison of the free energy of components for ion association process in different solvents permits us to estimate the energy of specific solvation interaction.

Electrical component of the change of free energy, depending on ion-ion interaction in accordance with the nature of ion association process, must exceed a sum of vacuum and covalent components in equation [9.52]. σ_{solv}^{el} for all above considered systems is higher than 85 - 90% because of the general change of the process free energy. The components of free energy of association of $CH_3(C_8H_{17})_3NOSO_3CH_3$ in different solvents[7] are presented in Table 9.9.

Evidently, the change of permittivity of the universal solvent is the most effective method of affecting the ion concentration. Using the equation relating ion concentration c_M^* for every type of 1-1 electrolyte with K_a and analytical concentration of electrolyte, c_M:

$$c_M = \left[\left(4K_a c_M^0 + 1 \right)^{1/2} - 1 \right] / 2K_a \qquad [9.107]$$

one can ascertain, that ε decrease from 185 to 6 changes the ion concentration of methyl octyl ammonium methyl sulfate in solution from 71 to 0.3%. In mixed solvent containing propylene carbonate, the ionic concentration of Et_4NBr is also changed from 80% (in propylene carbonate) to 3% (in pyridine), and even to 0.8% (in o-dichlorobenzene or acetic acid). Thus, affecting electrolyte strength by solvent choice permits to change a strong electrolyte into non-electrolyte.

A similar phenomenon is observed in conditionally-universal media A-B (A is solvate-active component, B is solvate-inert component). Association constant can be calculated from equations [9.56] or [9.104] for LiBr and KCNS solutions.[55,57]

Table 9.10. Coefficients of equations [9.56] and [9.106] for association constants of salts

| Solvent	[9.56]			[9.106] (296K)		
	a_{00}	a_{10}	a_{01}	a_{11}	a_{00}	a_{01}
Lithium bromide (298.15-323.15K)						
Propylene carbonate-o-dichlorobenzene	3.38	-808	-361	1.53×10^5	0.67	152.4
Propylene carbonate-pyridine	-5.56	2040	135	-6923	1.29	111.8
Propylene carbonate-acetic acid	-3.55	1617	70.1	-6160	1.87	49.4
Potassium thiocyanate (298.15-348.15K)						
Acetonitrile-chlorobenzene	3.80	-521	-25.4	3.26×10^4	2.05	84.0
Propylene carbonate-chlorobenzene	1.88	-229	-1.53	2.60×10^4	1.11	85.7
DMSO-chlorobenzene	6.18	-1580	-16.7	2.73×10^4	0.88	74.9
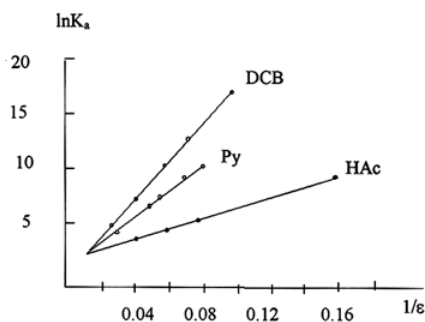
Figure 9.16. Dependence of $\ln K_a$ for lithium bromide on $1/\varepsilon$ in the mixed solvent based on propylene carbonate at 298.15K.

The dependence of $\ln K_a$ and $1/\varepsilon$ for LiBr in mixed solvent [9.53] shows an influence of solvate-active component on K_a. The difference of LiBr solvation energy in the presence of pyridine and acetic acid may be evaluated in accordance to [9.53], assuming low solvation energy of Li^+ by propylene carbonate in comparison with pyridine and negligible value of solvation energy of anion in solvents containing dichlorobenzene (DCB) and pyridine.

The data presented in Table 9.10 permit us to calculate the components of free energy for ion association processes. To interpret the data, one must take into account:

$$\sigma^{cov} = \Delta\sigma^v_{Cat\cdot An} + \left(\sigma_{sol,Cat\cdot An} - \sigma_{sol,Cat^+} - \sigma_{sol,An^-}\right)^{cov}$$

correspondingly:

$$\sigma^{el} = \left(\beta_{Cat\cdot An} - \beta_{Cat^+} - \beta_{An^-}\right)/\varepsilon$$

A small value σ^{cov} in all considered systems can be explained by low energy of interaction between the filled orbital of cation and anion. On the contrary, contribution of ion-ion interaction to the process energy leads to high value σ^{el} in comparison with the covalent component even in media of high permittivity (not to mention media of low permittivities).

From [9.106], isodielectric solution formed by two mixed solvents I and II follows the relationship:

$$\ln K_{a,I} = \left(a_{01,I} \,/\, a_{01,II}\right)\ln K_{a,II} - \left(a_{01,I} \,/\, a_{01,II}\right)a_{00,II} + a_{00,I} \qquad [9.108]$$

where:

      00, 01   subscripts of coefficients of approximation for dependence on temperature and permittivity

      I, II   subscripts for solvents I and II

The leveling (leveling solvent reduces differences between constants of ion association) or differentiating (differentiating solvent enhances these differences) effect of the first mixed solvent is defined by the ratio of coefficients of equation [9.106] or by the ratio of vacuum electrostatic component of free energy of association process, $\delta\Delta G^{el}_{\varepsilon=1}$.

One can calculate ratio $a_{01,\,PC\text{-}DCB}/a_{01,\,PC\text{-}Py} = 1.36$ using the data from Tables 9.10 and 9.11 and assess the leveling effect of the solvent propylene carbonate-pyridine on electrolyte strength. The ratio $a_{PC\text{-}DCB}/a_{PC\text{-}HAc} = 3.1$ indicates that propylene carbonate-acetic acid has more pronounced leveling effect on electrolyte strength than propylene carbonate-pyridine.

Table 9.11. The components of free energy change (kJ mol^{-1}) in ion association process of different salts in conditionally-universal media at 298.15K

Solvent	$-\sigma^{el}$		$-\sigma^{cov}$	$\sigma^{el}_{\varepsilon=1}$
	At max. ε	At min. ε		
Lithium bromide				
Propylene carbonate-o-dichlorobenzene	5.8	37.7	1.6	377
Propylene carbonate-pyridine	4.2	22.9	3.2	277
Propylene carbonate-acetic acid	1.9	20.0	4.6	122
Potassium thiocyanate				
Acetonitrile-chlorobenzene	5.7	37.1	5.1	208
Propylene carbonate-chlorobenzene	3.2	37.9	2.7	212
DMSO-chlorobenzene	4.0	33.1	2.2	185

ε change of the solvent and universal media affect the ion concentration in solution. The ion concentration in 0.1M solution of LiBr in the mixed solvent propylene carbonate-o-dichlorobenzene varies relative to its analytical concentration from 50% in propylene carbonate to 0.1% in dichlorobenzene. The ion concentration in 0.1M solution of KSCN in the solvent propylene carbonate-chlorobenzene varies from 60% in propylene carbonate to 0.06% in chlorobenzene.

The same effect can be obtained by means of solvent heating. For instance, LiBr solution in o-dichlorobenzene must be heated to $\approx 215°C$ to reach the same value of association constant as in propylene carbonate at room temperature. For this reason, solvent may be used as an effective means for tailoring electrolyte strength in conditionally universal media as well.

The influence of solvate active property of components of the mixed solvent is revealed in acid solution. The data for some acids in different mixed solvents are presented in Table 9.12.[7]

Table 9.12. The properties of ion association process of H-acids in conditionally universal media at 298.15K

Acid	Solvent	Coefficients of equation [9.106]		Components of energy of ion association process, kJ mol^{-1}			
				$-\sigma^{cov}$	$\sigma^{el}_{\varepsilon=1}$	σ^{el}	
		a_{00}	a_{01}			At max. ε	At min. ε
CH_3SO_3H	Methanol - n-hexanol	2.49	80.6	6.2	200	6.1	15.0
HSO_3F	Methanol-n-butanol	-1.50	165.0	3.7	408	12.5	23.9
CF_3COOH		4.86	190.9	12.0	473	15.5	26.7
H_2SO_4*		-1.82	165	-4.5	408	12.6	23.1
	DMSO - CCl$_4$	-1.55	215	-3.8	532	11.4	133
	DMSO-o-dichlorobenzene	-1.34	183	-3.3	453	9.7	75.6
	DMSO-benzene	0.55	145	1.4	359	7.7	120
	DMSO-1,4-dioxane	0.55	129	1.4	319	6.9	80
	DMSO-pyridine	1.50	90	3.7	223	4.8	15
	Propylene carbonate -DMSO	0.38	146	0.9	361	5.6	7.8
H_2SeO_4*	Methanol-n-butanol	-2.06	162	-5.1	401	12.3	22.7

*data for the first constant of ion association

The degree of ion association of acids as well as ionophores depends significantly on solvents` permittivity. The influence of the specific solvation by the solvate active component is pertinent from the comparison $\ln K_a$ - $1/\varepsilon$ isotherms for acid solutions in conditionally universal media $S^{(1)}$ - $S^{(2)}$, $S^{(1)}$ - $S^{(3)}$...

Figure 9.17[58] gives $\ln K_a$ - $1/\varepsilon$ relationships for solutions of sulfuric acid in binary solvent mixture containing DMSO and CCl$_4$, benzene, dioxane, pyridine. The increase in the second component basic capacity according to [9.50] leads to decrease in $\ln K_a$.

General analysis of the binary solvent mixtures formed by two solvate active components (these solvents are often used in analytical and electrochemistry) was conducted to evaluate their effect on H-acids.[59] The analysis was based on an equation which relates the constant of ion association, K_a, of the solvent mixture and constants of ion association of the acid K_a^A and K_a^B of each component of the mixed solvent, using equilibrium constants of scheme [9.105] - heteromolecular association constant, K_{add}; ionization constant of the
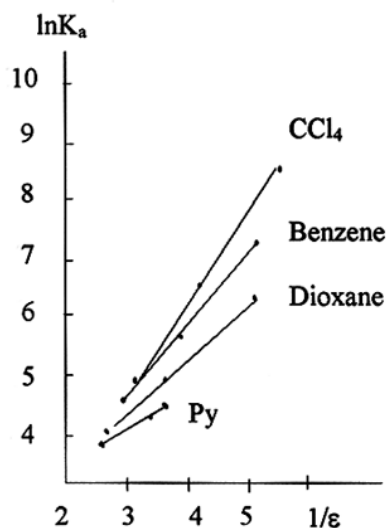
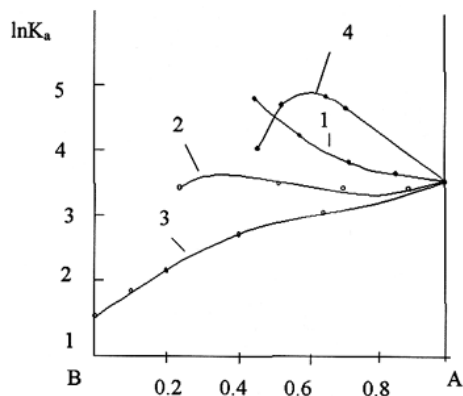Figure 9.17. Dependence of K_a of sulfuric acid on $1/\varepsilon$ in mixed solvents based on DMSO at 298.15K.

Figure 9.18. Dependence of K_a for HSO_3F on solvent composition in mixed solvents: A - n-butanol at 298.15K.[7] B : 1 - n-hexane; 2 - nitrobenzene; 3 - methanol; 4 - N,N- dimethyl aniline.

adduct, K_i; and resolution constant, K_{us}, (e.g., equilibrium constant of process $HA_n \cdot A + B \leftrightarrow HA_n \cdot B + A$), and with molar fractions of components of the mixed solvent x_A and x_B:

$$K_a = K_a^B + \left(K_a^B - K_a^A \right)\left[1 - \left(K_a^B / \left(1 + K_{add} x_B \left(1 + K_i \right) \right) \right) \right] \qquad [9.109]$$

The equation [9.109] changes into equation [9.100] when both components of the mixed solvent have donor character, e.i., $K_{us} = 0$. The analysis of equation [9.100][59] shows that the solvate active property of components of the mixed solvent A-B have to be changed to influence the dependence of K_a on composition of the mixed solvent. Some examples of such influence are presented in Figure 9.18.

## 9.4.6 SOLVENT EFFECT ON EXCHANGE INTERACTION PROCESSES

Chemical processes of exchange interaction, given by equation:

$$EF + HL \leftrightarrow EL + HF \qquad [9.110]$$

are common in research and technology, but the solvent effect on their equilibrium was not frequently studied. Let us systematize the existing experimental data on these processes.[60]

Systems with non-associated reagents

The process of exchange interaction between bis-(carbomethoxymethyl)mercury and mercury cyanide

$$(CH_3OCOCH_2)_2Hg + Hg(CN)_2 \leftrightarrow 2CH_3OCOCH_2HgCN \qquad [9.111]$$
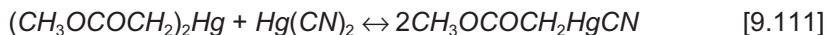
has been studied in the mixed solvent DMSO-pyridine. The components of solvent possess almost equal ability to specific solvation of mercury-organic compounds. This ability is

confirmed by equality of the constants of spin - spin interaction $^2I(^1H - {}^{199}Hg)$ for different organic compounds in these solvents. This was also confirmed[61] for participants of the equilibrium [9.111].

Systems with one associated participant of equilibrium

Methanolysis of triphenylchloromethane may serve as an example of such reaction:

$$Ph_3CCl + CH_3OH \leftrightarrow Ph_3COCH_3 + HCl \qquad [9.112]$$

This process has been studied in benzene, 1,2-dichloroethane, chloroform, trifluoromethylbenzene and in mixed solvents hexane - nitrobenzene, toluene - nitromethane, toluene - acetonitrile.

Low constant of the ion associate formation process of triphenylchloromethane, high constant of the ion association process, and low constant of the heteromolecular association process of HCl (HCl solutions in listed solvents obey the Henry's Law) show that only methanol is an associative participant of the equilibrium.

Systems with two associated participants of equilibrium

These systems have been studied be means of reaction of acidic exchange between acids and anhydrides with different acidic groups:

$$CH_2ClCOOH + (CH_3CO)_2O \leftrightarrow CH_2ClCOOCOCH_3 + CH_3COOH \qquad [9.113a]$$

$$CH_3COOH + (CH_2ClCO)_2O \leftrightarrow CH_2ClCOOCOCH_3 + CH_2ClCOOH \qquad [9.113b]$$

in binary mixed solvents formed from tetrachloromethane with chlorobenzene, trifluoromethylbenzene and nitrobenzene.

The system trifluoroacetic acid and methanol, undergoing esterification reaction:

$$CF_3COOH + CH_3OH \leftrightarrow CF_3COOCH_3 + H_2O \qquad [9.114]$$

also belongs to the group.

The equilibrium process has been studied in binary mixed solvents such as hexane-chloroform, hexane-chlorobenzene, chloroform-chlorobenzene. Also, re-esterification

$$CH_3COOC_3H_7 + CX_3COOH \leftrightarrow CX_3COOC_3H_7 + CH_3COOH \qquad [9.115]$$
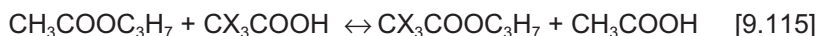
(where X is F or Cl) has been studied for the full concentration range of propyl acetate - trifluoro- and trichloroacetic acids.[62]

Etherification process of ethanol by caproic or lactic acids has been studied by these authors.[63] The reaction of acetal formation was studied[64]

$$RCHO + R'OH \leftrightarrow RCH(OR')_2 + H_2O \qquad [9.116]$$
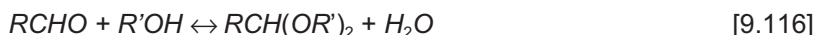
in systems of isoamyl alcohol-benzaldehyde (a) and ethanol - butyric aldehyde (b).

The relationship between the maximum output of the reaction of exchange interaction and associative state of equilibrium [9.110] participants follows the Gibbs-Dugem-Margulis equation:

$$x_s d \ln a_s + \Sigma x_i d \ln a_i = 0 \qquad [9.117]$$

where:

x_S, x_i molar fractions

a_s, a_i activity of the solvent and participants of the chemical process, correspondingly

Izmaylov[65] showed that maximum output of reaction depends on initial composition of reagents. Associative and dissociative processes of the chemical system components are accompanied by the change of their chemical potentials if the solvent potential depends on total activity of solution (it depends on concentration in dilute solutions):

$$\mu_s = \mu_s^o - RT \sum_{i=1}^{i} \ln c_i \qquad [9.118]$$

Hence the condition of chemical equilibrium in non-ideal (regular) systems is presented in the following form:

$$(\partial G)_{P,T} = (\partial G_S)_{P,T} + \sum (\partial G_i)_{P,T} \qquad [9.119]$$

$$\frac{\partial \ln K_{ch}}{\partial V} = n_s \frac{\partial \sum_{i=1}^{i} c_i}{\partial V} - \frac{\partial}{\partial V} \prod_{i=1}^{1} \gamma_i^{v_i} - \frac{\partial}{\partial V} \frac{\sum_{i=1}^{i} \mu_i^o v_i + n_s \Delta \mu_s^o}{RT} \qquad [9.120]$$

Inserting values of chemical potentials for equilibrium participants [9.110] and solvent in equation [9.119], one can obtain the equation relating the equilibrium constant, K_{ch}, change relative to the solvent composition (in volume parts, V), mol number, n_s, activity coefficients, γ_i, stoichiometric coefficients, v_i, of process [9.110] and chemical potential, μ_i^o, for every participant of equilibrium at concentration 1M.

Equation [9.120] changes to [9.121], if only EF and EL undergo homomolecular association:

$$\frac{\partial \ln K_{ch}}{\partial V} \approx 2 n_s \sqrt{c_{EF}^o} \frac{\partial}{\partial V} \left(\frac{1}{\sqrt{K_{dim}^{EL}}} - \frac{1}{\sqrt{K_{dim}^{EF}}} \right) + \frac{d K_{ch}}{d\varepsilon} \qquad [9.121]$$

where:

K_{dim} equilibrium constant of homomolecular association

Equations [9.120] and [9.121] describe the solvent effect on K_{ch} for a non-ideal liquid system. The dependence of $\ln K_{ch}$ and reciprocal ε is linear:

$$\ln K_{ch} = a_{00} + a_{01} / \varepsilon \qquad [9.122]$$

Coefficients of the equation and some thermodynamic properties of exchange interaction processes are presented in Table 9.13.

The degree of heteromolecular association of esters in reaction [9.121] is higher than for acids when K_{dim} values are equal. Thus the change of equilibrium constant according to [9.121] depends on electrostatic component. K_{ch} for these reactions also depends on exponentially reciprocal ε.
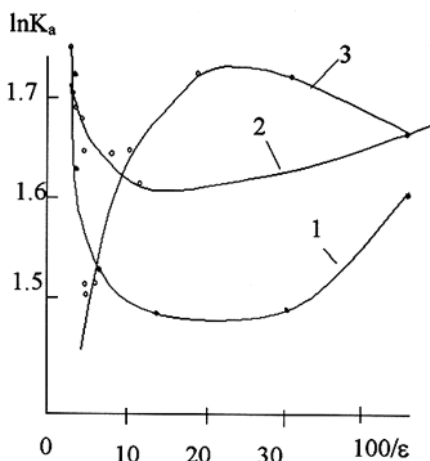
Figure 9.19. Dependence of equilibrium constants for triphenylchloromethane methanolysis on $1/\varepsilon$ of mixed solvent at 298.15K: 1 - hexane-nitrobenzene; 2 - toluene-nitromethane; 3 - toluene-acetonitrile.

The dependence of equilibrium constant for reaction [9.116] on ε is similar in a concentration range from 0.5 to 1.0 molar fraction of aldehyde, if the degrees of homomolecular association for aldehydes and acetals are smaller than for alcohol and water.

K_{ch} increase with increasing ε of media is a general property of all processes of exchange interaction presented in the Table 9.13. Dependence of lnK_{ch} - $1/\varepsilon$ for process [9.111] is not linear in all mixed solvents (Figure 9.19).

Extreme K_{ch} dependence on $1/\varepsilon$ is explained by chemical effect of solvation (it is explained in detail elsewhere[60]). Correlations with different empirical parameters of individual solvent parameters are held true for this process. The best of them is correlation (r=0.977) with parameter E_T.

Table 9.13. Characteristics of some processes of exchange interaction

Reaction	Coefficients of equation [9.122]		Free energy components, kJ/mol			
	a_{00}	$-a_{01}$	$-\sigma^{cov}$	$\sigma^{el}_{\varepsilon=1}$	σG at max. ε	σG at min. ε
[9.111]	2.40	97.6	5.9	241	5.2	19.0
[9.115], a, (F)	1.72	19.6	4.3	48.5	3.1	6.3
[9.115], b, (Cl)	2.55	17.1	6.3	42.3	5.1	7.0
[9.116], a	1.24	47	3.1	116.4	7.5	9.9
[9.116], b	2.47	16.7	6.1	41.3	3.4	4.1

The influence of molecular state of participants of exchange interaction on the process equilibrium is reflected in K_{ch} dependence (processes [9.113]) on the mixed solvent composition (Figure 9.20). The change of K_{dim} for acetic acid is less pronounced than for monochloroacetic acid, when CCl_4 is replaced by chlorobenzene. Thus K_{ch} should increase for reaction [9.113a] and it should decrease for reaction [9.113b], with ε increasing in accordance to equation [9.121].

Correlation of K_{dim} for acetic and monochloroacetic acid is obtained when chlorobenzene is replaced by nitrobenzene. This leads to decrease of K_{dim} when ε increases in the case of reaction [9.113a], and the opposite is the case for reaction [9.113b]. That is why a maximum is observed in the first process (see Figure 9.20 on the left hand side), and a minimum is observed for the second process.
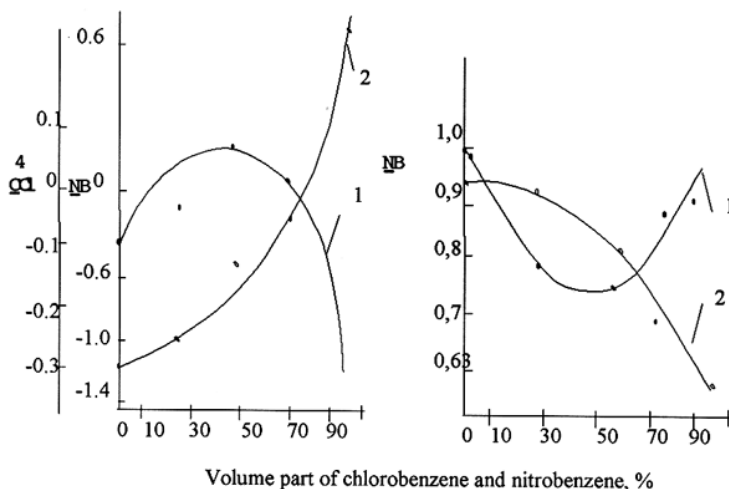
Figure 9.20. Dependence of K_{ch} on the mixed solvent composition for processes [9.113a] and [9.113b] at 298.15K: 1-tetrachloromethane-nitrobenzene; 2- tetrachloromethane-chlorobenzene.

At equilibrium [9.114] (with three associated participants), association degree of associated participants decreases with media polarity increasing. It leads to K_{ch} increasing and to K_{add} decreasing in the process of heteromolecular association of acid and alcohol.

Thus, K_{ch} depends to a low extent on the composition of studied mixed solvents. Vacuum component of free energy of processes of exchange interaction (Table 9.13) is low; σG^{el} values are low, too. This indicates, that ε change does not lead to the change of the reaction output. Solvent replacement leads to essential change of reaction output in process [9.111], characterized by the high value of σ^{el} (see Table 9.13), from 6% in pyridine to 60% in DMSO (in 0.1M solutions). K_{ch} increase in pyridine solution to its value in DMSO requires cooling to -140°C.

9.4.7 MIXED SOLVENT EFFECT ON PROCESSES OF COMPLEX FORMATION

Non-aqueous solvent effect on equilibrium and thermodynamic of complexation processes are summarized in monographs.[67-69]

The solvent effect on complex formation processes has two aspects. The first is a change of coordination sphere composition, changing participation of solvent as a chemical regent:

$$[ML_m]^{p+} \xleftrightarrow{+A} [ML_{m-1}A]^{p+} + L \longleftrightarrow \cdots \longleftrightarrow [MA_n]^{p+} + mL \qquad [9.123]$$
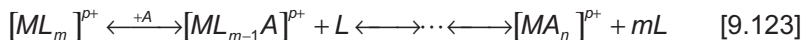
where:

  L_m a ligand in initial complex
  A, B   components of binary solvent

If both components of the mixed solvent are solvate-active, equilibrium [9.123] may be presented as:
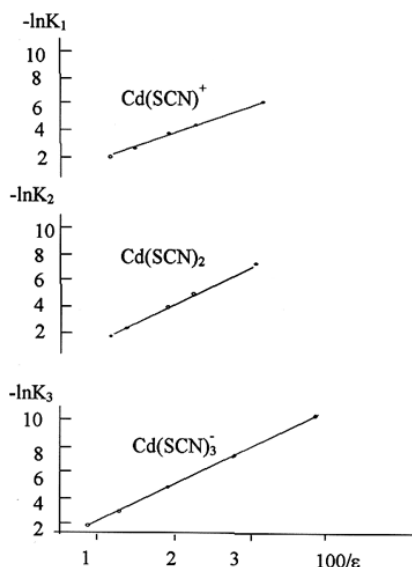
$$[ML_m]^{p+} \xleftrightarrow{+A+B} [ML_{m-2}AB]^{p+} + 2L \leftrightarrow \cdots \leftrightarrow [MA_{n-q}B_q]^{p+} + mL \quad [9.123a]$$
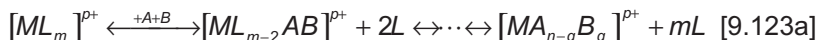
Figure 9.21. Dependence of stability constants for cadmium thiocyanate complexes on $1/\varepsilon$ in mixed solvent water-methanol at 298.15K.

Coordination solvents A and B taking part in the processes are the same ligands as L.

The second aspect of the solvent effect is related to the thermodynamic properties of the complex, such as formation constant. Discussing the problem of solvent effect on complex stability, authors often neglect the change of a complex nature, due to the change in solvent as follows from equations [9.123] and [9.123a]. These processes may also be regarded as resolution processes.

When the components of mixed solvate are solvate-inert in relation to the complex, equation [9.53a] takes the following form:

$$\ln K_k = a_{00} + a_{01} / \varepsilon \qquad [9.124]$$

Coefficient a_{00} has a physical meaning of logarithm of formation constant at $\varepsilon \to \infty$ related to the standard ionic strength $I = 0$. In Figure 9.21, this dependence is presented.

Table 9.14. Complexation process characteristics for system Cd^{2+}-thiourea in mixed solvent water-methanol at 298.15K

Constant	Coefficient of equation		Correlation coefficient r	Component σG, kJ/mol			
	a_{00}	a_{01}		σG^{cov}	$\sigma^{el}_{\varepsilon=1}$	$-\sigma G^{cov}$	
						in H_2O	in MeOH
K_2	-0.42	367.7	0.996	-1.0	910	11.6	27.9
K_3	1.07	561.9	0.987	2.6	1390	17.7	42.7
K_4	7.79	631.3	0.991	19.3	1563	19.9	47.9
K_5	2.72	837.0	0.988	6.7	2072	26.4	63.6

The data for cadmium thiourea complexes in water-methanol mixed solvent[70] are presented in Table 9.14. Dependence of stability constant on the solvent composition is very complex in the mixed solvents formed by two solvate-active components as defined by the relative activity, L, of A and B. Dependencies of stability constant for some complexes in water-B solution (where B is methyl acetate, methanol, etc.[69]) are presented in Figures 9.21 and 9.22 for complex $NiEn^{2+}$ (En=ethylenediamine) in water-non-aqueous solution (the constants are presented relative to stability constant in water).

9.5 THE MIXED SOLVENT EFFECT ON THE CHEMICAL EQUILIBRIUM THERMODYNAMICS

In most cases, thermodynamic characteristics of equilibrium processes are determined by temperature dependence of equilibrium constant $K = f(T)$, according to the classical equa-
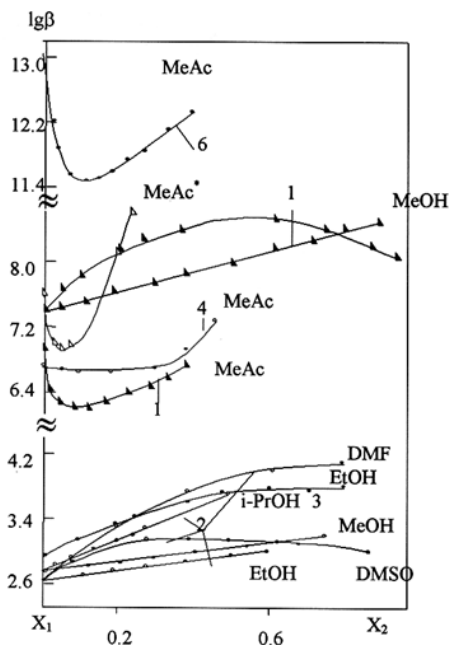
Figure 9.22. Stability constant of amine complexes of some $Ni(NH_3)^+$ in water-organic solvents: 1-$NiEn^{2+}$; 2-[N; $NH_3]^{2+}$; 3-[$CdCH_3NH_2]^{2+}$; 4-[$AgCH_3NH_2]^{2+}$; 5-[$AgEn_2]^{2+}$; 6-[$NiEn_2]^{2+}$.

Figure 9.23. Isotherms lnK - f(ε) for different temperatures ($T_1 < T_2 < T_3$).

tion: $\Delta H = RT^2(dlnK/dT)$ and $\Delta S = RlnK + T(dlnK/dT)$ or $\Delta S = \Delta H/T + RlnK$. Because equilibrium constant is a function of both temperature and permittivity [9.52a], i.e.,

$$K = f(T, \varepsilon) \qquad\qquad [9.125]$$

A change of constant during temperature change is a consequence of enthalpy of process (not equal to zero) and temperature dependence of permittivity. Thus, the change of equilibrium constant with temperature changing depends on both self-chemical equilibrium characteristics (here ΔH) and solvent characteristics (namely, solvent permittivity influence on equilibrium constant). This is pertinent from Figure 9.23, which shows dependence of equilibrium constant logarithm on reciprocal permittivity (isotherms). Equilibrium constants, obtained experimentally (dotted line a - b) correspond to various values of permittivity.

The thermodynamic characteristics of a chemical process, calculated from equilibrium constant polytherms, are integral characteristics (ΔH_i and ΔS_i), i.e., they consist of terms related to process itself (ΔH_T and ΔS_T) and terms depended on permittivity change with temperature changing (ΔH_ε and ΔS_ε):

$$\Delta H_i = \Delta H_T + \Delta H_\varepsilon \qquad\qquad [9.126a]$$

$$\Delta S_i = \Delta S_T + \Delta S_\varepsilon \qquad\qquad [9.126b]$$

The thermodynamic description of a process in a solvent has to lead to defined values of ΔH_T and ΔS_T, which are called van't Hoff or original parameters.[7] It follows from Figure 9.23 that one has to differentiate the equilibrium constant of polytherms corresponding to isodielectric values of the solvent on temperature (e.g., to equilibrium constant values of c-d dotted line).
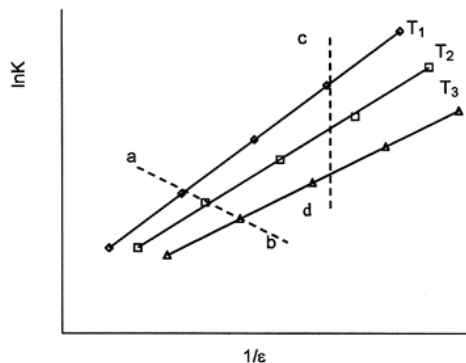
Division of equation [9.126] into the constituents must be done with full assurance to maintain influence of different solvents. For this reason, it is necessary to have a few iso-therms of equilibrium constant dependencies on permittivity (K=f(ε)T). We have developed an equation of a process depicted by scheme [9.45] after approximating each isotherm as lnK vs. 1/ε function and by following approximation of these equations for ε-1, ε-2, ε-3...ε-j conditions. We then can calculate the integral value of process entropy by differentiating re-lationship [9.55] versus T, e.g., ΔG= -RTlnK:

$$\Delta S_i = R\left[\sum_{\substack{i=0 \\ j=0}}^{\substack{i=m \\ j=n}} (1-i)a_{ji}\left(T^i\varepsilon^i\right) - j(d\ln\varepsilon/dT)/\varepsilon^{j-1}\sum_{\substack{i=0 \\ j=0}}^{\substack{i=m \\ j=n}} a_{ji}/T^{i-1}\right]/\varepsilon^i \quad [9.127]$$

Here, the first term of the sum in brackets corresponds to $\Delta S_T/R$ value and the second term to ΔS/R. We can determine "van't Hoff's" (original) constituents of the process en-tropy if all the terms containing dlnε/dT are equal to zero:

$$\Delta S_T = R\sum_{\substack{i=0 \\ j=0}}^{\substack{i=m \\ j=n}} (1-i)a_{ji}/\left(T^i\varepsilon^j\right) \quad [9.128]$$

Van't Hoff's constituent of enthalpy is determined in analogous manner as ΔH=ΔG+TΔS (ΔH$_T$):

$$\Delta H_T = -R\sum_{\substack{i=0 \\ j=0}}^{\substack{i=m \\ j=n}} a_{ji}/\left(T^{i-1}\varepsilon^j\right) \quad [9.129]$$

Such approach may by illustrated by dependence of formic acid association constant on temperature and permittivity in mixed solvents: water-ethylene glycol,[72] which is ap-proximated from equation

$$\ln K = a_{00} + a_{01}/T + a_{02}/T^2 + a_{10}/\varepsilon + a_{11}/(\varepsilon T)$$

where:

a_{00}	= 40.90
a_{01}	= -2.17×10^4
a_{02}	= 3.11×10^6
a_{10}	= -425.4
a_{11}	= 2.52×10^5

Hence

$$\Delta H_i = -R\left[a_{01} + 2a_{02}/T + a_{11}/\varepsilon + T(d\ln\varepsilon/dT)(a_{10}T + a_{11})/\varepsilon\right]$$

$$\Delta S_i = R\left[a_{00} - a_{02}/T + a_{10}/\varepsilon - (d\ln\varepsilon/dT)(a_{10}T + a_{11})/\varepsilon\right]$$

and consequently,

$$\Delta H_T = -R\left(a_{01} + 2a_{02} / T + a_{11} / \varepsilon\right) \quad \Delta S_T = R\left(a_{00} - a_{02} / T + a_{10} / \varepsilon\right)$$

Comparison of ΔH_i with ΔH_T and ΔS_i with ΔS_T shows that integral values of thermodynamic characteristics of the ionic association process for HCOOH are not only less informative than van't Hoff's characteristics, but they contradict the physical model of the process in this case. Indeed, corresponding dependencies of compensative effect are described by equations:

ΔH_i = -0.704ΔS_i + 22.87 *kJ/mol*

ΔH_T = 0.592ΔS_T - 22.22 *kJ/mol*

Thus, if the compensative effect for integral thermodynamic functions is interpreted, one should conclude that characteristic temperature (this is $\tan\alpha = \Delta H / \Delta S$) is a negative value, but that is, of course, devoid of physical sense.

In common cases, when the dependence [9.125] is approximated using equation [9.56], "van't Hoff's" (original) thermodynamic constituents of equilibrium process are equal to:

$$\Delta H_T = -R\left(a_{01} + a_{11} / \varepsilon\right) \tag{9.130}$$

$$\Delta S_T = R\left(a_{00} + a_{10} / \varepsilon\right) \tag{9.131}$$

As it is evident from [9.130] and [9.131], the original thermodynamic characteristics of the process are summarized by the terms where the first of them does not depend, and the second one depends, on permittivity. These terms accordingly are called covalent and electrostatic constituents of the process in solution, i.e.,

$$\Delta H^{cov} = -Ra_{01} \quad and \quad \Delta H^{el} = -Ra_{11} / \varepsilon \tag{9.132}$$

$$\Delta S^{cov} = Ra_{00} \quad and \quad \Delta S^{el} = Ra_{10} / \varepsilon \tag{9.133}$$

It should be emphasized that ΔG_T values are substantially more informative than integral thermodynamic values for thermodynamic analysis of chemical equilibrium in solutions of mixed solvents. Indeed, in frequent cases of equilibrium constant polytherm characterized by an extreme (i.e., sign of ΔH_i changes), one may arrive at the wrong conclusion that the process nature changes greatly at temperature of extreme value. As has been shown,[71] appearance of extreme value of equilibrium constant polytherms is caused in the majority of cases by temperature change of solvent permittivity. The condition of extreme appearance for the process described by equation [9.55] is:

$$a_{01} \exp\left(\alpha T_{extr} + \gamma\right) + \alpha a_{11} T_{extr}\left(a_{10} T_{extr} + a_{11}\right) = 0 \tag{9.134}$$

where:

α, γ	the coefficients of $\ln\varepsilon = \alpha T + \gamma$ equation
γ	activity coefficient
T_{extr}	temperature corresponding to extremum of isotherm of equilibrium constant

Let us illustrate the principle of integral thermodynamic characteristics of chemical equilibrium in mixed solvent based on the example of ionic association process of methylsulfuric acid HSO_3CH_3 and its tetraalkylammonium salt $CH_3(C_8H_{17})_3N + OSO_3CH_3$ in mixed solvent - methanol - n-butanol.[73] The dependencies of ionic association constants for these electrolytes on temperature and permittivity are described by equations based [9.56] the relationship:

$$K_{a,acid} = 14.53 - 3436/T - 130.28/\varepsilon + 5.84 \times 10/\varepsilon T$$

$$K_{a,salt} = 11.8 - 2514/T - 198.70/\varepsilon + 7.79 \times 10/\varepsilon T$$

Thermodynamic characteristics for these systems, calculated based on [9.130]-[9.133] equations, are given in Tables 9.15 and 9.16.

Table 9.15. Thermodynamic characteristics of ionic association process of HSO_3CH_3 in mixed solvent: methanol - n-butanol (298.15 K) (ΔH^{cov} = 28.56 kJ/mol, ΔS^{cov} = 120.8 J/(mol*K))

BuOH mol%	ε	ΔH, kJ/mol			ΔS, J/(mol* K)		
		ΔH_i	ΔH_T	ΔH_{el}	ΔS_i	ΔS_T	ΔS_{el}
60.39	20	20.62	4.29	-24.28	121.4	66.6	-54.1
51.60	22	20.90	6.50	-22.07	119.9	71.6	-49.2
37.24	24	21.19	9.89	-20.23	118.8	75.7	-45.1
25.32	26	21.49	8.34	-18.67	118.0	79.1	-41.7
15.82	28	21.79	11.22	-17.34	117.6	82.1	-38.7
8.76	30	22.09	12.38	-16.18	117.3	84.7	-36.1

Table 9.16. Thermodynamic characteristics of ionic association process of $CH_3(C_8H_{17})_3N + OSO_3CH_3$ in mixed solvent: methanol - n-butanol (298.15 K) (ΔH^{cov}=20.90 kJ/mol, ΔS^{cov}= 98.1 J/(mol K))

BuOH mol%	ε	ΔH, kJ/mol			ΔS, J/(mol K)		
		ΔH_i	ΔH_T	ΔH_{el}	ΔS_i	ΔS_T	ΔS_{el}
60.39	20	3.85	-11.23	-32.13	66.1	15.5	-82.6
51.60	22	5.00	- 8.31	-29.21	67.7	23.0	-75.1
37.24	24	6.00	- 5.88	-26.78	69.1	29.3	-68.8
25.32	26	6.90	- 3.82	-24.72	70.5	34.6	-63.5
15.82	28	7.70	-2.05	-22.95	71.8	39.1	-59.0
8.76	30	8.45	- 0.52	-21.42	73.1	43.0	-55.1

The analysis of data leads to conclusion that ΔH_i depends weakly on permittivity for both acids and salts. This contradicts the nature of the process. In contrast, the rate of ΔH_T

change is large enough. The analogous observations can be made regarding the character of ΔS_i and ΔS_T values changes along with permittivity change.

If considerable endothermic effect of the ionic association for acid can be explained by desolvation contribution of ionic pair formation (i.e., solvated molecule of acid), the endothermic effect of ionic pair formation by such voluminous cations contradicts the physical model of the process. Estimation of desolvation energy of ionic pair formation of salt ions according to the equation[74] shows that this energy is two orders of magnitude lower than the energy of heat movement of solvent molecules. For this reason, the process of ionic association of salt ions is exothermal, as seen from ΔH_T values. The exothermal character increases with permittivity decreasing, i.e., with increase of ion-ion interaction energy.

Dependencies ΔH_i on ΔS_i for salt and acid are not linear, i.e., the compensative effect is not fulfilled. Consequently, the substantial change of the ionic association process is due to change of solvent composition. Considering the same chemical characteristics of mixed solvent components, this conclusion is wrong because the compensative effect if fulfilled for van't Hoff's components is:

$$\Delta H_T = 0.448\ \Delta S_T - 28.5\ kJ/mol$$

$$\Delta H_T = 0.389\ \Delta S_T - 17.3\ kJ/mol$$

The smaller the magnitude of the characteristic temperature for salt (389K), in comparison to acid, the smaller the barrier of the ionic pairs formation process. That is true because the association process in the case of acid is accompanied by energy consumption for desolvation.

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