Substitution of Solvents by Safer Products and Processes

21.1 SUPERCRITICAL SOLVENTS

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21.1.1 INTRODUCTION

Significant and steady inroads towards wider and more effective utilization of supercritical fluids have been made over the last two decades, especially for high value added differenti-

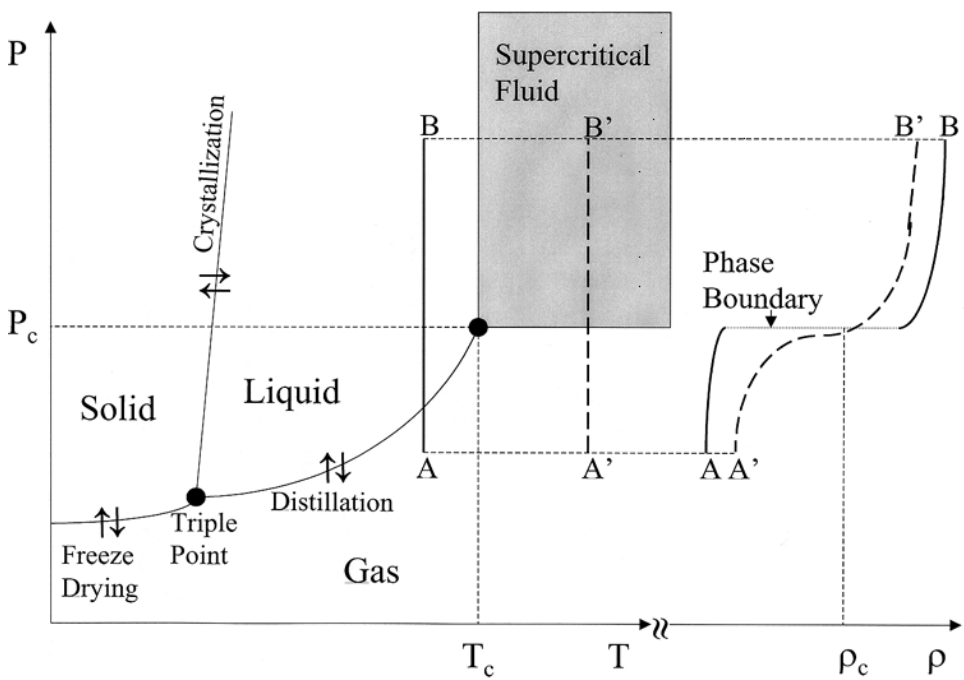

Figure 21.1.1. Pressure-temperature and pressure-density behavior of matter.

ated products. Furthermore, a new wave of second-generation supercritical technologies started to emerge, bringing forth new roles for dense gases. The motivation of this chapter is to assess the current status of the technology in an effort to extricate the challenges both in the current practice of processing with supercritical fluids and potential areas into which we have as yet to venture. The foundations including transport phenomena, reactions and thermodynamics as well as generic processing principles will be highlighted.

"Supercritical" refer to the state of the matter where the temperature and pressure of a single component fluid is above the critical point at which the phase boundaries diminish. A portfolio of chemical and physical operations carried out in the vicinity of this region defines Supercritical Fluid Technology (SFT). The pressure-temperature-volume (PVT) behavior of a substance can be best depicted by pressure-temperature and pressure-density (volume) projections, as shown in Figure 21.1.1. Pressure-temperature diagram identifies the supercritical fluid region, alternative separation techniques that involve phase transition including the associated phase boundaries, and the fact that an isotherm below critical (AB) involves phase transition while one above (A'B') does not. Pressure density projections illustrate tunability of the solvent density at supercritical conditions (A'B') and again the continuity of the isotherm that does not encounter any phase transition. The aforementioned behavior is for a pure component, solvent. The critical properties of various organic and inorganic substances are shown in Table 21.1.1.

Table 21.1.1. The critical properties of solvents

Solvents	Critical temperature, °C	Critical pressure, atm
Critical conditions for various inorganic supercritical solvents		
Ammonia	132.5	112.5
Carbon dioxide	31.0	72.9
Carbonyl sulfide	104.8	65.0
Nitric oxide	-93.0	64.0
Nitrous oxide	36.5	71.7
Chlorotrifluoro silane	34.5	34.2
Silane	-3.46	47.8
Xenon	16.6	58.0
Water	374.1	218.3
Critical conditions for various organic supercritical solvents		
Acetone	235.5	47.0
Ethane	32.3	48.2
Ethanol	243.0	63.0
Ethylene	9.3	49.7
Propane	96.7	41.9
Propylene	91.9	45.6

Solvents	Critical temperature, °C	Critical pressure, atm
Cyclohexane	280.3	40.2
Isopropanol	235.2	47.0
Benzene	289.0	48.3
Toluene	318.6	40.6
p-Xylene	343.1	34.7
Chlorofluoromethane	28.9	38.7
Trichlorofluoromethane	198.1	43.5

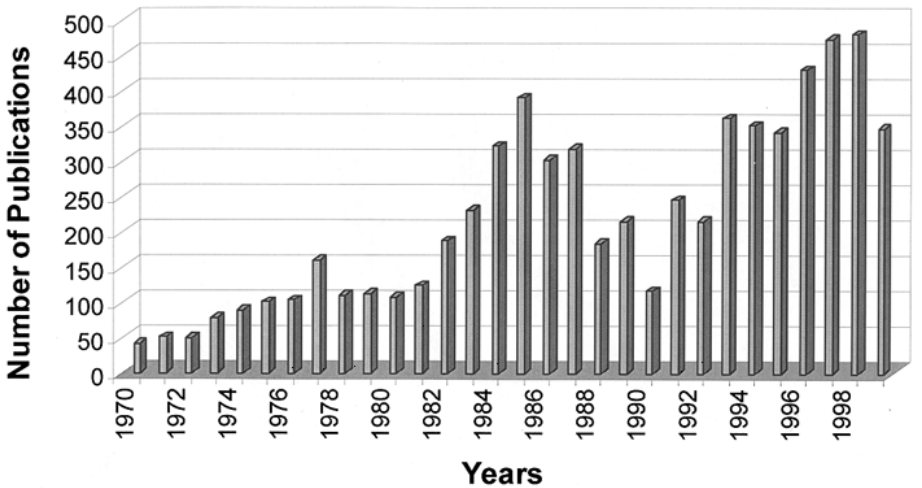

Figure 21.1.2. Annual number of publications related to supercritical fluids.

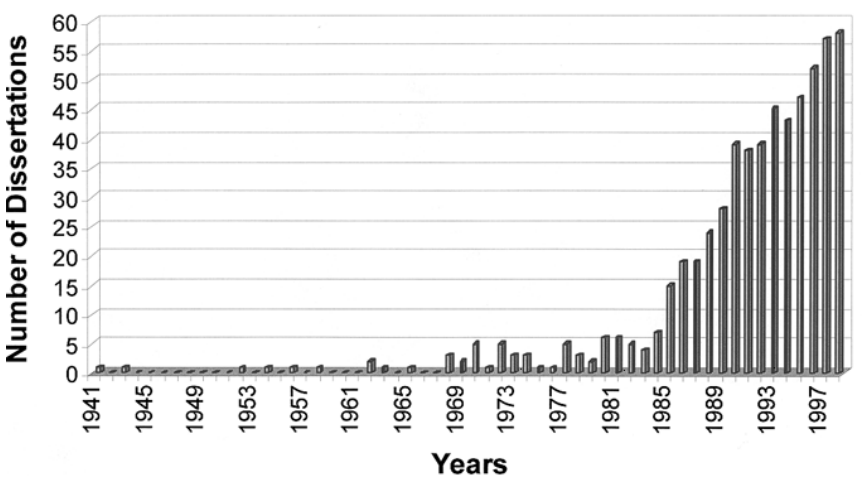

Figure 21.1.3. Annual number of dissertation related to supercritical fluids.

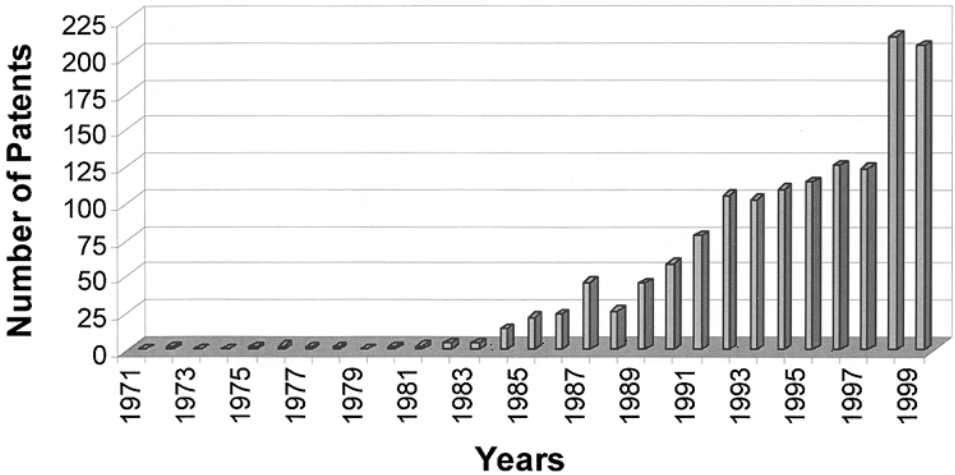

Figure 21.1.4. Annual number of patents related to supercritical fluids.

21.1.1.1 A promising path to green chemistry

One of significant paradigm shifts in chemical processing for the new millennium is the increased use of environmentally benign technology. The effectiveness of green solvents such as supercritical water and supercritical carbon dioxide for carrying out reactions, difficult separations, and materials processing is naturally very promising. The effectiveness of the supercritical solvents is related to their state, critical temperature, and pressure. Obviously, synergy between the physical characteristics of solvent and the conditions favorable for the desired chemistry is of paramount importance for the success of the application.

21.1.1.2 Unique and tunable physico-chemical properties

Supercritical fluids have the mobility of gases and the dissolving power of liquid solvents resulting in efficient penetration into porous matrices, high mass transfer rates, and high solvency. Furthermore, these properties are extremely sensitive to perturbations in temperature, pressure and composition resulting in innovative processing concepts. Furthermore, tailored products with tunable performance could be produced through synthesis and creative operating policies. Thus, over the last three decades, a spate of supercritical processes have been developed particularly for manufacture of high value added products that are superior in performance and exhibit conscious regard for a more socially responsible manufacturing practice.

21.1.1.3 Sustainable applications in many different areas

Despite the higher capital charges associated with relatively high pressures, the necessity to often add a new component into the processing environment, and operational challenges at conditions foreign to most process engineers, the interest in supercritical fluids had been growing steadily since the early eighties beyond the select number of areas. We see applications in the food and beverage industries, pharmaceutical, biomedical, micro-electronic industries, textiles, forest products, petrochemicals, chemicals, environmental clean-up, syn-fuel production, polymeric materials, ceramics, auto industry, coatings and paint industry, energetic materials, and fuels. As depicted in Figures 21.1.2-4, the number of the publications, dissertations, and patents in the area are still growing from one year to next.

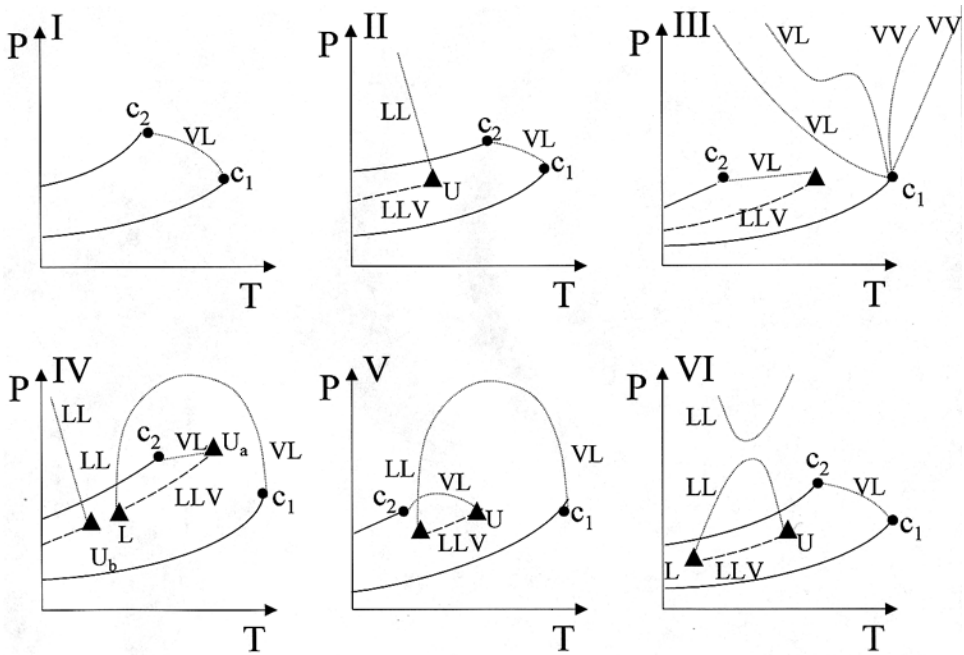

Figure 21.1.5 Classification of vapor-liquid phase behavior of binary systems.

21.1.2 FUNDAMENTALS

21.1.2.1 Phase behavior with supercritical solvents

The first recorded observation of supercritical fluid's ability to dissolve solids with low volatility goes back to 1879.[1] Since then, better understanding of high-pressure phase equilibrium emerged partially as a result of experiments of the last century, especially those of Timmermans,[2] Schneider,[3,4] Franck[5] on aqueous systems, McHugh[6] on polymeric systems and more recently the Delft group in Holland.[7,8] In classification of phase diagrams, one of the most important analytic contributions is due to Scott and Van Konynenberg.[9] They demonstrated that most of the experimental observations could be described qualitatively by the van der Waals equation of state. Their analysis of critical and three phase boundaries in temperature-pressure projection of the phase behavior led to their categorization of possible fluid phase equilibrium into five classes. Rowlinson and Swinton[10] later added a sixth class that occurs in some aqueous systems but is not predicted by the van der Waals equation of state. The classes described by Scott illustrate only a few of the known types of phase equilibrium and are shown in Figure 21.1.5. This classification scheme illustrates the principal lines (degrees of freedom = 1) and end points (degrees of freedom=0) that form the boundaries of pressure-temperature space of the surfaces that describe the equilibrium between two components. The types of boundaries are:

1. Solid lines (_____) are pure component vapor pressure curves.
2. The dashed lined (_ _ _ _ _) are for three phase lines.
3. The dotted lines (.....) are for critical lines.

The types of points are:

1. The filled circles are pure component critical points
2. The triangles are critical end points, lower (L) and upper (U)

Type I mixtures have continuous gas-liquid critical line and exhibit complete miscibility of the liquids at all temperatures. Mixtures of substances with comparable critical properties or substances belonging to a homologous series form Type I unless the size difference between components is large. The critical locus could be convex upward with a maximum or concave down with a minimum. Examples of Type I mixtures are: Water + 1-propanol, methane + n-butane, benzene + toluene, and carbon dioxide + n-butane.

Type II have systems have liquid-liquid immiscibility at lower temperatures while locus of liquid-liquid critical point (UCST) is distinct from gas liquid critical line. Examples include: water + phenol, water + tetralin, water + decalin, carbon dioxide + n-octane, and carbon dioxide + n-decane.

When the mutual immiscibility of two components becomes large, the locus of liquid-liquid critical solution moves to higher temperatures and it eventually interacts with gas-liquid critical curve disrupting the gas-liquid locus. This particular class is type III and some examples include: water + n-hexane, water + benzene, carbon dioxide + n-tridecane, and carbon dioxide + water.

Type IV systems have three critical curves, two of which are VLL. If the hydrocarbon mixtures differ significantly in their critical properties, they conform to type IV or V. The primary difference between Type IV and V is that type IV exhibits UCST and LCST while type V has LCST only. One important class of systems that exhibit type IV behavior is solvent polymer mixtures such as cyclohexane + polystyrene. Other examples of type IV include carbon dioxide + nitrobenzene and methane + n-hexane while ethane with ethanol or 1-propanol or 1-butanol exhibit type V behavior.

Type VI systems are composed of complex molecules with hydrogen bonding or other strong intermolecular forces and result in behavior where LCST and UCST are at temperatures well removed from gas-liquid critical temperature of the more volatile component.

Types IV and I are of particular interest in representing behavior exploited in supercritical extraction. There are many more possible classes and subclasses, especially where azeotropic behavior variations are involved, as discussed in the works of Rowlinson[10] and King.[11] More on the phase behavior applicable to dense gases can be found in reviews[12,13] and specialized texts[14] in this area.

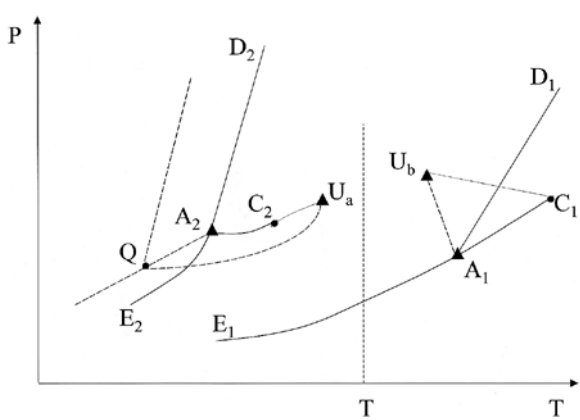

Figure 21.1.6 Phase behavior of dissimilar systems.

Supercritical extraction often involves separation of relatively non-volatile components, often in the solid phase, through selective solubility in the supercritical gasses. Thus, the critical temperatures of the pure components are likely to be significantly different and the critical temperature of the solvent is likely to be lower than the triple point temperature of the solute. The implication is that there is no common temperature range where both

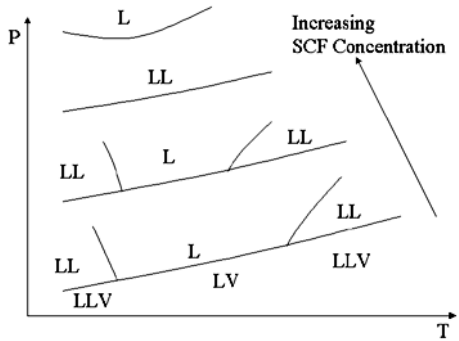

Figure 21.1.7. The effect of supercritical fluid concentration on polymer-solvent phase behavior.

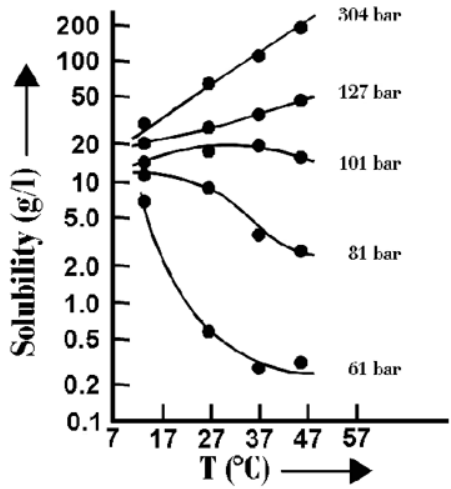

Figure 21.1.8 Solubility of naphthalene in supercritical ethylene.

components will be liquid. The phase diagram of systems with solid and supercritical fluid is shown in Figure 21.1.6.[15] The full lines are the sublimation, melting, and vapor pressure curves of the pure components, C_1 and C_2. Point Q is the quadruple point, where four phases S_1, S_2, L, and G are in equilibrium. If the temperature of C_2 lies far below of that A_1 (triple point of C_1), the three-phase region S_2, L, G curves upward and intersects the gas liquid line to form critical end points U_a and U_b. No liquid phase exits between the temperatures of U_a and U_b. The three-sided region $A_1C_1U_b$ is a region of gas-liquid phase separation. At temperatures between this region and U_a, the solid phase of component C_1 is in equilibrium with C_2 rich gas phase.

The polymer solution behavior is of significant importance due to large number of applications in the field. The supercritical fluids primarily follow class four behavior. An example related to the effect of supercritical solvent on phase behavior of such systems is shown in Figure 21.1.7. More comprehensive coverage of the field can be found in texts[6] and review papers.[16]

The unique behaviors of supercritical fluids relate to solubility enhancement and how the solubility varies with operating conditions. As can be seen from Figure 21.1.8, the solubility of a solid solute is enhanced several orders of magnitude over the ideal solubility.[17] Furthermore, the solubility decreases with increasing temperature at supercritical pressures somewhat above the critical, while at supercritical pressures above a "cross-over pressure", solubility of a solute increases with temperature. The crossover pressures are different for different solutes. As depicted in Figure 21.1.9, complete fractionation of solutes solubilized in the supercritical solvent is possible by slight increase in temperature.[18] Another unique behavior, called "barotropic effect", exists when highly compressed dense gas reaches pressures higher than the incompressible liquid. In such instances, dense gas phase is below the liquid or the second gas phase.

There are three essential elements that make up the thermodynamic foundations of supercritical fluids. These elements are experimental and identification techniques for elucidating the phase behavior, models for dense gases, and computation methods.

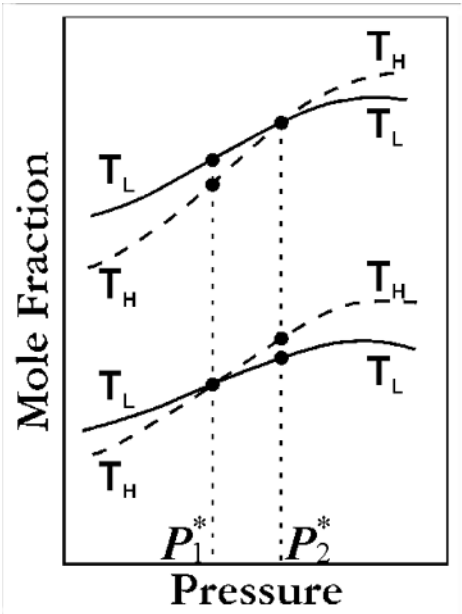

Figure 21.1.9 The crossover pressure and retrograde behavior.

21.1.2.1.1 Experimental methods

There are two basic approaches to experimental determination of the high-pressure phase behavior of a system, synthetic and analytic. In the synthetic approach, phase boundaries of a fixed (known) composition system are observed, usually visually, in a cell with sight windows, by manipulation of the system pressure and temperature.

In the analytical approach, the components are equilibrated and the compositions of the co-existing phases are determined either through sampling and off-line analysis or on-line spectroscopic techniques. A typical system for determination of vapor/liquid/liquid phase behavior is shown in Figure 21.1.10. The system is a double re-circulation variable volume system. A dynamic variant of this method is for the determination of the solubility of solids in a supercritical fluid. The stationary solid phase is contacted with a continuous supply of

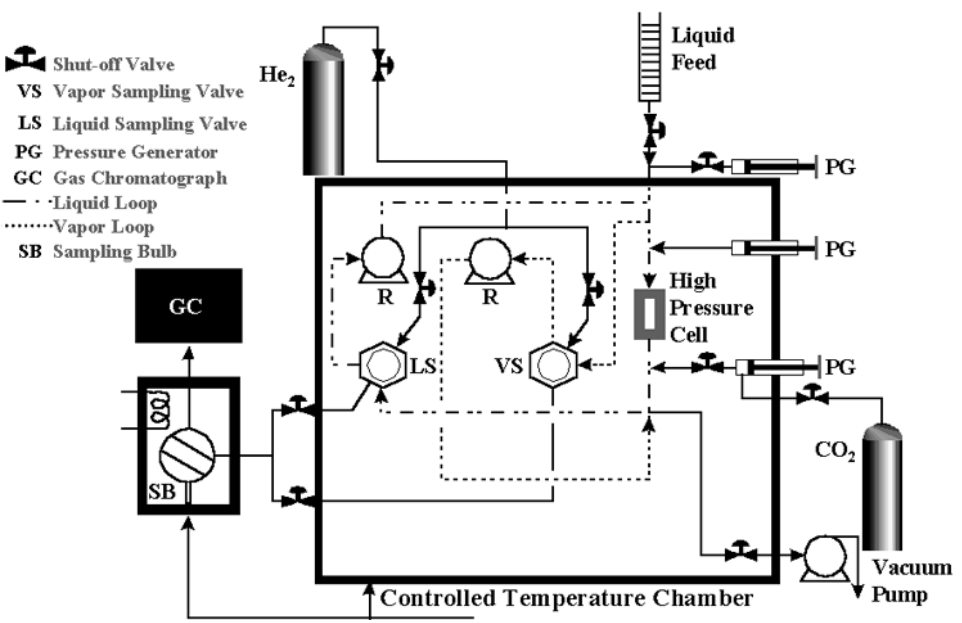

Figure 21.1.10. A high pressure fluid phase equilibrium measurement system.

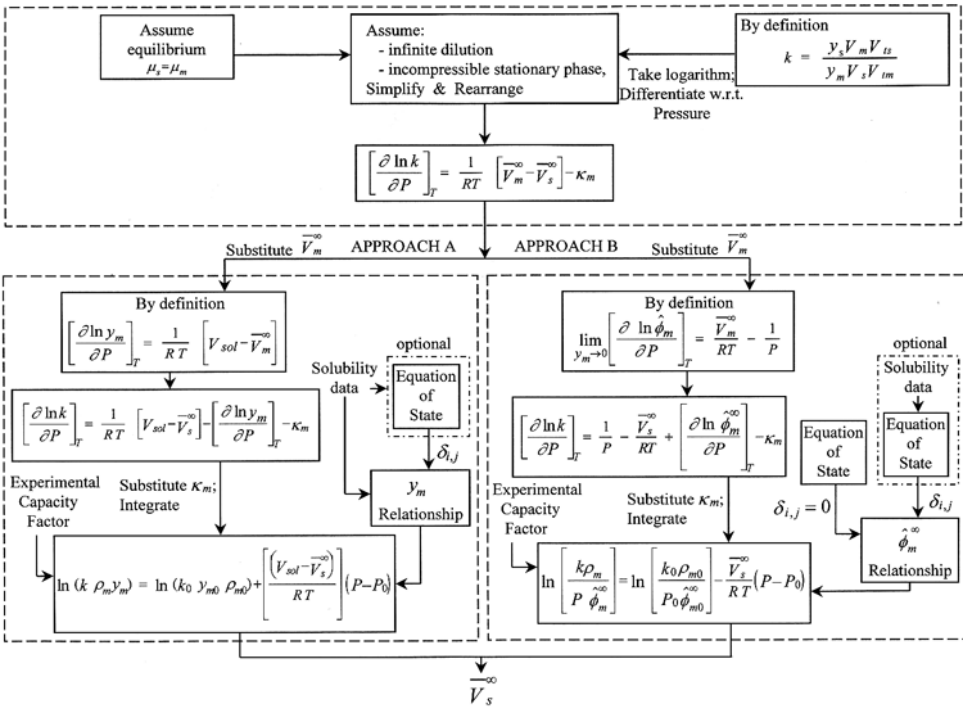

Figure 21.1.11. Estimation of solubility and partial molar volume using supercritical fluid chromatography.

supercritical fluid that is ensured to exit with an equilibrium amount of the solid.

The chromatographic and calorimetric information can also be used to infer phase behavior information. For example, solubility measurements can be performed on a Supercritical Fluid Chromatograph (SFC) where a relatively short fused silica capillary tubing system replaces the usual column. Sample is coated into this tubing using the same techniques that are used to coat a stationary phase on an analytical capillary column. Raising the solvent pressure stepwise from a selected starting point allows isothermal measurements of solubility. At each step, the ion current in the mass spectrometer, which is used as the detector, is monitored to determine the quantity of solute in solution. Also, solubility may be estimated from the last equations in Approach A and Approach B summarized in Figure 21.1.11.[19] This is true provided that the adsorbent is a solid and partial molar volume of the solute (e.g., naphthalene) in the stationary phase is equal to the solid molar volume of the solute.

It is worth noting that Supercritical Fluid Chromatography is an important experimental tool for measurement of a portfolio of physical-chemical properties as depicted in Table 21.1.2.

However, indirect approaches and methods that involve sampling suffer from magnification of propagated error due to the high sensitivity and non-linear nature of governing fundamental relations in the critical region.

Table 21.1.2. Classification of physicochemical properties that can be measured by SFC

Equilibrium properties	Kinetic and transport properties	Other properties
* Fluid phase interactions - Second virial coefficients * Solution interactions - Partial molar volumes - Solubilities * Surface interactions - Adsorption isotherms	* Diffusion coefficients * Mass transfer coefficients	* Molecular masses
	°Adsorption and desorption rate constants °Reaction rate constants	

*Properties determined by SFC; °Properties determined by GC and can be determined by SFC

Due to the inherent limitation of predictive methods, relative importance of experimental methods become very significant when compared to simple fluids at near ambient condition. Therefore, the area is a popular review[3,20] topic and is included in most texts[6,21] in the field.

21.1.2.1.2 Computational aspects

Computation and definition of critical phenomena is essential in prediction, modeling, and identification of various phases at high pressures. Gibbs presented the definition of critical state in his pioneering paper "On the Equilibrium of Heterogeneous Substances" in 1876.[22] For mixtures, mechanical and thermal stability criteria are not sufficient to describe the critical behavior and diffusional (material) stability criteria are required. Various investigators have transformed Gibbs' criteria to other variable sets and Reid and Beegle[23] have developed Gibbs' criteria in Legendre transforms with suggestions to overcome indeterminacy. Works of Michelsen[24] and Heidemann[25] combine algorithms with more convenient representation of Gibbs criteria.

Generation of complete phase diagrams is not a trivial task and may require utilization of either insight and heuristic guidance or global approaches coupled with Mixed Integer Non-linear Programming (MINLP) or intelligent search algorithms such as genetic algorithms and simulated annealing.

The methods used in generation of phase diagrams may either employ the more popular integral approach that is suitable for design purposes or the more insightful differential approach that is preferred for generation of phase diagrams.[26] The basic elements of integral approach are the determination of fluid phase partition coefficient, K, for each component as well as stability criterion coupled with a computational algorithm.

For determination of fluid phase partition coefficients, K, one may take a symmetric approach that uses Equation of States (EOS) for all fluid phases or an unsymmetrical approach that makes use of liquid activity models for the liquid phase retaining the equation of state models for the gas phase.

For symmetric approach:

$$K_i = \frac{\hat{\varphi}_i^{\beta}(T,P,x_i)}{\hat{\varphi}_i^{\alpha}(T,P,y_i)}$$

For the unsymmetrical approach:

$$K_i \frac{\gamma_i^{\beta}(T,P,x_i) f_i(T,P)}{\hat{\varphi}_i^{\alpha}(T,P,y_i)}$$

where:

K_i	partition coefficient of component i in phases α and β
$\hat{\varphi}_i^{\beta}$	fugacity coefficient of component i in mixture for phase β
$\hat{\varphi}_i^{\alpha}$	fugacity coefficient of component i in mixture for phase α
γ_i^{β}	activity coefficient of component i in mixture for phase β
f_i	fugacity of pure component i

If one assumes no solvent in the solid phase, the relation for solubility of the solid in the supercritical solvent reduces to:

$$y_i = \underbrace{\left(\frac{P_i^{sub}(T)}{P}\right)}_{A}\underbrace{\left(\frac{1}{\hat{\varphi}_i^{DG}}\right)}_{B}\underbrace{\exp\left(\frac{\overline{V}_i^{s}\left(P - P^{sub}(T)\right)}{RT}\right)}_{C}$$

where:

y_i	mole fraction of component i in gas phase
P_i^{sub}	sublimation pressure of component i
P	total pressure
$\hat{\varphi}_i^{DG}$	fugacity coefficient of component i in mixture for dense gas phase
$\overline{V}_i^{s}$	partial molar volume of component i in solid phase
R	universal gas constant
T	absolute temperature

The first term A is for ideal gas solubility, the second term B accounts for the non-ideality, while the third term C (Poynting correction) accounts for the pressure effects. The product of the second and third terms is often referred as the Enhancement Factor (over the ideal). In the absence of data, the sublimation pressure may be approximated through extrapolation of the vapor pressure information.

21.1.2.1.3 Modeling

The approaches to modeling the high pressure phase behavior follow either use of the equation of state models for fugacity coefficient determination or the treatment of the dense gas as an "expanded liquid" through an activity coefficient model, the former approach being more popular.

The macroscopic dense gas modeling approaches include van der Waals family of equation of states, virial family of equation of states, and non-classical approaches. The molecular/theoretical approaches and considerations contribute not only to more comprehensive models but also provide insight bringing forth sound parameters/terms to the macroscopic models. Computer simulation (molecular) can also be used to directly compute phase behavior with some success.[27,28] The virial family of equation of states finds limited use in supercritical applications due to the necessity for a large number of terms and

their inadequacy in representing the critical point. The non-classical scaling approaches[29,30] fail when extended beyond the very narrow critical region and their combinations with equations of state (crossover EOSs) are still far from having practical applicability. Therefore, we will focus on the van der Waals family of Equation of States.[31]

These equations of states have both a repulsive and an attractive term. The most popular variants differ in how the attractive terms are modeled. The success of more recent Peng-Robinson[32] (PR) and Soave-Redlich-Kwong[33] (SRK) equation of states in phase behavior representation is due to the added parameter, accentric factor that incorporates vapor pressure information into the model. The shortcomings around the critical point are mainly due to the enhanced contribution of repulsive forces that can be modified through Perturbed Hard Chain Theory (PHCT).[34] Naturally, one other inherent difficulty is due to the instability of high molecular weight compounds at their critical point. This implies use of other parameters or pseudo critical properties to model the compounds and their mixtures. These equations of states are better in representing molar gas volume then the liquid. The accuracy of molar liquid volume can be improved through volume translation.[35] The added terms and parameters naturally complicate the equation of state since the order of the equation increases above cubic.

Yet another essential dimension of the equation of states is their representation of mixture properties, which is achieved through mixing rules (models) that often include adjustable binary interaction parameters determined from multi-component, ideally binary, data. Most classical approaches fail to model mixing behavior of systems with dissimilar size components and hydrogen bonding, particularly if one expects to apply them throughout a wide pressure and temperature range that extends from very low to high pressures. Some of the empirical density dependent mixing rules such as Panagiotopoulos-Reid[36] can account for the relative size of the solute and the solvent but have theoretical shortcomings violating one fluid model. There are also approaches that combine equation of state with activity models by forcing the mixture EOS to behave like the activity models (G_E) at liquid densities.[31] EOS-G_E models can be combined with group contribution models to make them predictive. More recently, Wong-Sandler[37] mixing rules provide an avenue to incorporate more readily available low-pressure information into the equation of states extrapolate throughout the entire pressure range, as well as ensuring fundamentally correct boundary conditions.[38]

Considering the difficulty associated with representing fugacity coefficients that may vary over ten orders of magnitude by mere change in temperature, pressure and composition; a simple equation of state such as Peng-Robinson, which is given below, do very well in correlating the experimental data and representing the phase behavior well.

$$p = \underbrace{\frac{RT}{V_m - b}}_{\text{repulsive term}} - \underbrace{\frac{a}{V_m(V_m + b) + b(V_m - b)}}_{\text{attractive term}}$$

where:

$$b = \sum_i x_i b_i$$

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{0.5} (1 - k_{ij})$$

$$b_i = 0.07780\ (RT_{ci}/p_{ci})$$

$a_i = \alpha_i\, 0.45724\, (R^2T^2_{ci}/p_{ci})$
$\alpha_i = [1 + m_i(1 - T^{1/2}_{ri})]^2$
$m_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2$

where:

p	pressure
R	universal gas constant
T	temperature
V_m	molar volume
b	function of T_{ci} and P_{ci} and x_i
a	function of T_{ci}, P_{ci}, x_i and k_{ij}
α_i	a function of reduced temperature, T_{ri} and accentric factor, ω_i
m_i	a function of accentric factor of component i
ω_i	accentric factor of component i
k_{ij}	the interaction coefficient of the molecules i and j
T_{ci}, P_{ci}	critical temperature and pressure of component i
x_i	mole fraction of component i
T_{ri}	reduced temperature, T/T_{ci}

The polymer solutions[39] warrant use of a special class of lattice models such as Florry-Huggins. For correlation purposes Sanchez-Lacombe[40] method is sufficient but one may also use Statistical Association Fluid Theory[41] (SAFT) models to obtain a better representation.

21.1.2.2 Transport properties of supercritical solvents

The transport properties of the supercritical fluids fall somewhat in between the gas and the liquid and also depend on how removed one is from the critical point. Dense gasses have the solubilizing power of liquids and the mobility of gasses as depicted in Table 21.1.3. There are quite a few empirical correlations and theoretical models, which are primarily extensions of corresponding low-pressure liquid and gas counter parts. Similarly, of the classical experimental methods can be used for measurement of transport properties of supercritical fluids. A rather brief overview of the methods applicable for supercritical fluids will be presented since specialized reviews in the area give a good account of the state of the art.[30,42] For engineering purposes, one can use applicable property estimation methods available in flowsheet simulators[43] such as ASPEN PLUS, PROII, HYSIM, and CHEMCAD. These methods are discussed in a text classical in the field.[44]

Table 21.1.3. Transport properties of gases, liquids, and supercritical fluids

State	Condition	Property		
		Density, g/cm^3	Diffusivity, cm^2/s	Viscosity, g/cm-s
Gas	1 atm, 25°C	0.6-2×10^{-3}	1-4×10^{-1}	1-3×10^{-4}
Liquid	1 atm, 25°C	0.6-1.6	0.2-2×10^{-5}	0.2-3×10^{-2}
SC Fluid	T_c, P_c	0.2-0.5	0.5-4×10^{-3}	1-3×10^{-4}
SC Fluid	T_c, $4P_c$	0.4-0.9	0.1-1×10^{-3}	3-9×10^{-4}

21.1.2.2.1 Viscosity

Both the capillary viscometer (providing about 0.7% accuracy), the theory of which is based on the Hagen-Poiseuille equation and the oscillating disc viscometer (providing about 0.2% accuracy) are applicable to experimental determination of viscosity at high pressures and temperatures.

Most of the theoretically based estimation methods for viscosity of dense gases rely on modified Enskog theory. Corresponding states based methods are also popular but should be used with care due to their empiric nature.

21.1.2.2.2 Diffusivity

The experimental techniques used to measure the diffusion are based upon chromatographic methods,[19] NMR (for self-diffusion), and photon correlation spectroscopy.[45]

The so called chromatographic method for the measurement of diffusion coefficients, strictly speaking, is not a chromatographic method since no adsorption/desorption or retention due to partition in two phases are involved in the method. The experimental system used is however a chromatograph. Diffusion occurs in an empty, inert column on which the fluid phase is not supposed to be adsorbed. The fluid, in which the solute diffuses flows, continuously through the empty column and the solute, which is introduced into the column at one end, is detected at the other end as effluent concentration.

The theory of diffusion in flowing fluids is first given by Taylor[46] and Aris.[47] According to Aris, a sharp band of solute, which is allowed to dissolve in a solvent flowing laminarly in an empty tube, can be described in the limit of a long column as a Gaussian distribution, the variance of which, σ^2, in length units is:

$$\sigma(x)^2 = 2D_{eff}t$$

where:

t	time of migration of the peak
D_{eff}	effective diffusion coefficient given by,

$$D_{eff} = D_{12} + \frac{r^2u^2}{48D_{12}}$$

where:

u	average solvent velocity
r	inner radius of the tube
D_{12}	binary diffusion coefficient.

The first term describes the longitudinal diffusion in the axial direction. The second term is called the Taylor diffusion coefficient and describes band broadening due to the parabolic flow profile and therefore radial diffusion. The height equivalent to a theoretical plate, H, is a measure of the relative peak broadening and is defined as

$$H = \sigma(x)^2 / L$$

where:

L	length of the tubing.

Combining the above equations yields

$$H = \frac{2D_{12}}{u} + \frac{r^2u}{24D_{12}}$$

Bulk diffusivity can be calculated from the above equation.

The estimation of low pressure diffusivity is based on the corresponding states theory. The dense gas diffusion coefficient estimation is based on the Enskog theory. The binary diffusion coefficient D^v_{ij} at high pressures as modeled by the Dawson-Khoury-Kobayashi correlation, is next given as a representative model. For a binary system, the equations are:

$$D^v_{ij}\rho^v_m = \left[1 + a_1\rho^v_{rm} + a_2\left(\rho^v_{rm}\right)^2 + a_3\left(\rho^v_{rm}\right)^3\right] D^v_{ij}(p=0)\rho_m(p=1\,atm)$$

$$\rho^v_{rm} = V_{cm} / V^v_m, \quad \rho^v_m = 1/V^v_m, \quad V_{cm} = \frac{y_i V^*_{ci} + y_j V^*_{cj}}{y_i + y_j}$$

where:

ρ_m	molar density
ρ_{rm}	reduced molar density
a_1, a_2, a_3	constants
V_{cm}	critical molar volume
V_m	molar volume
V_{ci}	critical volume of component i
y_i	mole fraction of component i

D^v_{ij} (p=0) is the low pressure binary diffusion coefficient obtained from the Chapman-Enskog-Wilke-Lee model. The molar volume and the molar density are calculated with an equation of state model.

21.1.2.2.3 Thermal conductivity

Transient hot-wire and co-axial cylinder methods are typically applied for measurement of the thermal conductivity of supercritical fluids.[48]

The theory of thermal conductivity is based on the Enskog theory and a typical model for both vapor and liquid thermal conductivity is given by Chung-Lee-Starling. This model makes use of the PRWS (Peng-Robinson with the Wong-Sandler mixing rules) to provide a flexible and predictive equation of state. The main equation for the Chung-Lee-Starling thermal conductivity model is:

$$\lambda = \frac{31.2\eta(p=0)}{M} f_1 + f_2$$

where:

$f_1 = \mathrm{fcn}(\rho_{rm}, \omega, p_r, \kappa)$
$f_2 = \mathrm{fcn}(T_c, M, V_{cm}, \rho_{rm}, \omega, p_r, \kappa)$
$\psi = \mathrm{fcn}(C_v, \omega, T_r)$

η(p=0) can be calculated by the low pressure Chung-Lee-Starling model. The parameter p_r is the reduced dipole moment given by:

$$p_r = 4.152\frac{p}{\left(V_{cm}T_c^{1/2}\right)}$$

where:

λ	thermal conductivity
η	viscosity
M	molecular mass
ρ_{rm}	reduced molar density
ω	accentric factor
p	dipole moment
p_r	reduced dipole moment
V_{cm}	critical molar volume
T_c, T_r	critical and reduced temperature
κ	polar parameter

For low pressures, f_1 is reduced to 1.0 and f_2 is reduced to zero. This gives the Chung-Lee-Starling expression for thermal conductivity of low pressure gases. The molar density, ρ_{rm}, can be calculated using and equation of state model (for example, the Peng-Robinson-Wong-Sandler equation of state) where the mixing rule for b is obtained as follows. The second virial coefficient must depend quadratically on the mole fraction:

$$B(T) = \sum_i \sum_j x_i x_j B_{ij}$$

with:

$$B_{ij} = \frac{\left(B_{ii} + B_{ij}\right)}{2}\left(1 - k_{ij}\right)$$

The relationships between the equation of state at low pressure and the virial coefficient are:

$$B = b - \frac{a}{RT}; B_{ii} = b_i - \frac{a_i}{RT}$$

Wong and Sandler has shown that the following mixing rule does satisfy the second virial coefficient equation:

$$b = \frac{\sum_i \sum_j x_i x_j B_{ij}}{1 - \frac{A_m^E(p=\infty)}{\Lambda RT} - \sum_i x_i B_{ii}}$$

where:

B	the second virial coefficient
k_{ij}	the interaction coefficient of the molecules i and j
b	function of T_{ci} and P_{ci} and x_i
a	function of T_{ci}, P_{ci}, x_i and k_{ij}
A^E_m	Helmholtz free energy

The pressure correction to the thermal conductivity for a pure component or mixture at low pressure is given by:

$$\lambda^v = fcn\left(\lambda^v(p=0), \rho_{rm}, y_i, M_i, T_{ci}, V_{ci}, Z_{ci}\right)$$

where:

$$\rho_{rm} = \sum_i y_i \frac{V_{ci}}{V_m^v}$$

where:

λ^v	thermal conductivity
ρ_{rm}	reduced molar density for mixtures
y_i	mole fraction of component i
M_i	molecular weight of component i
T_{ci}	critical temperature of component i
V_{ci}	critical volume of component i
Z_{ci}	critical compressibility of component i

The vapor molar volume, V^v_m can be obtained from the equation of state models as described above.

21.1.2.2.4 Surface tension

Stability of phase boundaries depends on the surface tension. Surface tension in a supercritical fluid system is of major importance for drying, surfactant efficacy, and extraction. The surface tension of a gas increases with pressure and approaches zero at the critical point while the surface tension of liquid decreases with pressure resulting in dissolution of supercritical components in the liquid phase. The methods useful in correlating surface tension include Macleod-Sugden correlation and corresponding states theory.[21]

21.1.2.3 Entrainer (co-solvent effects) of supercritical solvents

Entrainers, modifiers, and co-solvents are basically mixed solvent systems and provide another dimension to supercritical fluid extraction. The entrainers enhance the solubility of the low volatile substance in the solvent, provide selective solubility in multi-solute instances, and enhance the sensitivity of the solubility and selectivity to temperature, pressure, and composition. The entrainers may be reactive and are also useful as slurrying media. Table 21.1.4 shows representative data on the effect of entrainers on vapor liquid systems that has been systematically studied by Brunner's group. Kurnik and Reid[50] as well as Johnston's group[51] present data for dense gas-solid systems.

Table 21.1.4. The effect of entrainers on separation factor (Adapted from Brunner[21])

Entrainer	α	Entrainer	α
Hexadecanol(1) - octadecane(2) - entrainer - nitrous oxide (120 bar, 70°C, y_0 = 1.5 wt%, a_0 = 2, $y_{(1)+(2)}$ = 2 wt%)		Octadecane(1) - salicylic acid phenal ester(2) - entrainer - nitrous oxide (120 bar, 70 °C, y_0 = 1.5 wt%, a_0 = 2, $y_{(1)+(2)}$ = 1.7 wt%)	
acetone	3	methanol	1.65
methanol	2.4	dichloromethane	1.5
dichloromethane	2.1	benzene	1.45
benzene	2	cyclohexane	1.4
methyl acetate	2	acetone	1.4
hexane	1.9	hexane	1.3
cyclohexane	1.7	methyl acetate	1.2

Entrainer	α	Entrainer	α
Hexadecanol(1) - octadecane(2) - entrainer - ethane (120 bar, 70°C, y_0 = 15 wt%, a_0 = 2.5, $y_{(1)+(2)}$ = 30 wt%)		Hexadecanol(1) - octadecane(2) - entrainer - carbon dioxide (120 bar, 70 °C, y_0 = 0.4 wt%, a_0 = 2.5, $y_{(1)+(2)}$ = 1 wt%)	
methanol	2.2	methanol	3.4
acetone	1.6	acetone	1.8
hexane	1.6	methyl acetate	1.6
(120 bar, 90°C, $y_{(1)+(2)}$ = 20 wt%)		hexane	1.4
methyl acetate	1.8		
benzene	1.2		
dichloromethane	1.1		

Separation factor, $\alpha = (y_2/x_2)/(y_1/x_2)$

Although entrainers provide the aforementioned added advantages, they also bring forth more complex process flowsheets. The separation of extract from entrainer and entrainer from the supercritical component are not as easy and as sharp as in the instances without entrainer. The selection of entrainer is based on thermodynamic, environmental, and economic considerations. The solute-entrainer and entrainer-supercritical separations are the key from the processing perspective.[52]

21.1.2.4 Reaction rate implication in supercritical solvents

Reactions in supercritical media utilize high pressures. Therefore, the effect of pressure on reaction equilibrium as well as reaction rate plays an important role in supercritical phase reactions.[53]

The kinetics of the reaction can be explained in terms of the transition-state theory. According to the theory, the reaction occurs via a transition state species M* and the generic elementary reaction can be written as:

$$aA + bB + \ldots\ldots\ldots\ldots \leftrightarrow M^* \rightarrow \text{Products}$$

The effect of pressure on the rate constant is given as:

$$\left(\frac{\partial \ln k_x}{\partial P}\right)_T = \left(\frac{\partial \ln K_x^*}{\partial P}\right)_T + \left(\frac{\partial \ln \kappa}{\partial P}\right)_T = \frac{\Delta \overline{V}^*}{RT} + \left(\frac{\partial \ln \kappa}{\partial P}\right)_T$$

where:

k_x	rate constant in mole fraction units
P	pressure
T	temperature
K^*_x	mole fraction based equilibrium constant for reaction involving reactants and transition state
κ_T	isothermal compressibility
$\Delta\overline{V}^*$	activation volume (difference between partial molar volumes of activated complex and reactants), $\Delta\overline{V}^* = \overline{V}^* - a\overline{V}_A - b\overline{V}_B - \ldots$
R	universal gas constant

The rate constant in the above equation is expressed in terms of pressure independent units (mole fraction). If the rate constant is expressed in terms of pressure dependent units (such as concentration), the relevant equation is:

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta \overline{V}^{\star}}{RT} + \left(\frac{\partial \ln \kappa}{\partial P}\right)_T + \kappa_T\left(1 - a - b - \cdots\right)$$

If the volume of activation is positive, the reaction is hindered by pressure. However, for high negative values of the volume of activation, the pressure enhances the rate of the reaction. Therefore, supercritical fluids that exhibit very high negative activation volumes for certain reactions will improve the rate of the reaction.

The volume of reaction, rather than activation, is crucial in determining the effect of pressure on the equilibrium constant.

$$\left(\frac{\partial \ln K_x}{\partial P}\right)_{T,x} = -\frac{\Delta \overline{V}_f}{RT}$$

where:

$\Delta \overline{V}_f$ reaction volume (difference between partial molar volumes of products and reactants)

If the equilibrium constant is expressed in terms of pressure dependent units (such as concentration), the relevant equation is:

$$\left(\frac{\partial \ln K}{\partial P}\right)_{T,x} = -\frac{\Delta \overline{V}_r}{RT} + \kappa_T \sum v_i$$

where:

v_i stoichiometric coefficient

As the above equation implies, supercritical fluids that exhibit very high negative activation volumes for certain reactions will improve the equilibrium conversion of the reaction.

21.1.2.5 Sorption behavior of supercritical solvents

Both adsorption from a supercritical fluid to an adsorbent and desorption from an adsorbent find applications in supercritical fluid processing.[54,55] The extrapolation of classical sorption theory to supercritical conditions has merits. The supercritical conditions are believed to necessitate monolayer coverage and density dependent isotherms. Considerable success has been observed by the authors in working with an equation of state based upon the Toth isoterm.[56] It is also important to note that the retrograde behavior observed for vapor-liquid phase equilibrium is experimentally observed and predicted for sorptive systems.

21.1.2.6 Swelling with supercritical solvents

As the pressure of the gas is increased, the solubility of the supercritical gas in the solid polymer increases resulting in swelling, a phenomena that could be advantageous in certain applications while its deleterious impact should be minimized, if not totally eliminated, in other instances.

The sorption of supercritical solvent and the resulting swelling could be very high, for example around 30% and 20% respectively for carbon dioxide in polymethylmethacrylate (PMMA). In such instances, the experimental information could be summarized using polymer equation of states such as Sanchez-Lacombe where a single mixture fitting parameter is used.[6]

Swelling can be advantageous in that it enables permeation and diffusion of the supercritical fluid into the polymer network. Fragrances, dyes, or medicinal substances loaded in the supercritical fluid can readily impregnate into the polymer and load the polymer with the aforementioned additives. Upon release of the pressure, only the supercritical fluid (i.e., carbon dioxide) flashes off. This avenue has led to a plethora of controlled (timed) release products.

Naturally, swelling may be undesirable in many instances as well. For example, swelling of organic polymer based membranes decreased selectivity. Other possible deleterious effects could include malfunctions due to solubilization and swelling of sealants such as gaskets or o-rings.

21.1.2.7 Surfactants and micro-emulsions

Most highly polar and ionic species are not amenable to processing with desirable solvents such as carbon dioxide or any other solvent such as water that has a higher critical temperature well above the decomposition temperature of many solutes. In such instances, the combination of the unique properties of supercritical fluids with those of micro-emulsions can be used to increase the range of applications of supercritical fluids.[57] The resulting thermodynamically stable systems generally contain water, a surfactant and a supercritical fluid (as opposed to a non-polar liquid in liquid micro-emulsions). The possible supercritical fluids that could be used in these systems include carbon dioxide, ethylene, ethane, propane, propylene, n-butane, and n-pentane while many ionic and non-ionic surfactants can be used. The major difference between the liquid based emulsions and the supercritical ones is the effect of pressure. The pressure affects the miscibility gaps as well as the microstructure of the micro-emulsion phase.

The incorporation of the micro-emulsion phase creates interesting potential advantages for reactions as well as separations. Isolation of components from fermentation broths and garment cleaning appear to be two of the more competitive applications of these systems.

21.1.3 SEPARATION WITH SUPERCRITICAL SOLVENTS

Supercritical fluids are effective at much lower temperatures than distillation, and their application in separation avoids degradation and decomposition of heat-labile compounds. Attractiveness of supercritical extraction processes are due to the sensitivity of responses to process variables, promise of complete and versatile regeneration of solvents, energy savings, enhanced solute volatilities, solvent selectivities, favorable transport properties for solvents, and state governed effectiveness of solvents which enables the use of low cost, non-toxic, environmentally acceptable solvents. The impact of inherent characteristics of supercritical fluids on separations is summarized in Table 21.1.5.

Table 21.1.5 The characteristics and challenges with supercritical separations

Inherent characteristics of systems @ supercritical conditions	Resulting promise	Challenges to be met
Enhanced solubility	Effective at lower temperatures	Recovery of substances inadvertently extracted
Favorable transport properties	High mass transfer rates especially in porous media	

Inherent characteristics of systems @ supercritical conditions	Resulting promise	Challenges to be met
Sensitivity of responses to process variables	Effective recovery of solvents, and innovative fractionation possibilities	Control and optimization
High pressure		High capital cost and need for recovery of mechanical energy
Dominance of physical characteristic on solvency over chemical	Expansion of solvent spate to environmentally benign, inexpensive, and non flammable solvents and their mixtures	

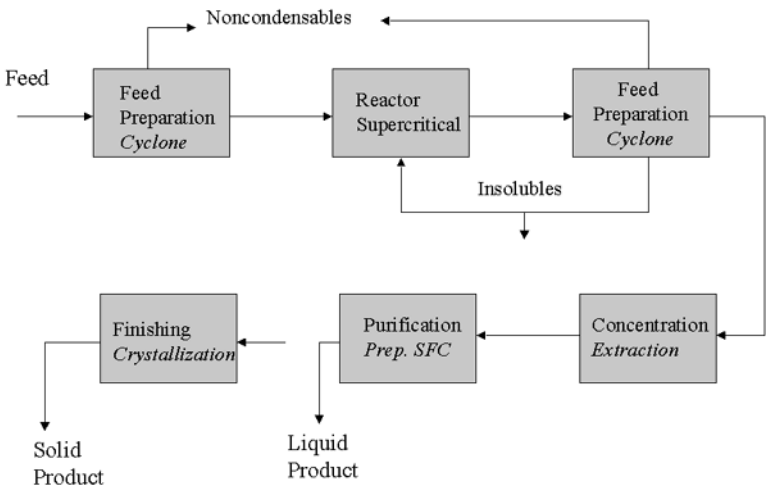

Figure 21.1.12. A generic process flow sheet.

There have been many useful attempts made to classify separation technologies. Supercritical fluids are applicable with both intra-phase and inter-phase separations. Due to the ease and flexibility in which a new phase can be formed for regeneration of the solvent, inter-phase is the more common. Furthermore, material solubility and swelling problems, particularly with organic-component based membranes, limit inter-phase separations. This is due to the enhanced solubility of these components in supercritical solvents.

Generic steps involved in a typical chemical process are shown in Figure 21.1.12, with each separation sub task type identified. Environmental processes are usually dominated by feed preparation tasks while biochemical processes utilize all of the four subtasks. Blending is considered a finishing task while splitting is considered a feed preparation task. The objective criteria used for the separation may vary according to the subtask. For example, in feed preparation, technical feasibility such as removal of the fines is more appropriate while the usual economic objectives subject to technical feasibility constraints become the goal for the purification and finishing stages.

The feed preparation task involves removal of insoluble components and at times non-condensable compounds. The technology selection and the scheduling of tasks are con-

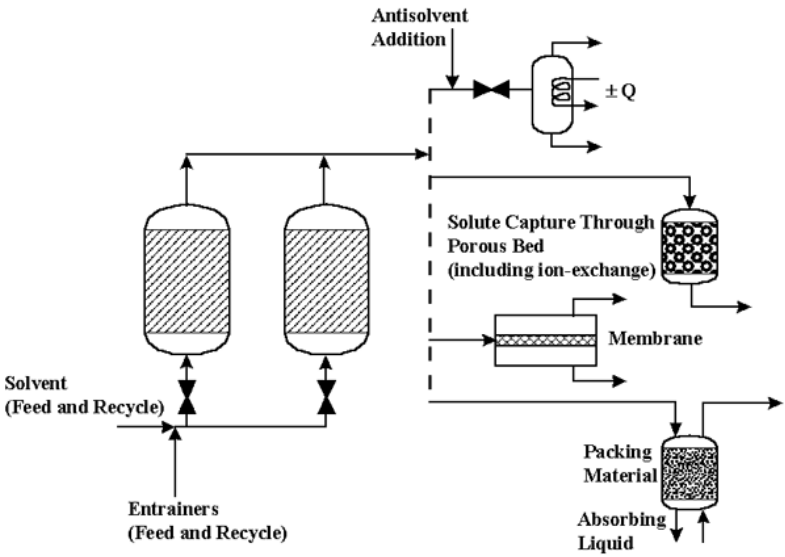

Figure 21.1.13. Supercritical leaching and options for supercritical solvent regeneration.

centration and particle size distribution dependent. These processes are usually physical/mechanical in nature. The feed preparation may be carried out in a unit designed particularly for the purpose or the function may be tied to another function within a single unit. For example, the fines, either nucleated through temperature and/or pressure perturbation, or particles suspended in the supercritical fluid can be readily separated through cyclones.

Concentration (or isolation) tasks are usually necessary with streams where the product concentration is very low (dilute). Adsorption and extraction are typical technologies utilized here. Energy considerations dominate the technology selection subject to product contamination and stability constraints. Thus, the base technology depends on the availability of the Mass Separating Agent (e.g., adsorbent or solvent) and its efficient recycle. Supercritical extraction of organic compounds from aqueous streams is a typical example of isolation step.

The candidate technologies for purification are many. Distillation, the work-horse of the chemical processes, leads the pack. Most of the synthesis effort to date has concentrated on the product purification step. This step is often the last step for liquid products especially in the chemical and petrochemical industries. The biochemical industry utilizes membrane and chromatographic processes more than the other industries due to the thermal stability and purity requirements. In the electronic industry, membrane processes are more prevalent due the ultra-purities necessary. Supercritical fractionation of alcohol water systems with the aid of a dense gas is an example of a purification step.

Crystallization, drying, and blending are typical operations necessary to polish (finish) the product to its final form. Particle nucleation from a supercritical fluid solution is an example of finishing. Each supercritical separation technique is identified on this generic process.

21.1.3.1 Leaching - generic application

Leaching is usually incorrectly referred to as extraction of a solid substrate, and is commercially the most significant application of supercritical fluids. A generic flowsheet, shown in Figure 21.1.13, illustrates the basic processing concepts. A heat labile natural substrate is usually contacted with a flowing supercritical fluid in a semi-continuous mode. The supercritical fluid may optionally be doped with an entrainer. Due to the stationary (batch) nature of the leaching stage, two or more parallel vessels loaded with the substrate may be utilized. The material leached is recovered and fractionated through pressure reduction, temperature perturbation, adsorption, membranes or through absorption. During the initial stages of leaching, the solute loading is high and may approach the equilibrium solubility limit, while at the latter stages kinetic and mass transfer limitations are responsible from relatively lower the concentration of the solute. Both coffee decaffeination[59] and hops extraction[60] are popular commercial successes of this application. Further, typical applications are given in Table 21.1.5.

Table 21.1.6. Leaching applications of supercritical fluids

Purpose	Supercritical medium	Substrate
Food processing[61]		
Food purification	CO_2	Coffee decaffeination Cholesterol removal from egg yolk
Essential oils[62]		
Leaching of natural products	CO_2	Oil from soybean, sunflower, spearmint, Camomile, thyme, rosemary sage, chervil
Leaching of natural products	CO_2, N_2O, CHF_3, SF_6	Fungal oil
Leaching of natural products	Methanol, ethanol, acetone	Liquid from hazelnut seed coat
Petrochemical		
Obtaining liquids from solid fuels[63]	Toluene, water, acetone, methanol, THF, tetralin, ethanol	Liquid from coal, lignite
Cleaning and upgrading solid fuels[64]	Toluene, methanol, ethanol, water, acetone, tetralin, CO_2	Sulfur, nitrogen, oxygen removal
Chemical[65]		
Cleaning of parts	CO_2	Oil from contaminated glass grinds, organic additives from extrusion-molded ceramic parts
Cleaning of parts	CO_2, fluorocarbon solvents	Particles from precision devices
Biochemical[66]		
Vitamin, pharmaceutical compounds	CO_2	Natural plants
Environmental[67]		
Extraction of soils	CO_2 + modifier	Polycyclic-aromatic hydrocarbons, pesticides

Purpose	Supercritical medium	Substrate
Extraction of soils	Nitrous oxide	Aromatic amines, pesticides
Extraction of soils	Water	Polycyclic-aromatic hydrocarbons
Polymer processing[6]		
Removal of trace compounds	CO_2	Siloxane oligomer, cyclic trimer, organic compounds from plastic, carbon tetrachloride from polyisoprene

21.1.3.2 Extraction - generic applications

Liquid streams containing close-boiling and heat-labile component can be fractionated with the aid of supercritical fluids or valuable components of aqueous streams could be isolated and concentrated using supercritical solvents. Entrainers could also be added to the solvent to enhance the selectivity, particularly in fractionation instances. The main reason for using entrainers for concentration purposes is to enhance solubility. One can also use membranes along with supercritical fractionator.[68] Typical applications of this process technology are given in Table 21.1.7 and Table 21.1.8 while several review papers and texts provide useful design information.[69-72]

Table 21.1.7. Extraction applications of supercritical fluids

Purpose	Supercritical medium	Substrate
Food processing		
Food purification	CO_2	Oil purification Cholesterol removal from milk fat
Flavor extraction	CO_2	Beer, wine and fruit flavor concentrates
Fractionation of food	CO_2	Oil, milk fat
Forest products		
Extraction of lignocellulosic materials and biomass	CO_2, SO_2, N_2O, H_2O, methylamine, ethanol, ethylene	Cellulose or ligno-cellulosic materials from wood or wood pulp
Biochemical		
Medicinal compound	CO_2	Fermentation broth
Petrochemical		
Purifying liquid fuels	CO_2	Deasphaltation, demetallization
Environmental		
Waste water extraction[73]	CO_2+entrainer	Aqueous toxic wastes, phenol, metabolic wastes
Essential oils		
Purification of essential oils	CO_2	Terpenes from orange, citrus and bergamot peel oil

Table 21.1.8. Fractionation applications of supercritical fluids

Purpose	Supercritical medium	Substrate
Essential oils		
Fractionation[74]	CO_2	Glycerol, fatty acids, glycerides
Chemical		
Fractionation	CO_2	Xylenes, glycerides, alkanes, aromatics
Fractionation	CO_2 + entrainer	Methyl esters, fullerenes
Petrochemical		
Fractionation	Toluene, pentane, propane,	Petroleum pitch, asphalt
Polymer processing		
	CO_2	Polydimethylsiloxane, fluoropolymers, polypropylene

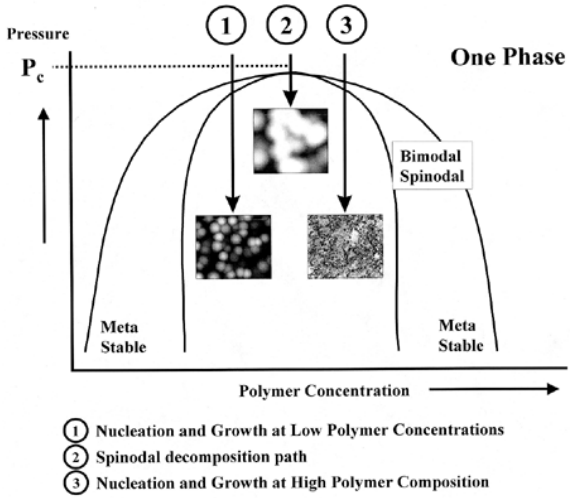

Figure 21.1.14. The pressure reduction path for nucleation of particles from supercritical fluids.

The methods useful in design of extraction systems are the same as those traditional methods applicable to liquid and gaseous systems and include Kremser, McCabe Thiele, Panchon Savarit (including Janecke), and more rigorous rate-based as well as equilibrium based methods. Due to the highly non-linear nature of the physical-chemical properties in the critical region, great care has to be taken in representing both the properties and the solution algorithms.

21.1.3.3 Crystallization - generic applications

Particles nucleated from supercritical fluids have unique particle size, shape, and particle size distributions.[75] The means of achieving nucleation and growth are many, and include pressure reduction, temperature perturbation, and addition of anti-solvents. Time profiling and staging have profound effect on the particle characteristics. The effect of pressure reduction on the resulting nucleated material for different solute concentrations[16] is illustrated in Figure 21.1.14.

21.1.3.4 Sorption - generic applications

The sorption applications[21] include regeneration of porous beds,[76] preparative scale supercritical chromatography,[21] simulated moving beds,[21] thermal swing schemes,[77] and adsorption/desorptions cycles. Although initial applications of supercritical fluids in this domain were on regeneration of porous beds, more recent emphasis on fractionation best reflects

where the true potential of this technique lies. Typical examples are provided in Table 21.1.9.

Table 21.1.9 Sorption applications of supercritical fluids[21,72]

Purpose	Supercritical medium	Substrate
Environmental		
Soil remediation	CO_2 + entrainers	Soil
Regeneration of adsorbents	CO_2	Polychlorinated biphenyls from adsorbents
Petrochemical		
Regeneration of adsorbents	CO_2	Benzene, toluene, ethyl acetate from activated carbon
Regeneration of catalysts	CO_2, THF, hexane, ethylbenzene, benzene	Hydrocarbon, coke removal from catalysts
Chromatographic fractionation	CO_2	Coal tar, mineral oil distillate
Essential oils[78]		
Chromatographic fractionation	CO_2 + alcohol	Black pepper, clove extract
Polymer processing		
Chromatographic fractionation	CO_2, n-pentane+methanol	Styrene oligomer
Biochemical		
Chromatographic fractionation	CO_2 + alcohol	Prostaglandis
Chromatographic fractionation	CO_2 + alcohol	Vitamins, polyunsaturated fatty acids
Chromatographic chiral separation	CO_2	Optical isomers

In synthesis of supercritical sorption processes and their operating policies, the synergy between the characteristics supercritical fluids and the sorption needs to captured. Naturally, the domain requires good distributed process models and solvers in addition to physical property models.

21.1.4 REACTIONS IN SUPERCRITICAL SOLVENTS

As stated in the previous sections, supercritical solvents are widely used for separation, especially for extraction of thermally labile compounds. Although the unique properties of supercritical fluids make them attractive as a reaction medium as well, the use of supercritical solvents as reaction medium is becoming more and more popular only in the recent years. The first review on reactions in supercritical fluids was presented by Subramaniam and McHugh,[79] whereas a more recent and through review was given by Savage et al.[80]

The motivations for using supercritical solvents in chemical reactions are many.[81,82] In this section, the motivations will be stated and explained with examples from each type of reaction. Emphasis in this chapter will be given to more recent examples, which were not included in the previous review papers.

Reasons for carrying out reactions in supercritical fluids:
There are several reasons for carrying out reactions in the supercritical phase. Naturally, some of the reasons are coupled. Nevertheless, they, in general, relate to control, favorable mass transfer and kinetic considerations.

- Enhanced reaction rate

The effect of pressure on the reaction rate and equilibrium constant at high pressures is described in Section 21.1.2.4. As can be perceived from this section, supercritical fluids that exhibit very high negative activation volumes for certain reactions will improve the rate and equilibrium conversion of the reaction.

- Homogenization

Reactions that otherwise would be carried out in more than one phase (heterogeneous reactions) can be transformed to homogeneous ones with the aid of supercritical fluids, so that inter-phase transport limitations are eliminated. This is realized due to enhanced solubilities of the reaction components in the supercritical fluids. Typical examples are reactions in water (supercritical water can solubilize organic compounds), homogeneous catalytic reactions, and reactions of organometallic compounds. Homogenizing one compound more than the others in a system may also affect relative rates in complex reactions and enhance the selectivity.

- Enhanced mass transfer

In many instances, reaction rates are limited by diffusion in the liquid phase. The rate of these reactions can be increased if the reaction is carried out in the supercritical phase. Typical examples are enzyme catalyzed reactions as well as some very fast reactions such as certain free radical reactions. Selectivity considerations usually dominate in complex reactions. If some steps of the complex reaction are controlled by diffusion, changing the diffusivity changes the relative rates of the reaction steps and affects the selectivity.

- Ease of down-stream separation

Another reason for using supercritical fluids as the reaction medium is to fractionate products, to purify the products or to remove unreacted reactants from the product stream. Supercritical fluids can be used as either a solvent or anti-solvent in these instances.

- Increased catalyst activity

Some heterogeneous catalytic reactions are carried out in the supercritical phase, in order to increase catalyst activity and life through in-situ regeneration of surfaces with tuning of operation conditions. For example, supercritical fluids are capable of dissolving carbon that may otherwise be deposited on the catalyst in the absence of the supercritical solvent.

- Tunable reaction rates through dielectric constant

Some properties of supercritical fluids can be monitored (manipulated) continuously by adjusting the density of the fluid. Dielectric constant is such a property and the solvent's dielectric constant can influence the rate of the reaction.

21.1.4.1 Homogenous reactions in supercritical solvents - examples

Homogeneous reactions carried out in supercritical fluids can be either catalytic or non-catalytic. The objective of carrying out both catalytic and non-catalytic reactions in supercritical fluids is to increase the overall rate of the reaction by eliminating the inter-phase transport effects.

21.1.4.1.1 Homogeneous reactions catalyzed by organometallic compounds

Homogeneous catalysts have advantages over heterogeneous catalysts such as possibility of carrying out the reaction at milder conditions, higher activity, and selectivity, ease of spectroscopic monitoring, and controlled and tunable reaction sites.

Organic reactants and products are not soluble in water while most catalytic materials are soluble in water. Therefore, homogenization of organic systems utilized environmentally undesirable organic solvents. An alternative to environmentally unacceptable organic solvents is a supercritical solvent that has added advantages over organic solvents such as increased reaction rate, higher selectivity and easy separation of reactants and products as well as of the catalyst after the reaction. Since the properties of supercritical solvents can be adjusted by manipulating the operating conditions, reaction rate and selectivity are better tunable in reactions carried out in supercritical solvents.

Carbon dioxide is the supercritical solvent that is most commonly used in homogeneous catalytic reactions. In addition to being environmentally acceptable (nontoxic, nonflammable), inexpensive, and available in large quantities, carbon dioxide does not participate in most reactions. It also has an ambient critical temperature. Although, supercritical carbon dioxide is more effective in dissolution of non-polar, nonionic and low molecular mass compounds, addition of co-solvents enhances the solubility of many otherwise insoluble compounds in supercritical carbon dioxide. A recent review by Noyori et al.[83] discusses homogeneous catalytic reactions under supercritical conditions.

When homogeneous reactions are carried out under supercritical conditions, gas/liquid interfacial transport is eliminated, which is an advantage for reactions such as hydrogenation, where diffusion of gas into the liquid may be limiting the reaction rate. In asymmetric hydrogenation reactions, hydrogen and the supercritical solvent are miscible and this results in better enantioselectivity. In Diels-Alder reactions, the advantage of the supercritical solvent is the higher selectivity obtained rather than increased rate of the reaction due to the solvent. Most of the oxidation reactions are carried out in supercritical water. Some heterogeneously catalyzed reactions are also carried out in supercritical carbon dioxide. Recently, homogeneously catalyzed reactions carried out in supercritical carbon dioxide have been reported. Examples of homogeneous catalytic reactions carried out under supercritical conditions are summarized in Table 21.1.10.

Table 21.1.10. Homogenous reactions in supercritical carbon dioxide catalyzed by organametallic compounds

Reaction	Catalyst
Isomerization	
1-hexene to 2-hexene	Iron catalyst
Hydrogenation	
CO_2 to formic acid	Ruthenium(II) phosphine complex
Asymmetric hydrogenation of tiglic acid	Ruthenium catalyst
Asymmetric hydrogenation of enamides	Cationic rhodium complex
Cyclopropene	Manganese catalyst

Reaction	Catalyst
Hydroformylation	
1-Octene	Rhodium catalyst
Propylene	Cobalt carbonyl
Olefin metathesis	
Ring opening metathesis polymerization	Ruthenium catalyst
Ring closing metathesis of dienes to cyclic olefins	Ruthenium catalyst
Diels-Alder reactions	
Synthesis of 2-pyrones	Nickel catalyst
Synthesis of cyclopentones	Cobalt catalyst
Cyclotrimerization of alkynes to substituted benzene derivatives	Cobalt catalyst
Oxidation	
Alkene epoxidation	Molybdenum catalyst
2,3-Dimethylbutene epoxidation	Molybdenum catalyst
Cyclooctene epoxidation	Molybdenum catalyst
Cyclohexene epoxidation	Molybdenum catalyst

21.1.4.1.2 Homogeneous reactions of supercritical water

Homogeneous reactions carried out in supercritical fluids are reactions in supercritical water, organo-metallic reactions and Diels Alder reactions. Reactions in supercritical water are well studied[84] and will be described in the following section.

Despite the higher temperature and pressures required in supercritical water applications, this solvent possesses unique properties that make it attractive as a reaction medium. Supercritical water has a lower dielectric constant as compared to liquid water, and the dielectric constant of supercritical water changes significantly with the density. Also, the effect of hydrogen bonding is less pronounced at supercritical conditions, one consequence of which is the high solubility of organics in supercritical water. The reactions in the supercritical water medium are carried out in a single phase, which implies high reactant concentration and negligible inter-phase mass transfer resistance. Also, the ion dissociation constant of water is higher in the critical region and is lower as supercritical conditions are accessed. These properties also vary continuously in the supercritical region, so that they can be tuned during the reaction by changing the temperature and/or pressure.

Examples of the homogeneous reactions are given in Table 21.1.11. In some of the reactions discussed in this category, acid or base catalysts were used to enhance the rates.[84]

Table 21.1.11. Homogeneous reactions of supercritical water

Reaction	Catalyst
C-C Bond formation	
Phenol and p-cresol alkylation	None

Reaction	Catalyst
Diels-Alder cycloaddition	None/NaOH
Ring opening of 2,5-dimethylfuran	Acid
Hydration/dehydration	
Conversion of tert-butyl alcohol to isobutylene	None/H_2SO_4/NaOH
Dehydration of cyclohexanol, 2-methyl cyclohexanol, 2-phenylethanol	Acid
Hydrolysis	
Esters to carboxylic acids and alcohols	Autocatalytic
Nitriles to amides and then to acid	Autocatalytic
Butyronitrile	Autocatalytic
Polyethyleneteraphthalate and polyurethane	None
Diaryl ether to hydroxyarene	None
Triglycerides into fatty acid	None
Decomposition	
Cellulose and glucose decomposition	None
Nitrobenzene	None
4-Nitroaniline	None
4-Nitrotoluene	None
Oxidation	
Phenols	None
Ethanol	None
2-Propanol	None
2-Butanol	None
Chlorinated hydrocarbons	None

21.1.4.1.3 Homogeneous non-catalytic reactions in supercritical solvents

The use of supercritical fluids as reaction media for organometallic species has also been investigated.[85] Reactions include photochemical replacement of carbon monoxide with N_2 and H_2 in metal carbonyls, where the reaction medium is supercritical xenon. Also, photochemical activation of C-H bonds by organometallic complexes in supercritical carbon dioxide has also been investigated. More recent studies on photochemical reactions also include laser flash photolysis of metal carbonyls in supercritical carbon dioxide and ethane[86] and laser flash photolysis of the hydrogen abstraction reaction of triplet benxophenone[87] in supercritical ethane and CHF_3.

21.1.4.2 Heterogeneous reactions in supercritical solvents - examples

Heterogeneous reactions in supercritical fluids can be catalytic or non-catalytic. Catalytic heterogeneous reactions are reactions carried out on solid catalysts and are of great impor-

tance in the chemical process industries. As described in the next section, the advantages of carrying out these reactions in a supercritical medium include enhanced inter-phase and intra-particle mass and heat transfer and in-situ regeneration of catalyst. Catalytic supercritical water oxidation will also be discussed. Other heterogeneous reactions that will be described are fuels processing and treatment of biomass.

21.1.4.2.1 Heterogeneous catalytic reactions in supercritical solvents

Obviously, a solid catalyzed reaction takes place only on the active sites of the porous catalyst with the implication of some mass and heat transport steps prior to and after the reaction. The first step is the diffusion of the reactants through the film surrounding the catalyst particle to the external surface of the catalyst, followed by diffusion of the reactants into the catalyst pore to the active site in the pores. These steps are limited by the diffusivity and viscosity of the reactants. In the case of a supercritical fluid phase reaction, the diffusivity is higher than the liquid diffusivity, viscosity is less than the liquid viscosity and therefore, the rate of transfer to the active site will be higher. After the adsorption, reaction and desorption steps, the products have to diffuse out of the pore, and again through the film surrounding the particle into the bulk fluid. Rates of these steps can be accelerated utilizing a supercritical medium for the reaction. Heat transfer effects are also important in a solid catalyzed reaction. Higher thermal conductivity of supercritical fluids is an advantage as well.[88]

For two-phase reactions (typically hydrogenation and oxidation reactions), the reaction steps include the diffusion of the gas reactant to and through the gas-liquid interface and then into the bulk liquid. This mass transfer limitation is also eliminated if the reaction is carried out in a supercritical medium where the reaction takes place in a single phase.[88]

Supercritical fluids bring other benefits to the solid catalyzed reaction rate besides eliminating or minimizing mass and heat transfer resistance. Supercritical solvents have the ability to regenerate the catalyst during the course of the reaction, which increases the catalyst life and activity, since undesirable deposits on the catalyst, such as carbon deposits, are soluble in the supercritical fluids. The rate of the intrinsic reaction is increased in supercritical fluids and tuning the properties of the supercritical medium can control the selectivity.[88]

Supercritical fluids may also bring opportunities in downstream separation of the reactants and products. Examples of solid catalyzed reactions in supercritical fluids are given in Table 21.1.12.[88]

Table 21.1.12. Solid catalyzed reactions in supercritical solvents

Reaction	Supercritical medium	Catalyst
	Hydrogenation	
Fats and oils	Propane, CO_2	Supported platinum, palladium catalysts
Acetophenone, cyclohexene	CO_2	Palladium on polysiloxane
Fischer-Tropsch synthesis	n-hexane, n-pentane, propane	Fe, Ru, Co/Al_2O_3, SiO_2
	Oxidation	
Toluene	CO_2	Co/Al_2O_3
Propene	SC reactant	CaI_2, CuI, Cu_2/MgO or Al_2O_3
Isobutane	SC reactant	SiO_2,TiO_3, Pd/carbon

Reaction	Supercritical medium	Catalyst
Cracking		
Heptane	CO_2	Zeolite
Isomerization		
1-Hexene	CO_2, and co-solvents	Pt/Al_2O_3
Xylene	SC reactant	Solid acid catalyst
Alkylation		
Benzene, ethylene, isopentane, isobutene, isobutane	CO_2 or SC reactant	Zeolite
Mesitylene, propene, propan-2-ol	CO_2	
Disproportionation		
Toluene to p-xylene, benzene	SC reactant	Zeolite
Ethylbenzene to benzene and diethylbenzene	Butane, pentane	Zeolite

Catalytic Supercritical Water Oxidation is an important class of solid catalyzed reactions that utilize advantageous solution properties of supercritical water (dielectric constant, electrolytic conductance, dissociation constant, hydrogen bonding) as well as the superior transport properties of the supercritical medium (viscosity, heat capacity, diffusion coefficient, density). The most commonly encountered oxidation reactions carried out in supercritical water are oxidation of alcohols, acetic acid, ammonia, benzene, benzoic acid, butanol, chlorophenol, dichlorobenzene, phenol, 2-propanol, (catalyzed by metal oxide catalysts such as CuO/ZnO, TiO_2, MnO_2, $KMnO_4$, V_2O_5, Cr_2O_3) and 2,4-dichlorophenol, MEK, and pyridine (catalyzed by supported noble metal catalysts such as supported platinum).[89]

21.1.4.2.2 Heterogeneous non-catalytic reactions in supercritical solvents

Use of the supercritical fluids as the reaction medium in synfuel processing is one of the earliest applications in the field. The advantage of the supercritical fluid as the reaction medium are again three-fold. During thermal degradation of fuels (oil-shale, coal), primary pyrolysis products usually undergo secondary reactions yielding to repolymerization (coking) or cracking into gas phase. Both reactions decrease the yield of the desired product (oil). To overcome this problem, a dense (supercritical) hydrogen donor (tetralin), or non-hydrogen donor (toluene), or an inorganic (water) medium is used.[63] Also, a supercritical medium provides ease of transport in the porous coal matrix. Finally, downstream processing (separation of the products) becomes an easier task when a supercritical medium is used. Kershaw[90] reviews the use of supercritical fluids in coal processing, while Sunol discusses the mechanism.[91]

The forest product applications in this category include biomass conversion[92] and delignification for pulping purposes.[93]

21.1.4.3 Biochemical reactions - examples

Due to their tunable properties, supercritical solvents provide a useful medium for enzyme catalyzed reactions.[94] The mechanism of enzyme-catalyzed reactions is similar to the mechanism described for solid catalyzed reactions. External as well as internal transport effects may limit the reaction rate. Utilizing supercritical fluids enhances external transport rate due to an increase in the diffusivity and therefore mass transfer coefficient. Internal transport rate depends on the fluid medium as well as the morphology of the enzyme. Supercritical fluids can alter both.

Water is known to be essential for the enzyme activity. Small amounts of water enhance enzyme activity, however excess water hinders the rate of some enzyme catalyzed reactions. The active site concentration on enzymes, hence the enzyme activity is found to be higher in the presence of hydrophobic supercritical fluids (ethane, ethylene) as compared to hydrophilic supercritical carbon dioxide.

The effect of pressure on enzyme catalyzed reactions can be explained in terms of the transition theory. Supercritical fluids that exhibit very high negative activation volumes for certain reactions are expected to improve the rate of the reaction.

Although, supercritical carbon dioxide has the advantage of being non-toxic and abundant, it is practically immiscible with water. Therefore, supercritical fluids used as the reaction medium in enzyme catalyzed reactions include fluoroform, sulfur hexafluoride and ethane, while lipases are the enzymes utilized in such reactions.[95]

21.1.4.4 Polymerization reactions - examples

Supercritical carbon dioxide is a promising green alternative to traditional solvents in polymer synthesis due to gas-like transport properties and liquid-like solubility. Supercritical carbon dioxide can be removed easily from the polymer solution by depressurization during drying of the polymer. Supercritical carbon dioxide provides easy separation of the polymer from the unreacted monomers and catalysts. Finally, supercritical carbon dioxide also exhibits Lewis acid-base interactions with electron donating functional groups of polymer chains.[96] Examples of homogeneous and heterogeneous polymerization reactions carried out in supercritical carbon dioxide are given in Table 21.1.13.

Table 21.1.13. Polymerization reactions in supercritical fluids

Polymerization mechanism	Substrate
Homogeneous, free radical/cationic polymerization	Amorphous fluoropolymers
Precipitation, free radical polymerization	Vinyl polymer, semicrystalline fluoropolymers
Dispersion, free radical polymerization	Polyvinyl acetate and ethylene vinyl acetate copolymer
Dispersion, cationic polymerization	Isobutylene polymer
Homogeneous/precipitation, cationic polymerization	Vinyl ether polymer
Transition metal catalyzed, ring opening methathesis polymerization	Norbornene polymer, polycarbonate

Butane, pentane, and propane are also used as the reaction medium in polymer synthesis.[97] Furthermore, some polymerization reactions (such as polyethylene synthesis) are carried out under supercritical conditions of the monomer.

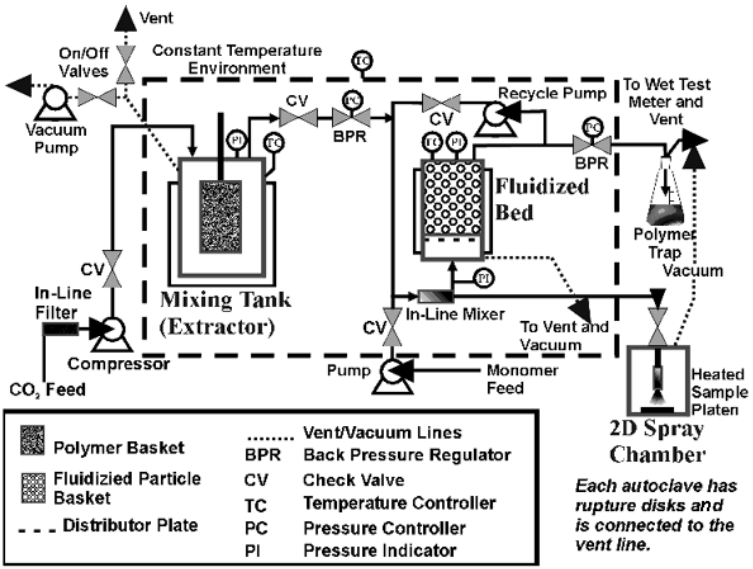

Figure 21.1.15. A flexible pilot plant for supercritical fluid aided materials processing.

21.1.4.5 Materials processing with supercritical solvents

The material field related applications of supercritical fluids are rapidly developing with exciting innovative developments continually emerging. The recent increase of activity in the supercritical field at large is partially due to these new horizons. Supercritical fluids are used to make highly porous material, aids in making uniform porous or non-porous films, to deposit solubilized components by diffusion and permeation into porous media resulting in composites with tailored characteristics or functionalized surfaces, is used to make particles with desired shape and particle size distribution, is used to encapsulate particles for time release applications, is used to fractionate macromolecules to desired dispersity and molecular weight distributions, and soon may be part of our household for cleaning/washing.

What makes supercritical fluids so attractive in this domain is their sensitivity to a large number of processing variables in a region where transition from a single or multiphase system into another is rather simple through a variety of paths.

One can start with a homogeneous phase and use pressure, temperature, mass separating agents, other external fields such as electromagnetic or irradiation, to nucleate and grow, or react or fractionate, to form new material with unique performance characteristics. In the homogenization step, supercritical fluids are used to solubilize. If solubilization in the supercritical fluid is not possible, the supercritical fluid can be used to induce phase separation as an anti-solvent in a subsequent step.

The supercritical fluids are effective in heterogeneous environments as well. They penetrate into porous environment loaded with additives or, used as a pure supercritical fluid to clean, dry (extract), coat, impregnate and process (e.g. extrude) a low viscosity solution.

A flexible pilot plant that addresses all the materials processing demands excluding extrusion is shown in Figure 21.1.15 while the modes for encapsulation and aerogel/impregnation are expanded upon Figures 21.1.16 and 21.1.17 respectively.

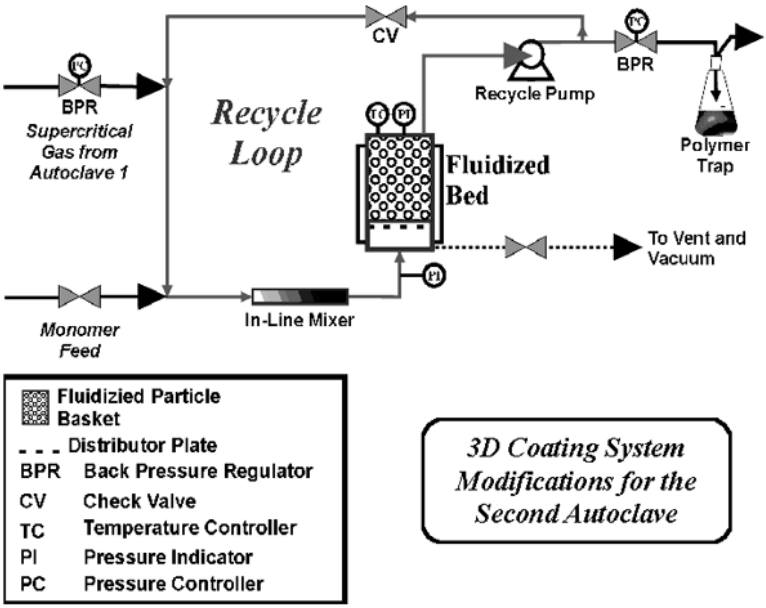

Figure 21.1.16. Particle coating section of the plant.

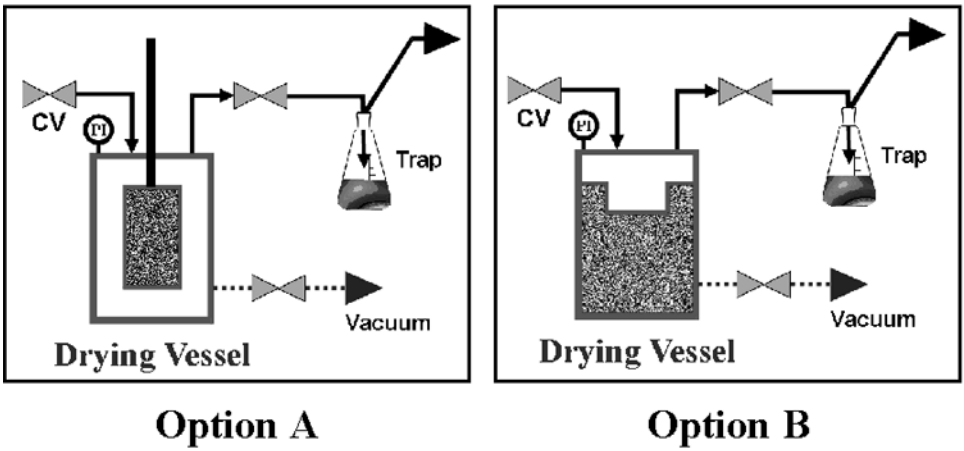

Figure 21.1.17. Supercritical drying section of the plant.

21.1.4.6 Particle synthesis - generic application

The routes to particle synthesis via supercritical fluids basically follow two paths, Rapid Expansion of Supercritical Solution (RESS) and Supercritical Anti-Solvent (SAS).[6,98] The basic processing steps are outlined in Figure 21.18 and Figure 21.19, respectively. RESS involves homogenization of the particles raw material in the supercritical fluid followed by rapid expansion of the solution through an expansion device such as a nozzle. Depending on the nozzle design, time-temperature and time-pressure profiles, and whether one uses

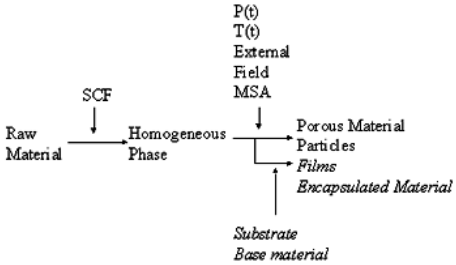

Figure 21.1.18. Homogeneous supercritical solution path to materials synthesis.

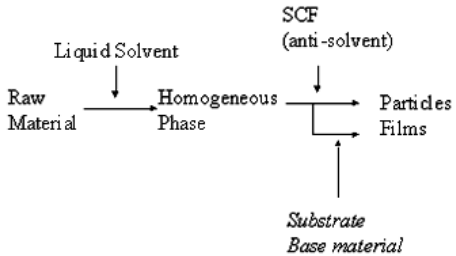

Figure 21.1.19. Anti-solvent path to materials synthesis.

entrainers or not, the particle size, shape, and particle size distribution changes. The primary particle creation mechanism is nucleation and growth. Usually the amount solubilized in the SCF is not very high for particle synthesis. For many applications such as pharmaceutical and energetic materials, the particle base material is not soluble in dense gasses. In those instances, these substances are solubilized in a liquid solvent and in a subsequent stage the supercritical anti-solvent is used for synthesis of particles.

21.1.4.7 Encapsulation - generic application

Micro-encapsulation of drug-polymer systems using the RESS (Rapid Expansion of Supercritical Fluid Solutions) techniques have been initiated with limited success due to poor understanding of the complex phenomena involved in co-nucleation of components. Not only do the particles have to be nucleated with the desired particle size and shape but also encapsulate the material simultaneously in an uniform fashion.

An alternative approach[99] depicted in Figure 21.1.17 involves a sequential method where synthesized particles are coated with polymeric thin films by simultaneous nucleation of polymeric material out of a supercritical fluid, encapsulating the particles fluidized in the supercritical fluid, followed by further polymerization and binding of the encapsulating material on the particle surface. The method involves a recirculatory system that includes dissolution of the polymer in the supercritical solvent and coating the particles through a temperature swing operation in the fluidized bed that contains the particles. The particulate material coated with the tailor polymeric material possesses unique timed-release characteristics, improved stability, and often-enhanced behavior.

21.1.4.8 Spraying and coating - generic application

The RESS and SAS approaches can be applied to coating and spraying applications if the inhomogenization step is exercised on a surface (a base material).

21.1.4.9 Extrusion - generic application

The addition of a supercritical fluid to a Newtonian or non-Newtonian fluid reduces the viscosity of the fluid improving its processibility and end materials morphology. Supercritical fluids can aid in food and polymer extrusion.

21.1.4.10 Perfusion (impregnation) - generic application

Excellent transport characteristics, solubilization power, and sensitivity to process variables all contribute to the success of the methodology. The generic scheme as shown in Fig-

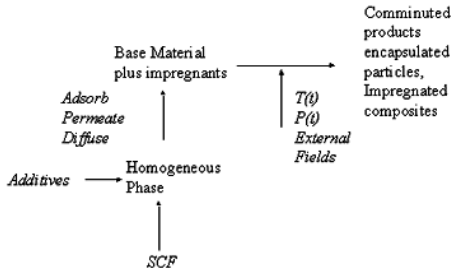

Figure 21.1.20. Supercritical fluid impregnation processes.

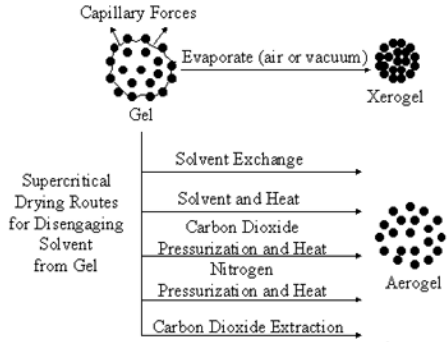

Figure 21.1.21. Sol-gel drying methods.

ure 21.1.20 involves homogenization, impregnation, deposition, and optional post treatment steps such as curing reactions. The mechanism of transport in the porous matrix is permeation and diffusion while the primary mechanisms for deposition are pressure reduction, temperature swing, sorption, and reaction (i.e., polymerization).

This process is a simplified version of impregnation process.[100] The impregnating solvent does not contain any material to be deposited and the pressure release causes disintegration of the impregnated material.[6,72]

21.1.4.11 Parts cleaning - generic application

In essence, the part cleaning process is basically extraction/leaching with or without surfactants. The basic steps are shown in Figure 21.1.13. Drying in the absence of capillary forces and solvent residue free substrate makes the technology attractive. The technology is comprehensive covered in a monograph[65] and there are many existing commercial applications.

21.1.4.12 Drying - generic application

A pilot plant used in drying is shown in Figures 21.1.15 and 21.1.17. The supercritical drying routes are particularly attractive in their ability to eliminate or at least minimize the capillary effect that cause non-uniformities in films as well as shrinkage and collapsing in pore structure. These supercritical avenues permit successful creation of highly porous structures such as foams, aerogels, coatings, and films.

The solvent can be removed from the wet gel using different methods. These methods and resulting gels are shown in Figure 21.1.21. If solvent is evaporated slowly from the gel, a xerogel is obtained. During evaporation, large capillary forces are exerted as the liquid-vapor interface moves through the gel. These forces cause shrinkage of the pores within the gel. Removal of the solvent (alcohol) from the gel under supercritical conditions results in the formation of the aerogel. Since this drying procedure eliminates the liquid-vapor interface, aerogels are formed in the absence of capillary forces. Aerogels retain the morphology of the original alcogel.

There are several methods developed for removing the solvent from the gel under supercritical conditions. The first one is the one suggested in the pioneering work by Kistler,[101] in which the solvent is brought to supercritical conditions in an autoclave and evacuated under these conditions. In order to pressurize the autoclave to a pressure above the critical value for the alcohol, more alcohol is added to the autoclave. Supercritical conditions of the solvent are reached by supplying heat to the autoclave. After the pressure

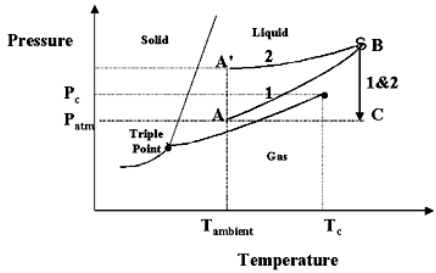

Figure 21.1.22. Pressure-temperature paths for supercritical drying.

reaches a preselected value, which is above the critical, the temperature is raised at constant pressure. Once the temperature is also above its critical value, the supercritical fluid is vented out of the autoclave at constant temperature.[102] The P-T behavior for this procedure is shown as route A-B (1) in Figure 21.1.22.

Van Lierop and co-workers later improved this method. In this improved version of the method, any boiling of the solvent was completely suppressed. This was done by introducing pressure of an inert gas into the autoclave prior to any heat treatment and furthermore, the autoclave was kept closed during heating until the temperature reached the predetermined value above the critical. The P-T behavior for this process is shown as route A'-B (2) in Figure 21.1.22.

In another method, developed by Jacobucci[104] and co-workers, alcohol is removed by supercritical CO_2 extraction in a semi-continuous system.

Solvent exchange is another method utilized to dry alcogels. The liquid in the pores (excess water of the hydrolysis) of the wet-gel is first displaced by alcohol and then alcohol is displaced by liquid CO_2 at about 16-20°C and 100 bar. After solvent exchange, the temperature of the system is increased to 40°C and supercritical carbon dioxide is vented out of the system.[105]

In yet another method, the system is pressurized with carbon dioxide prior to drying. Through partial solvent exchange during heating, drying of the gel at temperatures much lower than the critical temperature of the solvent (alcohol) can be achieved. Also, gels can be dried at a wide range of temperature and pressure combinations where optimum tunable conditions (resulting in optimum pore and surface characteristics) can be determined for a variety of objectives and cases.[106]

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21.2 IONIC LIQUIDS

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21.2.1 INTRODUCTION

The first question one would ask is "What is an ionic liquid?" Ionic liquids can be described, in the crudest terms, as room temperature molten salts. The term "ionic liquid" could therefore be applied to all molten salt systems such as cryolite (Na_3AlF_6) used in aluminum production or even molten table salt (NaCl). However the use of the word "molten" conjures up images of high temperature processes which are highly corrosive and difficult to design. In contrast to this, the ionic liquids discussed here are generally benign solvents which can be applied to a significant number of industrial processes leading to enhanced yields, greater recyclability and processes with an overall reduced environmental impact. Therefore an ionic liquid is normally described as a molten salts which is fluid at room temperature, or close to room temperature (salts melting below 100°C are often considered in this category). One only has to look at recent patent publications to discover that these solvents are finding

application in commercial sectors as diverse as the nuclear industry,[1,2] pharmaceuticals and fine chemicals,[3,4] as well as in mainstream petrochemical processes.[5-7] This contrasts with the unique perspective of Takahashi et al. who state that the two major applications are batteries and electrolytes, clearly unaware of the modern literature.[8] In a number of indicated cases, these processes have been taken through the development process to a point of industrial commercialization and represent first generation ionic liquid processes, principally based on chloroaluminate(III) ionic liquids which are currently ready for industrial uptake. Following this line, second generation ionic liquid processes based on other, more benign, ionic liquids are currently under investigation and development in a variety of laboratories around the world. Many of these processes utilize the ability of a range of ionic liquids to selectively immobilize transition metal catalysts for liquid-liquid two-phase catalysis while permitting easy, often trivial, extraction of products.[9-14]

So why have these solvents not been used to rapidly replace the current volatile organics currently found in industry? There are a number of answers to this, but the most significant reason is economics. By looking through any chemical catalogue, it is obvious that 1-methylimidizole (a precursor for the manufacture of ionic liquids) is considerably more expensive than standard solvents. By the time this compound is processed to the final ionic liquid product, its cost will have increased to many times that of normal solvents. This is not helped by the fact that at present there is a very limited market for these compounds, keeping retail prices high. It is envisaged that if ionic liquid technology does become widely accepted, then the cost of production will decrease rapidly. Other quaternary ammonium salts and those that are based around pyridinium are cheaper alternatives (principally due to the scale of manufacture), but economics is not the only problem. As yet, there is a significant deficit of raw physical property data for engineers to use when designing new processes or retrofitting old plants.

For the efficient design of any new industrial process incorporating ionic liquid technology, a complete understanding of the behavior of the solvent during operation is necessary. Physical properties such as viscosity, density, heat capacity and surface tension are all important during these early design stages. Others like electrochemical windows and electrical conductivities, will be important for more specific applications. With the advent of computers, chemical engineers have been able to use powerful process simulation software packages to estimate how a particular process will behave under certain operating conditions. These software packages, like the manual calculations which preceded them, predict the physical properties of organic solvents by using a number of empirical and semi-empirical equations which are available. Unfortunately these equations where developed for molecular compounds and tend to require the critical temperature and pressure data, information which does not apply to ionic liquids. In addition, other techniques for predicting physical properties like surface tension involve using group contribution methods, but again these fail to account for organic salts and therefore cannot

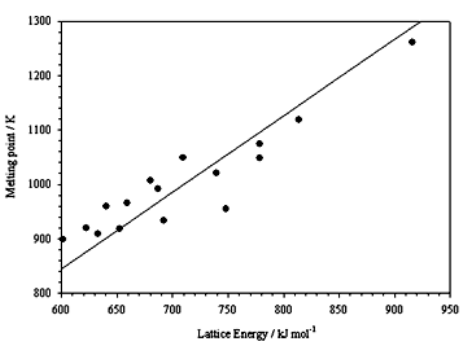

Figure 21.2.1. Showing the relationship between lattice energy[26] and melting point[27] for the Group 1 halide salts.

be used. This lack of predictive power and the overall general lack of physical property data in the literature will inevitably slow the transfer of ionic liquid technology into industrial processes.

21.2.2 FUNDAMENTAL PRINCIPLES OF THE FORMATION OF ROOM TEMPERATURE IONIC LIQUIDS

A number of detailed reviews and articles have been published recently on the theory and development behind ionic liquid technology.[15-25] However in order to develop a greater understanding and appreciation of these solvents, we will summarize the main points here. Therefore the purpose of this section is to give an introduction to the nature and properties of room-temperature ionic liquids, with particular emphasis being placed upon their potential as solvents for industrially relevant catalytic reactions, and (more generally) for clean technology.

21.2.2.1 Development of ionic liquids

To begin with, the melting point of a salt is related to its lattice energy. In fact, if one was to plot the lattice energy of a series of salts, for instance the Group 1 halides, against the melting points in Kelvin, then one can see that there is reasonable linearity between the melting point and the lattice energy (see Figure 21.2.1).

Although not particularly accurate, this simple approach will give an estimated melting point of the Group 1 salts if the lattice energy is known. The deviations from this treatment are frequent and are usually due to other forms of bonding within the structure, as shall be explained later. The first theoretical treatment of lattice energy began with Born and Landé, and was then further developed by Kapustinskii[28] into the what is know as the "Kapustinskii equation" (eqn. [21.2.1]):

$$U = \frac{287.2vZ^{+}Z^{-}}{r_0}\left(1 - \frac{0.345}{r_0}\right) \qquad [21.2.1]$$

where:

U	lattice energy
v	number of ions per molecule
r_0	sum of ionic radii
Z^+, Z^-	charge of the ionic species

Therefore by increasing the value of r_0, i.e., by using larger anionic and cationic components in the salt, it is possible to lower this energy and therefore reduce the melting point. This effect is shown Table 21.2.1.

Table 21.2.1. Melting points[27] of various inorganic salts, melting points given in ºC

Anion	Lithium	Sodium	Potassium	Rubidium	Caesium
Fluoride	842	988	846	775	682
Chloride	614	801	776	718	645
Bromide	550	747	734	693	636
Iodide	450	661	686	647	626

From this one can clearly see that as we increase both the size of the anion and the cation, the melting point decreases. From the Kapustinskii equation one must also note that by

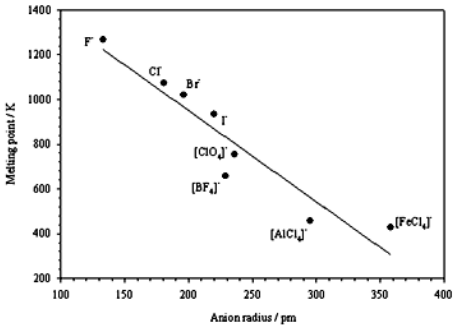

Figure 21.2.2. Showing the relationship between the size of similar anions containing halides and melting point of various sodium salts.

increasing the ionic charge will tend to increase the lattice energy of the crystal. However the effect on melting point is complicated by the fact that according to Fajans' rules an increasing charge also results in increasing covalency particularly for small cations and large anions. The effect of size can even be observed in the melting points of the lithium halide series, where the small size of the lithium ion leads to a greater covalent character in the lithium halide bond, reducing the melting point when compared to the other Group 1 salts.

For a given cation, and singly charged cations and ions, equation [21.2.1] demonstrates that the lattice energy will become only be a function of r_0, and since r_0 is the sum of r^+ and r^-, then the lattice energy is only dependant on anion size. The radius for simple anions can be found in a number of different sources.[27,29] However for more complex anions it becomes more difficult to assign unique values to the radii. Yatsimirskii[30] has shown that it is possible to determine the apparent values of the ionic radii of these ions indirectly from the lattice energy of the compounds containing them. These values are generally referred to as the thermochemical radii and a number are shown in Table 21.2.2. In most cases the fact that ions such as $[CNS]^-$ and $[CH_3COO]^-$, are markedly non-spherical makes these radii of limited use. However for the case of tetrahedral ions, the symmetry is sufficiently high enough for comparison purposes. If one were to plot the melting points a number of sodium salts against the opposing anions' thermochemical radius a clear relationship is observed (see Figure 21.2.2)

Table 21.2.2. Anionic and thermochemical radii

Name	Anion	r, pm	Name	Anion	r, pm
Tetrachloroferrate[31]	$[FeCl_4]^-$	358	Chlorate[33]	$[ClO_3]^-$	201
Tetrachloroborate[31]	$[BCl_4]^-$	310	Thiocyanate[33]	$[CNS]^-$	195
Tetrachloroaluminate[31]	$[AlCl_4]^-$	295	Borate[33]	$[BiO_4]^-$	191
Tetrachlorogallate[31]	$[GaCl_4]^-$	289	Bromate[33]	$[BrO_3]^-$	191
Trifluoromethylsulfonate[32]	$[CF_3SO_3]^-$	267	Nitrate[33]	$[NO_3]^-$	188
Hexafluoroarsenate[32]	$[AsF_6]^-$	259	Cyanide[33]	$[CN]^-$	181
Hexafluorophosphate[32]	$[PF_6]^-$	253	Iodate[33]	$[IO_3]^-$	181
Periodate[33]	$[IO_4]^-$	249	Cyanate[33]	$[CNO]^-$	160
Perchlorate[33]	$[ClO_4]^-$	236	Formate[33]	$[HCOO]^-$	160
Permanganate[33]	$[MnO_4]^-$	240	Acetate[33]	$[CH_3CO_2]^-$	156
Tetrafluoroborate[33]	$[BF_4]^-$	229	Nitrite[33]	$[NO_2]^-$	156
Trinitrophenoxide[33]	$[C_6H_2(NO_2)_3O]^-$	222	Amide[33]	$[NH_2]^-$	129

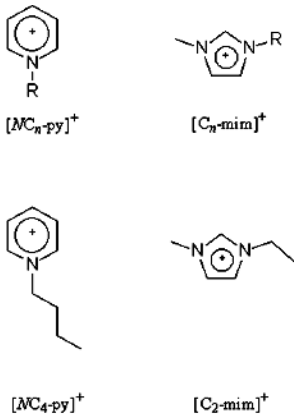

Figure 21.2.3. The aromatic heterocyclic N-butylpyridinium, 1-ethyl methylimidazolium cations, and general structural information for $[NC_n\text{-py}]^+$ and $[C_n\text{-mim}]^+$ based ionic liquids.

Table 21.2.3. Some melting points for various $[C_2\text{-mim}]$ salts

Salt	Melting point, ^oC
$[C_2\text{-mim}]Cl$[35]	84
$[C_2\text{-mim}]Br$[36,37]	81
$[C_2\text{-mim}]I$[36,37]	79-81
$[C_2\text{-mim}][PF_6]$[38]	62
$[C_2\text{-mim}][NO_2]$[39]	55
$[C_2\text{-mim}][GaCl_4]$[40]	47
$[C_2\text{-mim}][NO_3]$[39]	38
$[C_2\text{-mim}][AlCl_4]$[35]	7
$[C_2\text{-mim}][(CF_3SO_2)_2N]$[38]	-15

It should be noted that if one plotted the melting points and radii of the planar anions in Figure 21.2.2, they would not fall on the trend line. Since our desired goal is to produce a salt which melts at or around room temperature, we extrapolate that we would require an anion with a radius of at least 400 pm. The number of such large anions is limited, and they also have a relatively high degree of covalence associated with the structure. However, as clear from above, it is also possible to reduce the lattice energy by increasing the size of the cation. By moving to organic salts the effect can be demonstrated more easily. For example the organic salt $[EtNH_3][NO_3]$ was shown in 1914 to have a melting point of 12ºC and was hence the first room temperature ionic liquid.[34] This concept can be taken further and applied to other organic systems, such as, the cations "butylpyridinium" and "1-ethyl 3-methylimidazolium" ($[NC_4\text{-py}]^+$ $[C_2\text{-mim}]^+$), (see Figure 21.2.3). For the purpose of clarity we will simply refer to the length of the alkyl chain by the number of carbon atoms in that chain, hence ethyl is represented by C_2, butyl by C_4, etc.

In the case of the $[C_2\text{-mim}]^+$ cation it can be observed that it has the lowest possible symmetry making it even more difficult for a crystal to form. Given this argument one would expect the melting point of salts based around this cation to be low. Indeed Wilkes et al.[35] have shown that the melting point for $[C_2\text{-mim}]Cl$ is 84ºC significantly lower than any of the Group 1 halides. The melting points of a number of $[C_2\text{-mim}]^+$ salts have been reported over recent years, and some of these are summarized in Table 21.2.3.

In order to develop a greater understanding of these salts, the nature of the $[C_2\text{-mim}]^+$ cation and how it interacts with various anions has been explored in both solution[41] and solid[42] phases and via theoretical studies.[43] It is now possible to produce a similar plot to Figure 21.2.2 showing the effect of anion on the melting point of the $[C_2\text{-mim}]^+$ salts using the data in Table 21.2.3.

The $[AlCl_4]^-$ anomaly can be partly explained by the fact that in the ionic liquid an equilibrium existing between the $[AlCl_4]^-$ anion and the larger $[Al_2Cl_7]^-$ anion, is expected to be much higher than for the $[GaCl_4]^-$ ionic liquid. In addition results from our own research

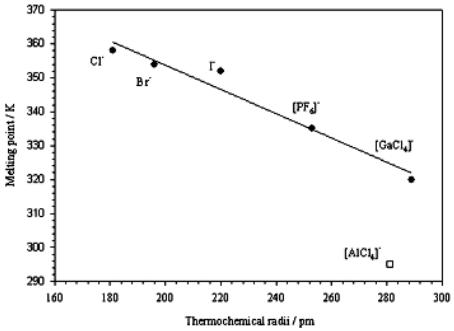

Figure 21.2.4. Relationship between the size of similar anions containing halides and the melting point of their $[C_2\text{-mim}]$ salts.

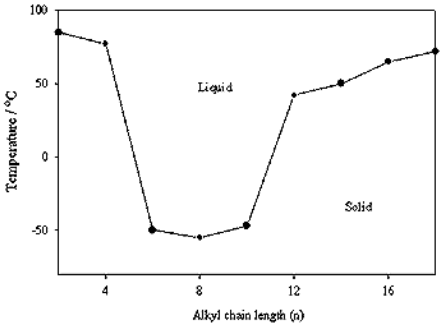

Figure 21.2.5. Phase diagram for the $[C_n\text{-mim}]Cl$ ionic liquids.[44]

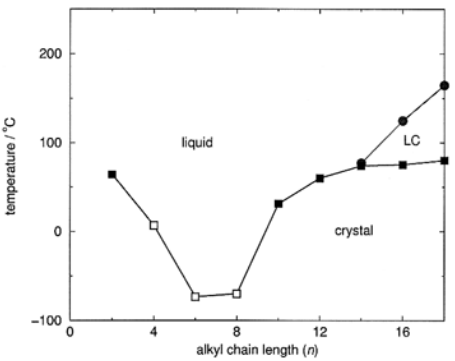

Figure 21.2.6. Melting point phase diagram for $[C_n\text{-mim}][PF_6]$ ionic liquids as a function of alkyl chain length n showing the melting transitions from crystalline (closed square) and glassy (open square) materials and the clearing transition (circle) of the liquid crystalline (LC) terms.

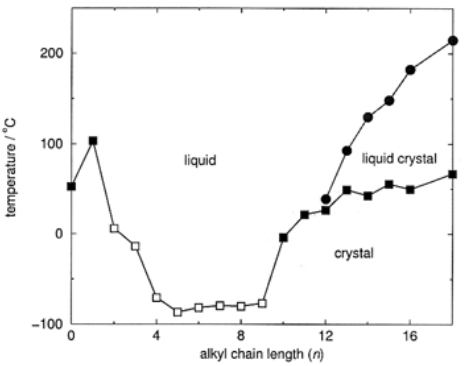

Figure 21.2.7. Melting point phase diagram for $[C_n\text{-mim}][BF_4]$ ionic liquids as a function of alkyl chain length n showing the melting transitions from crystalline (closed square) and glassy (open square) materials and the clearing transition (circle) of the liquid crystalline terms.

show that the melting point for the $[FeCl_4]^-$ ionic liquid does appear to follow the given trend.

In order to expand the number of potential ionic liquids the possibility also exists to increase the length of the alkyl group thereby further decreasing the lattice energy. For the $[C_n\text{-mim}]$ chlorides the result is a range of salts all of which have low melting points (some of which are below room temperature) as shown in Figure 21.2.5, though often at the cost of increased viscosity.

One can observe that there is a maximum chain length allowed before other forms of bonding begin to dominate and the melting point increases. The melting points indicated below the 0°C line are in fact glass transition temperatures rather than true melting points. As stated above, one point to note is that the viscosity of these room temperature "chloride" liquids is very high and they would therefore have to be used at relatively high temperatures if required in a process.

Figures 21.2.6 and 21.2.7 illustrate the significant variation in melting point which can be induced by simply changing the anion from $[C_n\text{-mim}][Cl]$ to the $[C_n\text{-mim}][PF_6]$ and

Table 21.2.4 Selected melting points of the Group 1 chloride mixtures[48]

System	Mole ratio	m.p., °C
LiCl-LiF	70:30	496
LiCl-LiI	35:65	368
LiCl-NaCl	25:75	551
LiCl-CsCl	60:40	355
NaCl-KCl	50:50	658
CsCl-KCl	35:65	610

Table 21.2.5. The melting points of selected tetrachloroaluminate(III) salts[48]

System	Mole ratio	m.p., °C
LiCl-$AlCl_3$	35:65	80
LiCl-$AlCl_3$	50:50	132
NaCl-$AlCl_3$	39:61	108
NaCl-$AlCl_3$	50:50	151
RbCl-$AlCl_3$	30:70	148
RbCl-$AlCl_3$	50:50	336

[C_n-mim][BF_4] ionic liquids.[45-47] This procedure has produced a lower melting point salt for example the [C_4-mim][PF_6] has a melting point of 5°C whereas the [C_4-mim][Cl] has a melting point of 80°C. These lower melting point liquids with the shorter alkyl chains lead to a much more fluid and easily managed liquid.

An interesting feature of these phase diagrams is the appearance of liquid crystalline phases with the longer alkyl chains, and this is confirmed when their optical textures are examined.[35] The implication of the existence of these stable phases has still to be explored in terms of stereochemical control of reactions.

From these figures it can be seen that those salts with short alkyl chains (n=2-10) are isotropic ionic liquids at room temperature and exhibit a wide liquid range, whereas the longer chain analogues are low melting mesomorphic crystalline solids which display an enantiotropic smectic A mesophase. The thermal range of the mesophase increases with increasing chain length and in the case of the longest chain salt prepared, [C_{18}-mim][BF_4], the mesophase range is ca. 150°C.

21.2.2.2 Binary ionic liquid systems

In Table 21.2.1 it was shown that the melting points of the Group 1 salts are significantly above room temperature, and far too high to form a generic medium for reactive chemistry. However by both increasing the size of the cation and the anion it has become possible to produce salts that are liquid at room temperature. It is well known that mixing together different salts deforms the crystal structure, leading to a lower lattice energy, and hence a lower melting point. At certain concentrations, referred to as eutectic points, the melting point has reached its minimum. This effect on melting point, obtained by combining the Group 1 chlorides into various mixtures can be seen in Table 21.2.4.

The melting points of the simple tetrachloroaluminate(III) salts of both the sodium and [C_2-mim] cations have been shown to be significantly lower than their respective chloride salts, indeed [C_2-mim][$AlCl_4$] was shown to be a liquid at room temperature. Such salts are produced by combining equimolar quantities of either NaCl or [C_2-mim]Cl with $AlCl_3$. However, as can be seen from Table 21.2.5, the 50:50 mole ratio does not usually correspond to the lowest melting point.

For the inorganic salts we now have melting points which are in the maximum range of some of the high-boiling organic solvents (e.g., 1,4-dichlorobenzene, b.p. 174°C). Hence given that the 50:50 mole ratio does not correspond to the lowest melting point of the inorganic salts, one would expect the same to be true for the organic cations. Figures 21.2.8 and

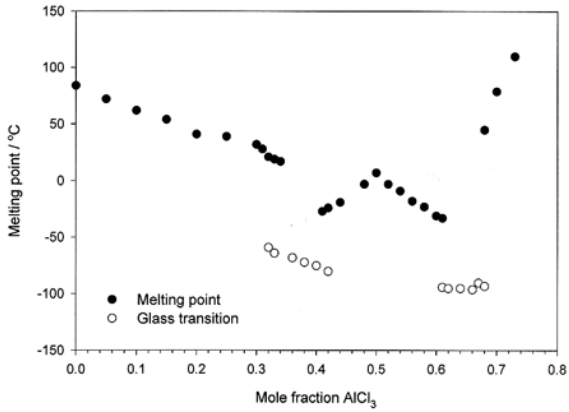

Figure 21.2.8. Phase diagram for the [C_2-mim]Cl-$AlCl_3$ system.[35]

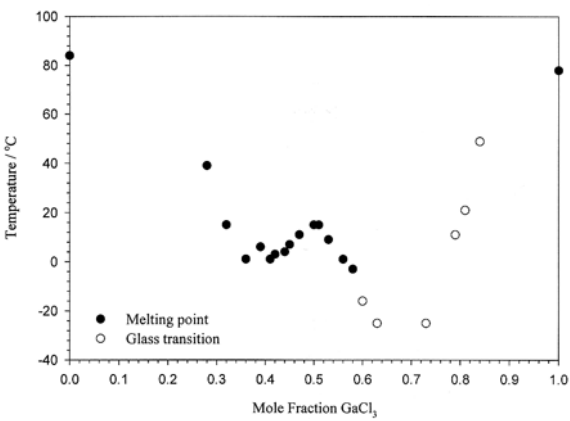

Figure 21.2.9. Phase diagram for the [C_2-mim]Cl-$GaCl_3$ system.[40]

21.2.9 show the phase diagrams of [C_2-mim]Cl when combined with varying quantities of $AlCl_3$ and $GaCl_3$.

Thus a large number of ambient temperature ionic liquids can be formed from a mixture of solid aluminium(III) chloride and solid 1-ethyl-3-methylimidazolium chloride. Mixing these two salts together results in an exothermic reaction and generation of a clear, colorless liquid, and an ambient temperature molten salt with low viscosity. We can see that depending on the proportions of the two components it is possible to obtain eutectics with melting points as low as -96°C.[35] These liquids are also thermally stable in excess of 200°C allowing for a tremendous liquidus range. When the molar proportions are equal, the system is a neutral stoichiometric salt 1-ethyl-3-methylimidazolium tetrachloroaluminate(III) chloride [C_2-mim][$AlCl_4$] which melts at its congruent melting point of about 7°C. The lowest melting point is achieved when the molar ratio of the system is 1:2 [C_2-mim]Cl:$AlCl_3$. Qualitatively these phase diagrams are similar to that reported by Hurley and Weir for the 1-ethylpyridinium bromide-$AlCl_3$ binaries[49] in that they all show a characteristic "W" shape.

It has been shown that if the butyl and ethyl groups are exchanged for a generic linear alkyl function then a series of cations can be generated. These can then be balanced against any one of a number of opposing anions to produce a final salt. Given that the range of available anions and cations has expanded enormously in the past decade it is possible to produce a number of combinations. Indeed, it is our best estimate that, if binary and ternary mixtures are included (and there are very good practical and economic reasons for doing that), there are approximately one trillion (10^{18}) accessible room temperature ionic liquids.[50]

21.2.3 CATALYSIS IN IONIC LIQUIDS

The wide range of reactions that have been undertaken in low temperature ionic liquid solvents is quite remarkable. It is limited simply by ones imagination. The specific and tuneable solvent properties of ionic liquids are a key feature for their use as solvents and have

been utilized, especially in combination with the catalytic properties of the chloroaluminate(III) ionic liquids, to develop a range of synthetically important catalytic reactions. Currently a number of these are being investigated as economically and environmentally viable alternatives to existing industrial processes. A number of reactions are summarized below; for a more detailed discussion in this area readers are recommended to the recent review by Holbrey and Seddon,[25] and to a forthcoming book in the NATO ARW series.

21.2.3.1 Reactions involving first generation chloroaluminate(III) ionic liquids

The chloroaluminate ionic liquid mixtures are governed by the following primary equilibrium, equation:[51]

$$2[AlCl_4]^- \leftrightarrow [Al_2Cl_7]^- + Cl^-;\ k \approx 10^{-16} \qquad [21.2.2]$$

This is an acid base equilibrium under the Franklin definition. The $[Al_2Cl_7]^-$ species is the "acid" and the Cl^- is the base. Note that this is an aprotic equilibrium. Therefore if the mole ratio of $[C_2\text{-mim}]Cl:AlCl_3$ is greater than, less than, or exactly equal to 50:50, the solvent behavior can be described as Franklin basic, Franklin acidic, or neutral.

Considering that aluminum trichloride is a very important commercial catalyst with over 25,000 tonnes produced annually in the USA alone, such liquids containing aluminum trichloride and allowing for differing levels of acidity have been extensively studied as first generation ionic catalytic solvents in a wide variety of synthetic and catalytic processes. Ionic liquids could therefore be used as substitutes for conventional solid or suspended sources of aluminum(III) chloride. As liquid phase catalysts, they allow for tremendous control of reactor inventories and can be cleaned and recycled with ease. Therefore, ionic liquids, in ideal cases, have no waste associated with them, whereas the supported aluminum(III) chloride catalysts will require large (and annually rising) waste disposal costs.

An industrial example of the use of chloroaluminate ionic liquids in alkene catalysts is the recent development of the IFP Difasol process[52] which is widely used industrially for alkene dimerization (typically propene and butanes). It was observed by Chauvin and coworkers[53-60] that chloroaluminate(III) ionic liquids would be good solvents for the nickel catalyst used in the reaction, and discovered that by using a ternary ionic liquid system ($[C_4\text{-mim}]Cl\text{-}AlCl_3\text{-}EtAlCl_2$) it was possible to form the active catalyst from a $NiCl_2L_2$ precursor and that, the ionic liquid solvent stabilized the active nickel species.

Overall they found that the nickel catalyst remains selectively dissolved in the ionic liquid phase to the extent that over 250 kg of propene could be dimerized per 1 g of nickel catalyst. In addition the product was insoluble in the ionic liquid, which made product recovery facile.

Other studies have shown that a wide range of acidic chloroaluminate(III) and alkylchloroaluminate(III) ionic liquids can be used to catalyze the dimerization and oligomerization of olefins.[61,62] In the reaction, the olefinic feedstock may be mixed with, or simply bubbled through, the ionic liquid catalyst to produce oligomeric products. A significant outcome of this reaction is that the product has a low solubility in the ionic liquid and separates as a less dense organic phase which is readily removed.

In addition to the above reactions it was shown that isobutene can be polymerized in an acidic ionic liquid to polyisobutene with a higher molecular weight than is formed using

other polymerization processes. Polyisobutene, traditionally prepared by the Cosden process, is a valuable lubricant, and also a route to higher value-added materials. In general it was observed that the catalytic activity of the ionic liquids increases towards higher degrees of polymerization from short-chain oligomers as the alkylchain length of the 1-alkyl-3-methylimidazolium or N-alkylpyridinium cation is increased.[63]

The ionic liquid process has a number of significant advantages over the industrial Cosden process. This system uses a supported or liquid phase aluminum(III) chloride catalyst.[63] Using the ionic liquid process, the polymer forms a separate layer, which is substantially free of catalyst and ionic liquid solvent. This effect greatly enhances the degree of control available to reduce undesirable secondary reactions (i.e., isomerization) without requiring alkali quenching of the reaction.

In addition Ziegler-Natta polymerization reactions have also shown some success when carried out in ionic liquids.[64] The most common production methods for this form of polymerization involve the use of triethylaluminium catalysts at ca. 100°C and 100 atmospheres pressure. Advances have been developed through the use of organometallic transition metal catalysts, typically nickel or titanium. Given the solvent characteristics of ionic liquids it should be possible to effectively immobilize such catalysts in an ionic liquid solvent. Indeed, Carlin and Wilkes[64] have reported the Ziegler-Natta polymerization of ethene in an ionic liquid solvent. In these reactions an acidic [C_2-mim]Cl-$AlCl_3$ ionic liquid solvent was used to support dichlorobis(η^5-cyclopentadienyl)titanium(IV) with an alkylchloroaluminium(III) co-catalyst.

Electrophilic substitution[65] and other reactions of naphthalenes (alkylation, acylation, condensation and migration in acidic ionic liquids[66,67] have been reported. Anthracene undergoes photochemical [4+4] cycloaddition reactions[68,69] in acidic chloroaluminate(III) ionic liquids. One interesting study included a one-pot synthesis of anthraquinone from benzene giving a 94% yield. In general a much wider range of redox products are formed than occur in conventional solvents; the strong Brønsted acidity of the ionic liquid induces protonation of anthracene, by residual traces of HCl, to form an anthracenium species which couples readily via photochemically driven electron transfer mechanisms.

Both the Friedel-Crafts alkylations and acylations are of great importance to the fine chemical and pharmaceutical industries. Typically, these reactions are run in an inert solvent with suspended or dissolved aluminum(III) chloride as a catalyst, and may take six hours and go only to 80% completion giving a mixture of isomeric products. In addition, there are a number of problems, especially with misnamed "catalytic" Friedel-Crafts acylation reactions, which are actually stoichiometric, consuming 1 mole of $AlCl_3$ per mole of reactant. Annually, massive quantities of aluminum(III) chloride are consumed in these reactions causing a number environmental problems through waste disposal. Both alkylation and acylation reactions under Friedel-Crafts conditions have been demonstrated using chloroaluminate(III) ionic liquids as both solvent and catalysts.[66-77] Here it has been shown that reaction rates are much faster with total reagent conversion and often with surprising specificity to a single product.

Boon et al. have reported the alkylation of benzene with a wide number of alkyl halides in acidic chloroaluminate(III) ionic liquids[73] and general organic reactions in low melting chloroaluminate ionic liquids have also been described,[75,78] which include chlorinations and nitrations in acidic ionic liquids.[72,73,76]

One specific example is the alkylation of benzene with chloroethane which gives a mixture of mono- to hexa-substituted products. The ionic liquid solvent/catalyst activates the reaction and the alkylation can be performed even at temperatures as low as -20°C in the ionic liquid solvent. Again it was shown that the products have a low solubility in the ionic liquid leading to facile separation.

Many acylation reactions have been demonstrated in acidic chloroaluminate(III) ionic liquids liquids.[70,74] However as described above these processes are essentially non-catalytic in aluminum(III) chloride which necessitates destroying the ionic liquid catalyst by quenching with water to extract the products. However, regioselectivity and reaction rates observed from acylation reactions in ionic liquids are equal to the best published results. The Friedel-Crafts acylation of benzene has been shown to be promoted by acidic chloroaluminate(III) ionic liquids.[74] It was observed that the acylated products of these reactions have high selectivities to a single isomer for example toluene, chlorobenzene and anisole are acylated in the 4-position with 98% specificity. Naphthalene is acylated in the 1-position which is the thermodynamically unfavored product. In addition to benzene and other simple aromatic rings, a range of organic and organometallic substrates (e.g., ferrocene)[79,80] have been acylated in acidic chloroaluminate(III) ionic liquids.

21.2.3.2 Reactions in neutral or second generation ionic liquids

Acidic $[C_2\text{-mim}]Cl\text{-}AlCl_3$ mixtures have been shown above to be very useful catalytic solvents for a number of industrially relevant reactions. However, reactions catalyzed by aluminum trichloride, whether used in an ionic liquid or as a solid phase reactions have one significant disadvantage, they are air and moisture sensitive. Using such liquids within an industrial process will therefore require that reactants are kept as dry as possible, adding to the overall process cost. We have seen how the activity and properties of the liquid can be readily controlled by both changing the anion or the cations present. By switching to neutral ionic liquids containing for example $[BF_4]^-$, $[PF_6]^-$ and $[SbF_6]^-$ anions, the reactive polymerization and oligomerization reactions of olefins catalyzed by acidic anions is not observed and more controlled, specific reactions can be catalyzed.

Since these ionic liquids cannot support the existence of reactive Lewis acid conjugate anions (such as $[Al_2Cl_7]^-$ i.e. there is no analogous mechanism to support $2[BF_4]^- \leftrightarrow [B_2F_7]^- + F^-$), they are much less reactive when used as solvents. Under these conditions, many conventional transition metal catalysts can be utilized. Again modification of the ionic liquid solvents allows the potential to immobilize catalysts, stabilizing the active species and to optimize reactant/product solubilities and to permit facile extraction of products. In general it has been found that charged, especially cationic transition metal complexes are most effectively "immobilized" in the ionic liquid solvents. In addition ionic liquids can immobilize less complex catalysts than two-phase aqueous-organic systems, where expensive, unstable, synthetically challenging ligands are often required.

Hydrogenation of olefins catalyzed by transition metal complexes dissolved in ionic liquid solvents have been reported using rhodium-,[81] and ruthenium- and cobalt-containing catalysts.[82] In these studies it was shown that hydrogenation rates where up to five times higher than the comparable reactions when carried out in propanone. The solubilities of the alkene reagents, TOFs, and product distributions where all strongly influenced by the nature of the anion in the ionic liquid solvent.

Chauvin et al. reported the asymmetric hydrogenation of acetamidocinnamic acid[83] to (S)-phenylalanine with a cationic chiral rhodium catalyst in [C_4-mim][SbF_6] ionic liquid, more recently the 2-arylacrylic acid has been produced with a reasonable 64% yield[84] using a chiral ruthenium catalysts in [C_4-mim][BF_4] ionic liquids. Palladium catalysts[85] immobilized in an ionic liquid-polymer gel membrane[86] containing either [C_2-mim][CF_3SO_3] or [C_2-mim][BF_4] have also been reported as catalysts for heterogeneous hydrogenation reactions.

Fuller et al have also reported the hydroformylation[86] of pent-1-ene in [C_4-mim][PF_6] using a rhodium catalysts showing both a high catalytic activity and product separation as a second organic phase. However it was observed that a small quantity of the neutral catalyst leached into the organic phase.

Other commercially important reactions include the hydrodimerization of 1,3-butadiene to octa-2,7-dien-1-ol[87,88] carried out using palladium catalysts in [C_4-mim][BF_4]. The catalyst precursor [$Pd(mim)_2Cl_2$] was prepared *in situ* from an imidazolium tetrachloropalladate(II) salt, [C_4-mim]$_2$[$PdCl_4$], dissolved in the ionic liquid solvent. The reaction proceeds in a liquid-liquid two-phase system, where the products separate from the catalytic reaction mixture as a separate layer on cooling.

Ionic liquids have been demonstrated as effective solvents for Diels-Alder reactions[89-91] where they have shown significant rate enhancements as well as high yields and selectivities when compared with the best results obtained in conventional solvents. To date, the biggest developments in Diels-Alder chemistry have come through reactions in Li[ClO_4]-Et_2O, where the high electrolyte concentrations are cited as beneficial through "salt-effects" and the high internal pressure of the solvent. However the use of such mixtures of perchlorate salts with organic molecules could cause a number of hazards when used on an industrial scale. Hence there is considerable potential for ionic liquids in this area.

The stability of the neutral ionic liquids allows them to be used in environments unsuitable to the tetrachloroaluminate(III) based ionic liquids. As such they offer considerable advantages allowing them to be used with "wet" process streams. The use of the fluorinated anions as shown in Figures 21.2.6 and 21.2.7, i.e., [PF_6] and [BF_4], introduces the concept of hydrophilic ionic liquids which are partially immiscible with water. In fact all [PF_6] liquids are found to be immiscible with water and all [BF_4] liquids with chain lengths greater than C_4 will form two separate phases with water at sufficient concentrations. This property has prompted investigation into the application of these solvents as extraction solvents for a number of materials. Rogers et al.[92] has studied the partition of benzene with water and has recently studied the relationship between pH and extraction efficiency.[93] Figure 21.2.10 il-

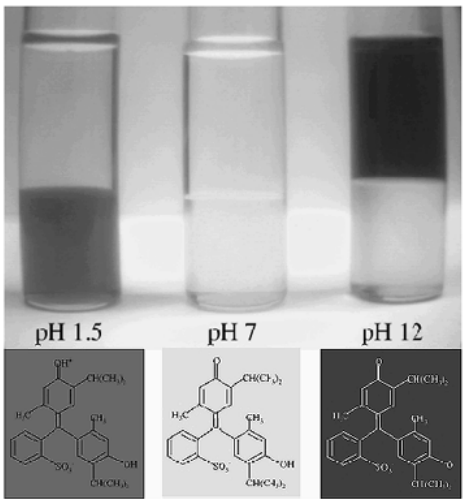

Figure 21.2.10. The phase preference of the three forms of thymol blue in [C_4-mim][PF6].[93]

lustrates the qualitative partitioning of thymol blue in its three forms between aqueous (top) and [C_4-mim][PF_6] (bottom) phases, as aqueous phase pH is changed from very acidic, to very basic. At low pH the thymol blue exists in its red form as a neutral zwitterion which prefers the ionic liquid phase. As the pH is increased via the addition of NaOH, the yellow monoanion forms with some detectable increase in concentration in the aqueous phase. The blue dianion, above pH = 10, partitions quantitatively to the aqueous phase. The same result was also obtained by bubbling CO_2 and NH_3 through the ionic liquid phase.

Lye[94] has also studied the use of ionic liquids in the extraction of erythromycin-A for the *Rhodococcus* R312 catalysed biotransformation of 1,3-dicyanobenzene (1,3-DCB) in a liquid-liquid two-phase system. Here it was found that the ionic solvent was less harmful to the system than conventional molecular solvents with the specific activity of the biocatalyst in the water-[C_4-mim][PF_6] system being almost an order of magnitude greater than in the water-toluene system. In addition, recent reports have effectively shown the potential for combining ionic liquid-and supercritical CO_2 systems for product extraction and separation[95] of naphthalene. Here it was found that the CO_2 was highly soluble in [C_4-mim][PF_6] reaching a mole fraction of 0.6 at 8 MPa and after separation there was no detectable ionic liquid in the extract. Another recent example is a paper by Armstrong et al.,[96] where ionic liquids ([C_4-mim][PF_6] and [C_4-mim][BF_4]) where used as stationary phases for gas chromatography. From these studies it was concluded that the ionic liquids act as nonpolar stationary phases when separating nonpolar analytes, however they are highly interactive and retentive when used to separate molecules with somewhat acidic or basic functional groups.

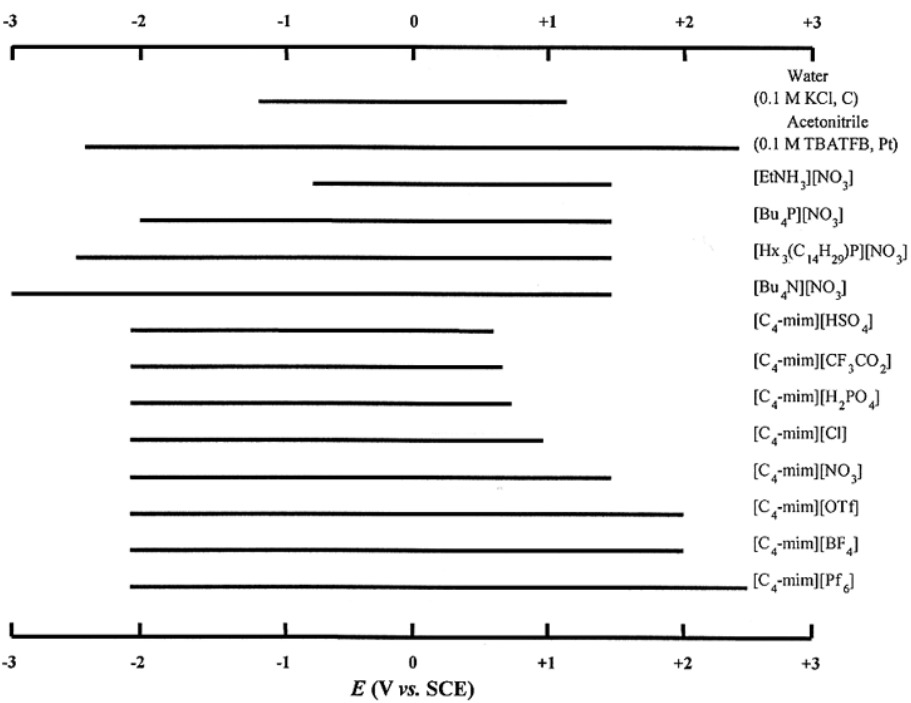

Figure 21.2.11. The electrochemical windows of a number of ionic liquids.[97]

21.2.4 ELECTROCHEMICAL APPLICATIONS

Since ionic liquid where first developed as an adjunct to the U.S. Naval program for use as battery electrolytes it seems only fair to begin this discussion by firstly looking at the electrochemical properties. One of the most important electrochemical properties of a solvent is its electrochemical window, the range of potentials over which a solvent system (including the solvent and any supporting electrolyte) is inert. The cathodic limit results from reduction of the solvent system; the anodic limit from its oxidation. Electrochemical windows are somewhat arbitrary as they are dependent upon the amount of background current which can be tolerated. Figure 21.2.11 shows the electrochemical windows of a range of ionic liquids as well as more commonly used solvents such as water and acetonitrile. The electrochemical windows shown in Figure 21.2.11 were determined using cyclic voltammetry at a glassy carbon disc electrode and are referenced against the Ag(I)/Ag couple (versus Ag(I)/Ag) and converted to the equivalent SCE potential. The reference electrode consisted of a silver wire immersed in a 0.1 M solution of $AgNO_3$ dissolved in [C_6-mim][NO_3]. In chloroaluminate ionic liquids, the most common reference electrode is an aluminum wire immersed in neat acidic ionic liquid (versus Al(III)/Al).

It can be seen from Figure 21.2.11 that the [C_4-mim] cation has a cathodic limit of approximately -2 V versus SCE and that this value is essentially the same for all of the [C_n-mim] cations. Given that the deposition potentials for many metals will fall positive of this potential, it becomes possible to use ionic liquids as electrolytes for metal plating and other similar processes. The broad electrochemical windows (in some cases, over 4 V) indicate that a variety of organic and inorganic electrochemical oxidations and reduction should be possible in ionic liquids.

A wide variety of metals can be electrodeposited from room-temperature ionic liquids. The electrodeposition mechanisms of transition metals, lanthanides and Group 13 metals have been investigated[98-103] as have cobalt,[104-107] iron,[108] manganese,[109] tin,[110] gold,[111,112] silver,[113-116] palladium,[117,118] mercury,[119] cerium,[120] and lead,[121] and the actinides.[122] In addition, ionic liquids have been used extensively to study the electrochemistry and spectrochemistry of metal-chloride complexes.[123-131]

Chloroaluminate ionic liquids have been used in the electrodeposition of aluminum and aluminum-transition metal alloys.[132] Transition metal-aluminum alloys are valued for their corrosion resistance and magnetic properties. A convenient method for creating thin alloy films is through the electrodeposition of two or more metals. The electrodeposition of aluminum and aluminum alloys from aqueous solutions is complicated by the fact that dihydrogen is evolved before aluminum is deposited. However, these materials can be electrodeposited from aprotic non-aqueous solvents or high temperature molten salts. The electrodeposition of aluminum alloys such as Cr-Al,[133] Mn-Al,[134,135] Ni-Al[136] and Ti-Al[137] have been demonstrated from inorganic chloroaluminate molten salts, mainly Franklin acidic ($AlCl_3$-rich) $AlCl_3$ - NaCl. One unfortunate drawback to the use of alkali-chloride based chloroaluminates such as $AlCl_3$-NaCl for the electroplating of

Table 21.2.6. Diffusion coefficients and Stokes-Einstein products of a number of species studied in the 40-60 mol% [C_2-mim]Cl-$AlCl_3$ ionic liquids at 40ºC

	D_o 10^{-7} cm^2s^{-1}	ηD_o T^{-1}, 10^{-10} g cm s^{-2} K^{-1}
Co(II)	6.6	2.6
Cu(I)	2	0.7
Ni(II)	10	3.5
Zn(II)	6.7	2.3

these alloys is the substantial vapor pressure of Al_2Cl_6 associated with the acidic region of these melts.

This is of course not the case when working with room temperature ionic liquid systems. Electrochemical and spectroscopic studies of cobalt,[138] copper,[139] and nickel,[140] have been carried out in the $AlCl_3$-butylpyridinium chloride molten salt system. The direct current and pulsed current electrodeposition of Ni-Al alloys has also been shown in acidic $AlCl_3$-butylpyridinium chloride ionic liquids. This particular alloy has also been shown to be successful in $AlCl_3$-[C_2-mim]Cl as have Co-Al and Cu-Al.[141] Electrochemical techniques can also be used to calculate the diffusion coefficients of metal ions. Table 21.2.6 shows the calculated diffusion coefficients and stokes-Einstein products of cobalt(II),[104] copper(I),[142] nickel(II)[143] and zinc(II)[144] in the 40-60 mol% [C_2-mim]Cl-$AlCl_3$ ionic liquid.

21.2.4.1 Electrosynthesis

Electrosynthesis provides an attractive alternative to conventional methods used for performing synthetic chemistry. It can effect the clean, complete conversion of starting material to product without using hazardous or toxic experimental conditions. Ionic liquids possess many advantages over conventional solvents typically used in electrochemical experiments. Their polar nature allows them to dissolve large concentrations of a wide variety of organic and inorganic compounds. They possess no vapor pressure, are stable on heating and because they are completely ionized the need for a supporting electrolyte is eliminated. Such benefits are not associated with many of the non-aqueous systems employed in electrochemical applications.

Electrochemical studies in ionic liquids are common;[145-148] however the application of this technology to molecular synthesis remains largely unexplored. Some of the examples to date deal with electro-polymerizations. Osteryoung et al. prepared polyaniline on platinum and glassy carbon electrodes by anodic oxidation of the monomer in imidazolium based chloroaluminate ionic liquids.[149] Elsewhere the formation of polyfluorene was achieved by Janiszewska and Osteryoung.[150] Actual transformation of an organic moiety was achieved electrochemically in 1-methyl-3-butylimidazolium chloroaluminate systems. The reactions studied dealt with the reduction of aromatic ketones.[151] Reductions of perylene and phenazine have also been achieved electrochemically in basic mixtures of aluminum trichloride and 1-ethyl-3-methylimidazolium chloride.[152,153] The use of a neat ionic liquid 1-ethyl-3-methylimidazolium hydrogen dichloride [C_2-mim][HCl_2] was also investigated with regard to the reduction of phenazine.[152] Most of the work in electrosynthesis has been carried out in air- and moisture-sensitive ionic liquids, those containing chloroaluminates and $[HCl_2]^-$; little investigation into the electrosynthetic possibilities presented by air and moisture stable ionic liquids has been attempted.[154]

21.2.5 PHYSICAL CHARACTERIZATION

21.2.5.1 Viscosity

Viscosity is probably the most important physical property for initially determining the "processability" of a solvent. It is necessary for all calculations involving fluid flow, (pumping, mixing, etc.) as well as in the estimation of heat transfer and diffusion coefficients. Information on the change in viscosity as a function of temperature, solvent or reagent addition is required for the efficient and design of any handling equipment. Ideally one would like the viscosity of a fluid to be as low as possible allowing for the fluid to be

pumped easily. In addition it is desired for the fluid to have only small changes in viscosity through the normal operating temperature range.

In general, the published data on the viscosity of ionic liquids is scarce. Most of this published literature on ionic liquids viscosity deals with the first generation ionic liquids. The viscosity of any fluid is highly dependent on both the measuring technique used and the purity of the samples. Given this difficulty the reported values in the literature are often neither comparable or reproducible.

Once again, the first studies of the viscosity where related to the development of ionic liquids as nonaqueous battery electrolytes. Hussey et al.[155] reported the viscosity of several N-alkylpyridinium chloroaluminate salts over a temperature range of 25 to 75°C where they observed an increase in viscosity with alkyl chain length and concluded that the temperature dependence of the viscosity could be fitted to the Arrhenius type equation, i.e.,

$$\eta = \eta_0 \exp\left(E_\eta / RT\right) \qquad [21.2.3]$$

where:

E_η is the energy of activation for viscous flow
R is the gas constant
T is the absolute temperature

This conclusion was supported by the linearity of the ln η vs. 1/T plots for the studied temperature range. The above equation can be modified to give;

$$\ln\eta = A_\eta + B_\eta / T \qquad [21.2.4]$$

where:

A_η = ln η_0
B_η = E_η/R

The fitted parameters, along with the values of E_η, appear in Table 21.2.7.

Table 21.2.7. Parameters for Arrhenius equations for viscosity

Melt	Mol ratio	- A_η	E_η
$[NC_1\text{-py}]Cl\text{ -}AlCl_3$	1:2	4.801	4.639
$[NC_2\text{-py}]Cl\text{ -}AlCl_3$	1:2	4.355	4.276
$[NC_3\text{-py}]Cl\text{ -}AlCl_3$	1:2	4.734	4.523
$[NC_4\text{-py}]Cl\text{ -}AlCl_3$	1:2	5.314	4.950
$[NC_2\text{-py}]Br\text{ -}AlCl_3$	1:2	5.575	5.136

The viscosities of the 1,3-dialkylimidazoilium aluminium chloride[156] and 1-methyl-3-ethylimidazolium aluminium bromide[157] ionic liquids have also been reported for different compositions and temperatures. For both the chloroaluminate and bromoaluminate ionic liquids the temperature dependence was found not to have an Arrhenious type curve, with non-linear plots of ln η vs. 1/T. In these studies the temperature range used was wider than that of the N-alkylpyridinium. This non-Arrhenius behavior is characteristic of glass forming melts. Here the three parameter Vogel-Tammann-Fulcher (VFT) equation:

$$\ln\eta = K_\eta / (T - T_0) + \tfrac{1}{2}\ln T + \ln A_\eta \qquad [21.2.5]$$

where:

A_η is a scaling factor
T_0 is the "ideal transition temperature" and
K_η is a constant characteristic of the material

can be used for such fluids, with K_η being the formal analogue of the Arrhenius activation energy. The parameter T_0 has been given a quasi-theoretical significance by the free volume theory of Cohen and Turnbull. According to this theory, T_0 represents the temperature at which the free volume of the liquid disappears and liquid transport becomes impossible.[155,157] Alternatively, it has been interpreted by Adams and Gibbs as the temperature at which the configuration entropy of the supercooled liquid becomes zero.[155,157]

The fitted parameters for the VFT equation are displayed in Table 21.2.8 for the 1,3-dialkylimidazolium chloride-aluminium chloride systems.

Table 21.2.8. Fitted parameters for the VFT equation for some $AlCl_3$ systems[156]

Melt	Mol ratio	T_0, K	K_η, K	- ln A_η
[C_1-mim]Cl- $AlCl_3$	1:2	109.1	1024	5.444
	2:1	194.8	811	4.739
[C_3-mim]Cl- $AlCl_3$	1:1	141.5	879	5.157
	1:2	160.0	608	4.351
	2:1	185.0	958	5.208
[C_4-mim]Cl- $AlCl_3$	1:1	184.5	484	3.819
	1:2	154.8	666	4.537
	2:1	165.4	1261	5.793
[C_4-bim]Cl- $AlCl_3$	1:1	156.5	792	4.811
	1:2	150.7	750	4.765

These systems show a strong dependence of the composition for the basic range, with an increase in viscosity as the aluminum trichloride mole fraction decreases. In the acidic range the viscosity seems almost independent of the composition, nevertheless showing a slight decrease with increasing aluminum trichloride mole fraction. However it was also observed that increased viscosities where associated with longer alkyl chain lengths.

In the study of the 1-methyl-3-ethylimidazolium bromide - aluminum bromide systems, the VFT parameters for the different compositions were fitted as a function of X ($AlBr_3$ mole fraction) to cubic polynomial equations of the form

$$F(x) = c_0 + c_1 X + c_2 X^2 + c_3 X^3 \qquad [21.2.6]$$

in neutral and basic melts and to second order equations of the form

$$F(x) = c_0 + c_1 X^{-1} + c_2 X^{-2} \qquad [21.2.7]$$

in acidic melts. The values generated for these constants are displayed in Table 21.2.9.

Table 21.2.9. Parameters for 1-ethyl-3-methylimidazolium bromide/aluminum bromide systems[157]

Melt composition	VFT Parameter	c_0	c_1	c_2	c_3
Neutral and basic melts $0.35 \leq X \leq 0.50$	T_0	2.1405×10^3	-1.5128×10^4	3.9396×10^4	-3.4596×10^4
	K_η	-1.4147×10^4	1.1709×10^5	-3.0743×10^5	2.6769×10^5
	$\ln A_\eta$	-1.3581×10^1	1.8522×10^2	-5.1772×10^2	4.7652×10^2
Acidic melts $0.50 < X \leq 0.75$	T_0	-3.8691×10^2	7.6383×10^2	-2.6176×10^2	-
	K_η	6.6201×10^3	-7.8145×10^3	-2.5214×10^3	-
	$\ln A_\eta$	2.5515×10^1	-2.2656×10^1	7.3019	-

In this case, the viscosity showed a minimum at X =0.50, with the viscosity rising as X is either increased or decreased; displaying an irregular increase in the acidic range. This result is somewhat different for the chloroaluminate analogue discussed above.

It is important to note that in all the studies described above, different types of capillary viscometers were used for measuring the viscosity. This technique generates a kinematic viscosity, ν, that has to be multiplied by the density, ρ, of the melt to obtain the absolute viscosity, η.

Other viscosity studies in ionic liquids were carried out by Grätzel et al.[158] as part of a research program for the application of ionic liquids as solvents for a dye-sensitized nanocrystalline solar cell.

A series of imidazolium based salts with various alkyl substituents and different anions were characterized in terms of viscosity in order to establish a correlation between chemical structure and physical properties. The results are summarized in Table 21.2.10.

Table 21.2.10. Viscosity at 20°C, cps. TfO^-: triflate; NfO^-: nonaflate; Tf_2N^-: bis(tryfil)amide; TA^-: trifluoroacetate; HB^-: heptafluorobutanoate; AcO^-: acetate[158]

Imidazolium cation		TfO^-	NfO^-	Tf_2N^-	TA^-	HB^-	AcO^-
3-Methyl	1-Methyl			44			
	1-Ethyl	45		34	35	105	162
	1-Butyl	90	373	52	73	182	
	1-i-Butyl			83			
	1-MeOEt	74		54			
	1-CF_3CH_2			248			
3-Ethyl	1-Ethyl	53		35	43		
	1-Butyl		323	48	89		
1-Ethyl-2-methyl	3-Methyl			88			
1-Ethyl-5-methyl	3-Methyl	51		37			
	3-Ethyl			36			

According to this study, the viscosity of ionic liquids is mainly controlled by hydrogen bonding, van der Waals forces, molecular weight, and mobility.

In respect to the cation structure, alkyl lengthening or fluorination make the salt more viscous. Also the reduction of freedom of rotation (from butyl to isobutyl) increased the viscosity. Unexpectedly, methylation at the C_2(H) of the imidazolium ring increased viscosity even if it suppressed the position most likely to hydrogen bond with the anion.[158]

In respect to the anion, from TfO^- to NfO^- and from TA^- to HB^-, the increase of van der Waals attraction dominates over the H-bonding decrease due to the better charge delocalization. However, from TfO^- to Tf_2N^-, the almost complete suppression of H-bonding seems to influence more than the increase in Van der Waals attractions smaller anion weight of TfO^-. On the other hand, comparing TA^- and AcO^-, the H-bonding strength of AcO^- is more important than its smaller size. The salts with lower viscosity are TA^-, with minimal anion weight and moderate basicity, and Tf_2N^-, with minimal basicity and moderate anion weight.[158]

Table 21.2.11. Viscosity of some ionic liquids at 25°C. For the binary mixtures the ratio means the proportion of AlX_3 to ImX or TMSuX

Cation	Anion	η, cps at 25°C
[C_2-py]	$Br/AlCl_3$ (ratio 2:1)	22.5[155]
	$Br/AlBr_3$ (ratio 2:1)	~50[159]
[C_2-mim]	$Cl/AlCl_3$ (ratio 2:1)	13.5[156]
	$Br/AlBr_3$ (ratio 2:1)	31[157]
	BF_4	37.7 (22°C)[160]
	Triflate (CF_3SO_3)	43[161]
	Mesylate (CH_3SO_3)	160[161]
[C_4-mim]	BF_4	233 (30°C)[162]
	PF_6	312 (30°C)[162]
Trimethylsulfonium	$Cl/AlCl_3$ (ratio 2)	39.3[163]
	$Br/AlCl_3$ (ratio 2)	54.9[163]
	$Br/AlBr_3$ (ratio 2)	138[163]

Clearly, many structural parameters affect the viscosity of ionic liquids and a more exhaustive study is needed to rationalize the different trends and to establish a correlation model for prediction.

Finally, there are some scattered data on viscosity of other ionic liquids which are summarized in Table 21.2.11, together with the most relevant data from the studies cited above.

As it was mentioned above, care must be taken when comparing or using these data as different measuring techniques can yield different viscosity results and furthermore, our recent investigations (to be published shortly) have shown that the presence of traces of water or other impurities like Cl^- can have a dramatic effect on viscosity.

Table 21.2.12. Densities of the [C_4-mim][PF_6] and [C_4-mim][BF_4] ionic liquids when compared against other solvents at room temperature

Solvent	ρ, kg m^{-3}
trichloromethane	1483
[C_4-mim][PF_6][164]	1372
dichloromethane	1327
[C_4-mim][BF_4][164]	1208
water	1000
diethyl ether	714
toluene	867
2-propanol	786
benzene	877

21.2.5.2 Density

Information on solvent density is also another important physical property. This is a particularly used in fluid flow calculations and for the design of liquid/liquid two phase mixer-settler units. Given that many of the ionic liquids have a "heavy" anion it would be expected that their density would be relatively high when compared to normal industrial solvents. However it can be seen from the Table 21.2.12 that the density of the [C_4-mim][PF_6] and [C_4-mim][BF_4] ionic liquids fall within the region of the chlorinated solvents.

Overall the density of ionic liquids is somewhat easier to model than the viscosity. In general the change of density with temperature has been fitted to linear equations of the form

$$\rho = a + b \times T \qquad [21.2.8]$$

where a and b are constants.[155-157]

The fitted parameters for N-alkylpyridinium are displayed in Table 21.2.13. The bromide containing melts showed a much higher density than the chloride ones which is to be expected. It has also been shown that the lengthening of the alkyl chain smoothly decreases the density.[155,156]

Table 21.2.13. Fitted parameters for the density of N-alkylpyridinium[155]

Melt	Mol ratio	a	$-b \times 10^3$	Temp range, °C
[NC_1-py]Cl -$AlCl_3$	1:2	1.4625	0.87103	25-75
[NC_2-py]Cl -$AlCl_3$	1:2	1.4307	0.91446	25-67
[NC_3-py]Cl -$AlCl_3$	1:2	1.3973	0.8847	26-75
[NC_4-py]Cl -$AlCl_3$	1:2	1.3680	0.86042	31-76
[NC_2-py]Br -$AlCl_3$	1:2	1.5473	0.93059	25-32

The variation of density with different concentrations of aluminum trichloride in 1,3-dialkylimidazolium chloride- aluminum chloride melts is not however a smooth function.[156] In the study carried out by Wilkes et al. on the density of 1-methyl-3-ethylimidazolium bromide aluminum bromide systems, the change of the parameters a and b with composition, X, were successfully fitted to polynomials of third order. The constants obtained from this study are shown in Table 21.2.14.

Table 21.2.14. Calculated constants for third order polynomial

		c_0	c_1	c_2	c_3
Neutral and basic melts $0.35 \le X \le 0.50$	a	1.0588	3.8594	-2.8945	0.00
	b	1.2907×10^{-3}	-1.0448×10^{-2}	1.1519×10^{-2}	0.00

		c_0	c_1	c_2	c_3
Acidic melts 0.5 0< X ≤ 0.75	a	-5.8410	37.009×10^{1}	-56.829×10^{1}	30.474×10^{1}
	b	1.7946×10^{-2}	-9.0089×10^{-2}	1.4121×10^{-1}	-7.4099×10^{-2}

Grätzel et al.[158] has also measured the densities for the different ionic liquids with the results are shown in Table 21.2.15.

Table 21.2.15. Density at 22°C or indicated temperature, g cm^{-3}. TfO$^-$: triflate; NfO$^-$: nonaflate; Tf$_2$N$^-$: bis(tryfil)amide; TA$^-$: trifluoroacetate; HB$^-$: heptafluorobutanoate; AcO$^-$: acetate[158]

Imidazolium cation		TfO$^-$	NfO$^-$	Tf$_2$N$^-$	TA$^-$	HB$^-$
3-Me	1-Me			1.559		
	1-Et	1.390		1.520	1.285	1.450
	1-Bu	1.290[20]	1.473[18]	1.429[19]	1.209[21]	1.333
	1-i-Bu			1.428[20]		
	1-MeOEt	1.364		1.496		
	1-CF$_3$CH$_2$			1.656[20]		
3-Et	1-Et	1.330		1.452[21]	1.250	
	1-Bu		1.427[18]	1.404[19]	1.183[23]	
1-Et-2-Me	3-Me			1.495[21]		
1-Et-5-Me	3-Me	1.334		1.470		
	3-Et			1.432[23]		

As with viscosity, there are some scattered data on density of other ionic liquids which is summarized in Table 21.2.16, together with the most relevant data from the studies cited above.

Table 21.2.16. Density of some ionic liquids at 25°C. For the binary mixtures the ratio means the proportion of AlX$_3$ to ImX or TMSuX

Cation	Anion	ρ, g cm^{-3} at 25°C
1-ethylpyridinium	Br/AlCl$_3$ (ratio 2)	1.52[155]
	Br/AlBr$_3$ (ratio 2)	2.20[159]
1-ethyl-3-methylimidazolium	Cl/AlCl$_3$ (ratio 2)	1.39[156]
	Br/AlBr$_3$ (ratio 2)	2.22[157]
	BF$_4$	1.24 (22°C)[160]
	Triflate (CF$_3$SO$_3$)	1.38[161]
	Mesylate (CH$_3$SO$_3$)	1.24[161]
1-butyl-3-methylimidazolium	BF$_4$	1.17 (30°C)[162]
	PF$_6$	1.37 (30°C)[162]

Cation	Anion	ρ, g cm^{-3} at 25°C
1-butyl-3-ethylimidazolium	Triflate (CF_3SO_3)	1.27[161]
	Mesylate (CH_3SO_3)	1.14[161]
1-dodecyl-3-ethylimidazolium	Triflate (CF_3SO_3)	1.10[161]
Trimethylsulfonium	$Cl/AlCl_3$ (ratio 2)	1.40[163]
	$Br/AlCl_3$ (ratio 2)	1.59[163]
	$Br/AlBr_3$(ratio 2)	2.40[163]

21.2.6 SUMMARY

In summary ionic liquids have a proven ability to enhance current industrial chemistry. Within current industrial processes using conventional solvents, selectivities, TOF and reaction rates are effectively uncontrolled: however by using ionic liquid media for the catalysis, it is possible to have a profound influence on all these factors. Tailoring of the ionic liquid by a combination of subtle (i.e., changing cation substitution patterns) and gross (anion type) modifications can permit very precise tuning of reactions.

Ionic liquids have a proven ability to be used as effective solvents and catalysts for clean chemical reactions; as replacements for volatile organic and dipolar aprotic solvents (i.e. DMF, DMSO) and solid acid catalysts in reactions whether being used at the laboratory or industrial scale. Many of their physical properties are in the same region as organic solvents and as such could easily be incorporated into any future processes. Properties such as negligible vapor pressure and high density/variable interfacial tension offer considerable advantages in the design of unit operations such as evaporators, mixer-settlers and reactors. It is envisaged that as more information is gathered on their physical properties it will be possible to accurately design and optimize entire plants around these novel solvent systems. In a time where considerable emphasis is being placed on clean reactions and processes with minimal waste and efficient product extraction ionic liquids have emerged as a novel and exciting alternative to modern production methods. They are truly designer solvents.

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21.3 OXIDE SOLUBILITIES IN IONIC MELTS

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21.3.1 METHODS USED FOR SOLUBILITY ESTIMATIONS IN IONIC MELTS

Processes of the dissolution of metal oxides in ionic melts are accompanied by interactions between ions of dissolved substance with ions of the melt (solvation). The superimposition of the mentioned processes results in the formation of metal complexes with the melt anions and cation complexes with oxide-ions. Therewithal, the definite part of the oxide passes into the solution without dissociation as uncharged particles. Thus, in saturated solution of oxide the following equilibria take place:

$$MeO_s = MeO_l \qquad [21.3.1]$$

$$MeO_l = Me^{2+} + O^{2-} \qquad [21.3.2]$$

$$Me^{2+} + iX^{k-} = MeX_i^{2-ik} \qquad [21.3.3]$$

$$O^{2-} + nKt^{m+} = Kt_nO^{nm-2} \qquad [21.3.4]$$

where:

s and l	subscripts denoting solid and dissolved oxide, respectively,
Me	the designation of two-valent metal
Kt^{m+}	the melt cation (such as Cs^+, K^+, Na^+, Ba^{2+}, Ca^{2+}, etc.),
X^{k-}	the melt anion (Cl^-, Br^-, I^-, SO_4^{2-}, PO^{3-}, etc.)

Since at the dissolution of any oxide in melts a degree of interaction "Kt^{m+} - O^{2-}" should be the same and the complexation with melt anions for cations of oxide may be assumed as closed,[1] therefore, it can be believed that oxide solubilities depend mainly on the degree of interactions [21.3.1] and [21.3.2], latter may be considered as an acid-base interactions as proposed by Lux.[2] The constant of [21.3.2]

$$K_{MeO} = \frac{a_{Me^{2+}} a_{O^{2-}}}{a_{MeO}} \approx \frac{m_{Me^{2+}} m_{O^{2-}}}{m_{MeO}} \qquad [21.3.5]$$

where:
a and m activities and molarities of the particles noted in the subscripts

may be considered as a measure of acidic properties of the cation if reaction [21.3.2] is homogeneous. However, a majority of oxides possess limited solubilities in molten salts and the excess of the oxide should precipitate. In this case the fixation and removing oxide ions

from melt took place not only because of the cation acidity but owing to formation of new phase - the precipitate of the oxide. Therefore, works in which the estimations of cation acidities were based on measurements of changes in oxide concentration before and after cation addition[3] or by interactions between, e.g., carbonates with Lux acids[4,5] contained distorted results. The latter works[4,5] contain the additional error - insoluble metal carbonates $MeCO_3$ after interaction with acid $K_2Cr_2O_7$[4] or $NaPO_3$[5] were transformed into insoluble chromates or phosphates - all reactions were heterogeneous. The above may be also referred to works of Slama[6,7] where cation acidities were estimated on the base of reactions

$$Me^{2+} + NO_3^- = MeO\downarrow + NO_2^+ \qquad [21.3.6]$$

$$NO_2^+ + NO_3^- = 2NO_2\uparrow + \tfrac{1}{2}O_2 \qquad [21.3.7]$$

there was no evidence of homogeneity of reaction [21.3.6].

The mentioned method seems to have no wide usage for studying behavior of oxides in molten salts, solubility studies by isothermal saturation and potentiometric titration methods are more precise and informative.

From the listed above scheme of equilibria [21.3.1-21.3.4] it follows that the fixation of oxide ions by metal cations is in common case a heterogeneous process resulting in the formation of a new phase and cation acidity may have no connection with the completeness of interaction Me^{2+} - O^{2-} in molten salts.

From eq. [21.3.1] it is clear that molecular oxide concentration in the saturated solution is not dependent on the constituent ion concentrations but connected with the precipitate properties, mainly with the molar surface of the deposit, σ.

Since the concentration of the non-dissociated oxide in the saturated solution, as a rule, is hardly determined, for practical purposes the solubility product, the magnitudes of PMeO (used below pP≡-logP),

$$P_{MeO} = a_{Me^{2+}} a_{O^{2-}} \approx m_{Me^{2+}} m_{O^{2-}} \qquad [21.3.8]$$

are usually employed for the description of the saturated solutions. The known values of P_{MeO} and K_{MeO} give possibility to estimate the concentration of the non-dissociated oxide, s_{MeO}, in the saturated solution:

$$s_{MeO} = \frac{P_{MeO}}{K_{MeO}} \qquad [21.3.9]$$

It should be noted, however, that there was no reliable method for determining dissociation constants and s_{MeO}. Let us consider two generally accepted methods for oxide solubility determinations.

21.3.1.1 Isothermal saturation method

This method is simple enough and includes some modifications:

1. placing baked sample of the oxide in the melt-solvent and regular tests of the metal concentration in the melt up to the saturation. Known test routines are either radiochemical[8] or complexonometric[9] analysis of cooled samples of the saturated solutions;

2. the addition of known weights of oxide to the melt up to the saturation detected by a potentiometric technique.[10,11]

The sum of molecular and ionic form concentrations in the saturated solution, Σs_{MeO}, is obtained as the main result of such investigations, this magnitude may be expressed by the following equation:

$$\sum s_{MeO} = \sqrt{P_{MeO}} + \frac{P_{MeO}}{K_{MeO}} \qquad [21.3.10]$$

Since Σs_{MeO} is the main result of this method, there exists a possibility to determine the dissociation constant according to routine 2 if an oxygen electrode was preliminary calibrated by known additions of the completely dissociated Lux base. But there is no information about such studies.

Studies connected with the analysis of cooled samples allow to obtain thermal dependencies of oxide solubilities by analysis of the saturated melt heated to the definite temperature. Main disadvantages of isothermal saturation method are:

- the inclusion of suspended particles of oxide in the sample for analysis and following overvaluing of the results;
- the magnitude determined is the concentration but not its logarithm; range of oxides available for this routine is essentially narrowed and this method is unsuitable for studies of practically insoluble substances. The presence of oxygen impurities in the melt studied leads to lowering the calculated solubilities, especially, if oxide solubility is of the same order as initial oxide concentration since oxide admixtures suppress the oxide dissolution.

21.3.1.2 Potentiometric titration method

This method is more frequently used than the previously described one. It may be employed for oxide solubility studies in a wide range of concentrations of saturated solutions. This method allows to determine solubility products of oxides and in some cases (the existence of the non-saturated solution region) dissociation constants may be calculated.

As compared with isothermal saturation a potentiometric method possesses the following advantages:

- e.m.f. values are linearly dependent on logarithm of O^{2-} concentration; it is possible to measure the latter even in solutions with extremely low potential-determining ion concentrations;
- simplicity of e.m.f. measurements and good reproducibility of the experimental values;
- possibility to made studies *in situ*, i.e., without any effect on the process studied.

Main limitations of the potentiometric titration are due to the potential of liquid junction, however, the latter is negligible in molten salts,[10] and the absence of reliable and generally accepted methods for calculation of activity coefficients for oxide ions and cations.

As for determination of solubility and dissociation parameters it should be noted that this method allows to determine values K_{MeO} only if the potentiometric curve contains the non-saturated solution region. Studies in the wide temperature range are impeded as compared with the isothermal saturation method.

21.3.2 OXYGEN-CONTAINING MELTS

Frederics and Temple studied CuO, MgO, PbO and ZnO solubilities in molten equimolar mixture KNO_3-$NaNO_3$ in the range 290-320ºC.[12] The solubilities were determined by isothermal saturation method with the potentiometric control of solubilities. Solubility products were 2.24×10^{-13} for CuO, 2.2×10^{-13} for ZnO, 2.16×10^{-14} for MgO and 4.34×10^{-12} for PbO. The increase of the temperature to 320ºC led to the increase of the solubilities by 6-10 times.[12]

Individual Lux acids derived from B_2O_3 (borax) and P_2O_5 (sodium metaphosphate) are interesting since they are often used as acidic components of different fluxes. Delimarsky and Andreeva[10] determined PbO solubility in molten $NaPO_3$ at 720ºC by isothermal saturation method with the potentiometric control of saturation. The concentration cell with oxygen electrodes $Pt(O_2)$ was used. PbO solubility was estimated as 31.6 mol%.

Nan and Delimarsky investigated solubilities of acidic metal oxides (MoO_3, WO_3, TiO_2) in molten borax at 900ºC by a similar method.[13] The control of saturation was performed by a gravimetric analysis. Solubilities of the oxides deviated from those predicted by Shreder's equation, because of chemical interactions between the substances dissolved and the solvent. Oxide solubilities increased with the reduction of melting point of oxide. Solubilities were 66.1 mol% for MoO_3, 63.2 mol% for WO_3 and 21.2 mol% for TiO_3.

21.3.3 HALIDE MELTS

21.3.3.1 The eutectic mixture KCl-LiCl (0.41:0.59)

Delarue[14,15] performed qualitative studies on oxide solubilities in the melt at t~500ºC by visual method. The experiments consisted of addition of potassium hydroxide, KOH, to the metal chloride solution in KCl-LiCl. If there were no formation of the oxide deposit then the oxide was considered soluble, in other cases, oxide was referred to slightly soluble or insoluble depending on the amount of oxide deposited. CdO, PbO, BaO, CaO and Ag_2O belonged to the group of soluble oxides, CoO, NiO, ZnO were examples of slightly soluble oxides and MgO, BeO and Al_2O_3 were insoluble. Copper (II) oxide was unstable in molten chlorides since its dissolution was accompanied by the reduction of Cu^{II} to Cu^{I}. This transformation has been demonstrated[16] to be substantial even under the partial pressure of chlorine equal to 1 atm. The similar behavior is typical of other transition cations in the highest degree of oxidation, e.g., Tl^{III}, Fe^{III}, and Au^{III}. The addition of corresponding chlorides to the saturated solutions formed by non-oxidizing cations resulted in dissolution of latter due to reactions similar to:

$$2CuCl_2 + ZnO\downarrow \rightarrow 2CuCl + ZnCl_2 + \tfrac{1}{2}O_2\uparrow \qquad [21.3.11]$$

An important feature of oxide solubilities[14,15] was the essential difference of solubility values of "powdered" (added as powder) and prepared *in situ* oxide solubilities. Solubilities of latter samples have been found to be considerably greater (CaO, CdO), although there was no explanation to this observation. Quantitative characteristics of oxides solubilities in KCl-LiCl were not presented.[14,15]

Laitinen and Bhitia[17] determined solubility products for certain oxides at 450ºC in order to evaluate possibility to use corresponding metal-oxide electrodes for oxoacidity measurements in molten salts. Oxide solubilities were as the following (mole/kg): NiO - 3.3×10^{-4}, BiOCl - 6.8×10^{-4}, PdO - 9.4×10^{-3}, PtO - 3.32×10^{-2}, Cu_2O - 3.8×10^{-2}.

The important fact found was the relatively high PtO solubility, therefore, platinum gas oxygen electrode, sometimes considered as metal-oxide one, cannot be used for measurement of pO in strongly acidic media because of complete dissolution of the oxide film over its surface. Pt|PtO electrode was attempted for pO index measurements in buffer solutions Ni^{2+}/NiO.[18]

Shapoval et al.[19-21] studied saturated solutions of different oxides by polarographic technique. A degree of interaction between oxide dissolved and the melt has been estimated taking into account potential and polarogram shifts and their deviations from theoretical ones. Rate of cation reduction has been found to be limited by the acid-base dissociation stage. Stability constants of some oxides have been found to be (in mol%): CoO - $(9.9\pm1.9)\times10$, NiO - $(6.8\pm0.8)\times10^3$, PbO - $(3.4\pm1.3)\times10^3$, Bi_2O_3 - $(8.7\pm3.5)\times10^3$. Cadmium, copper (I) and silver oxides have been shown to completely dissociate under the experimental conditions (400-600°C) this was in a good agreement with Delarue's results.[14,15]

Stabilities of iron (II) and (III) oxides in the chloride melt at 470°C have been investigated.[22,23] Oxide precipitation by carbonate $CO_3^{2-} \equiv O^{2-}$ has been shown by potentiometric and diffractometric data to result in formation of FeO from Fe^{II} solutions. Fe^{III} precipitation led to formation of solid solutions $LiFeO_2$-$Li_yFe_{1-y}O$. Solubility products in molarity scale have been determined as FeO-$10^{-5.4}$, Fe_3O_4-$10^{-36.3}$, Fe_2O_3-$10^{-29.16}$. Cations Fe^{3+} have been found to oxidize chloride melt with chlorine evolution, that is in good agreement with the results of other studies.[14,15] Carbonate ion as oxide donor had its dissociation to O^{2-} essentially incomplete and, therefore, obtained solubility products gave systematic error.[20,21]

Cherginets and Rebrova[24,25] studied oxide solubilities in this melt at 700°C. Solubility products of CoO (pP=4.43±0.11) NiO (pP=5.34±0.2) and MgO (pP=5.87±0.05) were higher than those in molten eutectic KCl-NaCl. The shift of the solubilities in molar fraction scale was ~3.36 log units and allowed to estimate solubilities of other MeO oxides on the base of the known values in KCl-NaCl. It has been shown that acidic properties of Pb^{2+} and Cd^{2+} cations were suppressed by those of Li^+, therefore, these cations and Ba^{2+} and Sr^{2+} did not change oxoacidic properties of the molten KCl-LiCl.

21.3.3.2 Molten KCl-NaCl (0.50:0.50)

One of the first works devoted to oxide solubilities determination in this melt has been performed by Naumann and Reinhardt.[8] CaO, SrO and BaO solubilities have been determined by isothermal saturation technique with isotopic control of the saturation in temperature range from melting point to 900°C. KCl-NaCl and individual molten chlorides, KCl and NaCl, have been used as solvents. Oxide solubilities have been stated to increase in the sequence CaO<SrO<BaO and solubility product values in KCl-NaCl and KCl were similar, and the values for NaCl were higher. A comparison of experimental and thermodynamic data for MeO and Me^{2+}+O^{2-} solutions have shown that the solubility values are between values calculated for solutions of completely dissociated and completely molecular oxide. It means that these constituents were present simultaneously.

Similar investigations have been done in the temperature range 700-800°C by Volkovich.[9] Saturated solutions were prepared by placing pressed oxide tablets into the melt and holding them for 2-3 h. The analysis of solution samples was performed by complexometric titration.

Potentiometric studies of cations Ca^{2+}, Li^+ and Ba^{2+} were conducted to determine acidic properties at 700°C; the calculated dissociation constants (in mol%) were 2.8×10^{-3} for

Li_2O, and 1.2×10^{-2} for BaO, these values showed that all studied cations had considerable acidic properties.[26,27]

Ovsyannikova and Rybkin[3] developed the cation acidity scale in molten KCl-NaCl at 700°C on the basis of e.m.f. shifts after addition of metal sulfates. Acidic properties of the main subgroup elements decreased with the increase of their atomic numbers and there was no similar relationships for side groups and transition metals. Quantitative data elucidation according to acid-base equilibrium [21.3.2] in this melt is affected by additional reaction:

$$SO_4^{2-} = SO_3 \uparrow + O^{2-} \qquad [21.3.12]$$

caused by additions to chloride melts of the corresponding sulfates. The use of sulfates may cause SO_3 formation from highly acidic cation solutions. In particular, Na^+ is the most acidic cation of KCl-NaCl melt, therefore, additions of more basic oxides than Na_2O should result in oxide ion exchange:

$$Me_2^{I}O + 2Na^+ \rightarrow 2Me^+ + Na_2O \qquad [21.3.13]$$

which is shifted to the right. Similar considerations have been made for K^+ - Na^+ - O^{2-} system in molten KCl-NaCl.[28] From [21.3.13] it follows that any solution of cations in Na-based melts cannot create oxide ion concentration exceeding that of equimolar addition of corresponding salt of the most acidic cation of the melt (Na^+). However, the oxide ion concentration in $BaSO_4$ solution has been shown[3] to be 10 times higher than in K_2SO_4 and Na_2SO_4 (ΔE=0.11 V). Similar deviations for other cations are smaller, e.g., Cs - 0.49 V, Sr - 0.30 V, Rb - 0.1 V.

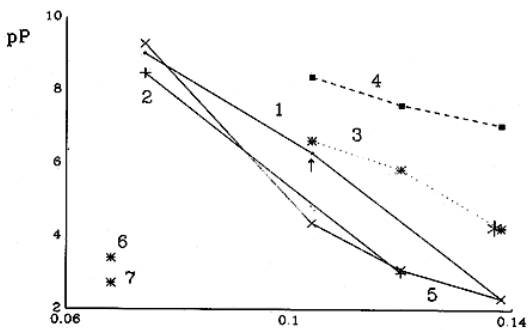

Figure 21.3.1. Alkaline oxide solubilities in KCl-NaCl: 1[11,28-32] at 1000K; 2;[29] 3;[8] 4;[9] 5;[33,38] 6;[40,41] 7;[42] at 700°C.

A potentiometric study of ZnO, MgO, NiO and SrO solubilities at 700°C have been conducted[29] by direct and reverse titrations of cation by KOH. These measurements have resulted in a set of characteristics corresponding (by the calculation formula) to solubility products and dissociation constants. The averaging or another procedure of data treatment were not included. Oxide solubilities have been found to increase in sequence: MgO<NiO<ZnO<SrO.

Oxide solubilities in the chloride melt at 1000 K were studied.[11,28-32] MgO is neutralized in two stages: first stage product was Mg_2O^{2+} and end product was MgO.[11] It should be noted, however, that although MgO solubilities were investigated in similar manner in KCl-NaCl,[29,33] CsCl-KCl-NaCl[34-36] and $BaCl_2$-$CaCl_2$-NaCl[37] no pronounced first stage was detected. Thermal dependence of CaO solubility has been determined by isothermal saturation method[31,32] to be approximated by the following plot $pK_{s,CaO}$=10800/T-5.8. We have studied solubilities of 11 oxides in this melt at 700°C and developed the methods of saturation detection to determine in some cases dissociation constants.[33,38]

Thermal dependence of ZrO_2 solubility (molar fraction, N) in molten KCl-NaCl was evaluated in the temperature range of 973-1174 K:[39] N=(-5.7±3.1)×10-6 + (7±3)×10^{-9}×T. ZrO_2 solubility at t~700ºC was negligible.

Barbin et al.[40,41] determined thermal dependence of Li_2O solubility in equimolar mixture KCl-NaCl by isothermal saturation technique in temperature range of 973-1073 K: N=0.107-5.221/T, in this range the solubility varied from 0.52 to 0.86 mol%. In earlier work by Kaneko and Kojima,[42] the solubility at 973 K was lower (0.31 mol%). The solubility of lithium oxide was close to that for BaO.

Solubility products of some oxides in molten KCl-NaCl in molarity scale are presented in Table 21.3.1 and plotted in Figure 21.3.1 (data obtained by same authors are connected by lines).

Table 21.3.1. Oxide solubilities in molten KCl-NaCl at 700°C (-log P, molarities)

Oxide	pP[11,28-32]	pP[29]	pP[8]	pP[9]	pP[33,38]
MgO	9.00±0.15	8.46			9.27±0.06
CaO	~6.29		6.62	8.36	4.36±0.06
SrO		3.00	5.84	7.60	3.08±0.40
BaO	2.31±0.05		4.22	7.05	2.30±0.15
NiO	11.2	8.32			9.03±0.06
ZnO		6.18			6.93±0.20
Cu_2O	5.4				4.17±0.30
MnO					6.78±0.05
CoO					7.89±0.03
CdO					5.00±0.03
PbO					5.12±0.05

Two groups of values are presented: obtained from isothermal saturation and potentiometric results. The precision of results from isothermal saturation is worse. The potentiometric results should give lower values than isothermal saturation because it includes molecular oxide concentration. Figure 21.3.1 shows that results have opposite trend to [21.3.10].

The following explanation of the above discrepancy is proposed.[43,44] Let us consider the chemical potential, μ, of oxide in its saturated solution:

$$\mu_{MeO,s} = \mu^0_{MeO,l} + RT \ln s_{MeO,l} \qquad [21.3.14]$$

From this equation it follows that the oxide solubility should be constant. But every precipitate possesses a definite surface, hence, the effect of latter should be taken into account, too:

$$\mu_{MeO,s} + \sigma S = \mu^0_{MeO,l} + RT \ln s_{MeO,l} \qquad [21.3.15]$$

where:

σ the surface energy
S molar surface square of the precipitate

Since for the same oxide σ is constant, the increase of the precipitate square should result in the increase of precipitate solubility.

Similar considerations were included in well-known Ostvald-Freundlich equation.[45] For substances having 1:1 dissociation, a similar equation can be written in the following form:

$$\frac{RT}{M}\ln\frac{s_1}{s_2}=\frac{RT}{M}\ln\frac{P_1}{P_2}=\frac{\sigma}{d}\left(\frac{1}{r_2}-\frac{1}{r_1}\right) \qquad [21.3.16]$$

where:

s_1, s_2	the solubility of crystals with radii r_1 and r_2, respectively
P_1, P_2	corresponding solubility products
M	molecular weight
d	density

From this equation, it follows that the increase of crystal size reduces its solubility. Oxide particles deposited from more concentrated cation solution, should possess larger sizes due to the so-called "deposit ageing", than those obtained from mere diluted solutions. Therefore, results of Delimarsky et al.[29] obtained from 0.01 mole/kg solutions should be higher that those obtained in other works[11,33,38] using 0.05 mole/kg solutions. In the first case solubility was greater approximately by half-order of the magnitude than in second one. Oxide formed from more concentrated solution should have less surface and, hence, less solubility. Data obtained in works[11,33,38] practically coincide although we[33,38] have used NaOH as titrant similarly to other study.[29]

Sedimentational titration results in formation of fine dispersed oxide which immediately begins to age because of the recrystallization, i.e., the growth of larger crystals and disappearance of smaller ones, this process leads to the surface energy, σS, decrease. Continuous holding at high temperature and high solution concentration favors this process. In particular, samples used for isothermal saturation technique studies exposed to high temperatures for a long time, and tablets obtained are held in the contact with the melt for some hours. High concentration solutions favor transfer of substance from small to large crystals (diffusion). The differences between data in references 8 and 9 may be explained by different conditions of the powder calcination. During the annealing of the oxide sample recrystallization processes occur, which lead to the reduction of surface square of the powder and the decrease of solubility. The differences in data for KCl-NaCl are caused by the differences in crystal sizes of solid oxide being in equilibrium state with the saturated solution.

21.3.3.3 Other chloride-based melts

ZrO_2 solubilities in molten mixtures KCl-KPO_3 at 800°C have been investigated.[46] Zr^{IV} concentration in pure KPO_3 was 1.34 wt%, and in the equimolar mixture KCl-KPO_3 concentration was 3.25 wt%. A reason for solubility increase is in the depolymerization of PO^{3-} which may be schematically described by the following equation:

$$(PO_3)_n^{n-}=nPO_3^- \qquad [21.3.17]$$

and increase in acidic properties of melt. The increase of KCl molar fraction over 0.6 led to sharp reduction of ZrO_2 solubility because the decrease of acid (PO^{3-}) concentration could not be compensated by the depolymerization process [21.3.17].

Deanhardt and Stern[47,48] studied solubilities of NiO and Y_2O_3 in molten NaCl and Na_2SO_4 at 1100°C. Y_2O_3 solubility product was $(1.4\text{-}2.2)\times10^{-36}$ and $(4.5\text{-}6.4)\times10^{-31}$ in the chloride and the sulphate melt respectively. The formation of YO^{2-} was observed when oxide ion was in excess. The formation of peroxide ions in the presence of O_2 over melt was favored by thermodynamic properties. Watson and Perry[49] have studied ZnO solubility in molten KCl and found that it was 2.3×10^{-8} mole/kg for ZnO and 3.2×10^{-12} for K_2ZnO_2.

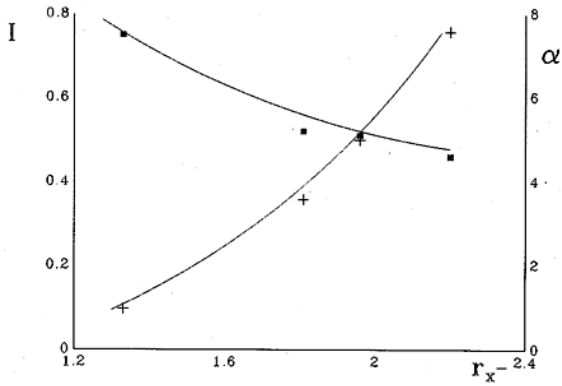

Figure 21.3.2. The formal ionic moments (I, $r_{x^-}^{-1}$, $Å^{-1}$) and polarizations (α) of halide-ions.

We have studied oxide solubilities in molten CsCl-KCl-NaCl at 600 and 700°C in order to estimate oxide solubility changes with temperature.[34-36,50] Oxide solubilities were lower than those predicted by Shreder's equation but estimations of their thermal changes usually were in a good agreement with those calculated from Shreder's equation. Oxides solubilities (in molar fractions) in KCl-NaCl and CsCl-KCl-NaCl have been found to be close at the same temperature.

Some works are related to oxo-acidity studies in alkaline chloride melts with cations of high acidity: $MgO\text{-}BaCl_2\text{-}CaCl_2\text{-}NaCl$,[37] $CaO\text{-}CaCl_2\text{-}KCl\text{-}NaCl$,[51] $CeCl_3\text{-}KCl\text{-}NaCl$,[52] ZnO-NaCl-ZnCl.[2.53,54] Acidic cations have been found to affect acid-base interactions by fixing oxide ions. Oxide solubilities[37,51] were higher than those for alkaline chloride mixtures without acidic admixtures. The same conclusions came from studies[55] on MgO solubility in $CaCl_2$-CaO mixture, $K_s=10^{-6.2}$ at 1133 K. The oxide solubility products in Ca-based chlorides are increased by 4 orders of magnitude.

Solubilities (as pP) of MgO (7,61±0,06), NiO (7,44±0,09), CoO (6,25±0,12), MnO (5,20±0,17), ZnO (4,97±0,07) and CdO (3,21±0,07) in molten eutectic $SrCl_2$-KCl-NaCl (0.22:0.42:0.36) at 700°C have been determined.[56] The precipitation of PbO from solutions containing Pb^{2+} was not observed although these cations demonstrated appreciable acidic properties (pK=2,58±0,05). The oxide solubility products in molar fractions have been increased by 1.95 orders of the magnitude for all the oxides.

A similar study was performed in two Ba-based melts: $BaCl_2$-KCl-NaCl (0.43:0.29:0.28) and $BaCl_2$-KCl (0.26:0.74) at 700°C.[57] Solubility products in molar fractions of CdO were 5.43 and 5.62, for ZnO these magnitudes were 6.97 and 7.14 in molten $BaCl_2$-KCl-NaCl and $BaCl_2$-KCl, respectively. The corresponding pP in KCl-NaCl were 2.01 and 1.83. The oxide solubility products in alkaline earth and Li-based chlorides are presented in Table 21.3.2.

Table 21.3.2. Solubility products of some oxides in melts based on moderately acidic cations at 700°C (molar fractions, at the confidence level 0.95)

Oxide/composition	KCl-LiCl[24,25]	$SrCl_2$-KCl-NaCl[56]	$BaCl_2$-KCl-NaCl[57]	$BaCl_2$-KCl[57]
	0.4:0.6	0.22:0.42:0.36	0.43:0.29:0.28	0.26:0.74
MgO	8.38±0.05	9.63±0.06	9.76±0.12	
MnO		7.32±0.17	7.38±0.06	
CoO	6.94±0.11	8.37±0.12	8.12±0.12	
NiO	7.85±0.2	9.56±0.09	9.26±0.11	
ZnO		7.09±0.07	6.97±0.1	7.11±0.1
CdO		5.33±0.07	5.43±0.2	5.62±0.2

21.3.3.4 Other alkaline halides

NiO solubility in molten KF-LiF at 550°C determined by potentiometric method is 1.3×10^{-6}.[58] This value considerably exceeds values obtained for the above chloride melts. The increase of NiO solubility occurred due to formation of fluoride complexes which are more stable than chloride ones.

Demirskaya, Cherginets and Khailova conducted oxide solubility studies in molten CsBr·2KBr[59-61] and CsI[62] at 700°C. Results are presented in Table 21.3.3. These data are useful to evaluate the effect of halide ion of melt on changes of oxide solubilities. There is a significant reduction of oxide solubility with anion exchange $Cl^- \rightarrow Br^-$, pP changes were of order of 1-2 units for all oxides studied, a degree of dissociation decreases simultaneously. Oxide solubilities in molten CsI possess intermediate values (Table 21.3.3.).

The changes of solubility in halide melts may be explained by changes of complexation abilities of halide ions. In general, the complexation ability increases together with the formal ionic moment, $r_{X^-}^{-1}$, $Å^{-1}$, and the polarization, α, $Å^3$, of anions. In the sequence $F^- > Cl^- > Br^- > I^-$ the formal ionic moments decrease and polarization increases as in Figure 21.3.2. The superimposition of these factors leads to the extremum in the bonding energy in the halide complexes, therefore, its minimum for chloride or bromide complexes should be expected. The studies[33,59-62] show that this leads to minimal solubilities in molten bromides.

Table 21.3.3. Solubility products, of some oxides in molten alkaline halides (molar fractions).[After references 33,59-62]

Oxide	CsCl-KCl-NaCl (0.45:0.25:0.30)		CsBr-KBr (0.66:0.34)	CsI
MgO	12.68±0.11	11.68±0.04	12.76±0.06	
CaO	7.73±0.05	6.86±0.13	9.93±0.06	7.50±0.14
SrO	5.81±0.40	5.54±0.13	6.82±0.12	6.28±0.30
BaO	4.75±0.10	4.50±0.20	5.16±0.30	4.98±0.15
MnO	9.73±0.15	9.49±0.14	10.70±0.04	
CoO	10.92±0.06	10.50±0.03	11.33±0.20	
NiO	12.60±0.08	11.42±0.06	12.71±0.30	

Oxide	CsCl-KCl-NaCl (0.45:0.25:0.30)		CsBr-KBr (0.66:0.34)	CsI
Cu_2O	6.95±0.10	6.35±0.05		
ZnO	8.80±0.07	8.15±0.03	11.03±0.16	
CdO	7.54±0.48	7.09±0.05	9.35±0.16	8.00±0.06
SnO	11.28±0.05			
PbO	8.21±0.05	7.04±0.05	8.52±0.07	7.80±0.10

21.3.4 ON THE POSSIBILITY TO PREDICT OXIDE SOLUBILITIES ON THE BASE OF THE EXISTING DATA

Studies[33,59-62] show that the estimation of oxide solubilities in non-studied halide melts are possible, at least, for 1:1 oxides, i.e., MeO.

21.3.4.1 The estimation of effect of anion

It has been found that oxide solubilities (pP) are related to cation radius.[33] For Na- and K-based halide melts, a plot for solubility products expressed in molar fractions is described by the following equation:

$$pP_N = pP_{N,0} + a\, r_{Me^{2+}}^{-2} \qquad [21.3.20]$$

where:

$r_{Me^{2+}}$ the cation of oxide radius, nm.

The value of a is ~0.053 and values of $pP_{N,0}$ are 1.8, 3.2 and 2.6 for chloride, bromide and iodide melts, respectively. The accurate values are presented in Table 21.3.4.

Table 21.3.4. Coefficients of plots [21.3.20] for molten alkaline halides at the confidence level 0.95. After references [38,59-62]

Melt	t, °C	$pP_{N,0}$	a
KCl-NaCl	700	1.8±0.9	0.053±0.01
CsCl-KCl-NaCl	600	1.7±2.0	0.057±0.01
CsCl-KCl-NaCl	700	1.7±0.3	0.054±0.02
CsBr-KBr	700	3.2±1.8	0.053±0.01
CsI	700	2.65±0.58	0.052±0.01

21.3.4.2 The estimation of effect of melt acidity

Papers[25,26,57,58] give us the possibility to estimate the oxide solubilities for melts with cations more acidic than Na^+. For acidic melts the following equation applies:

$$pP_N = pP_{N,KCl-NaCl} - pI_I \qquad [21.3.21]$$

where pI_I is ~3.5 for KCl-NaCl, ~2 for $SrCl_2$-KCl-NaCl, ~4 for $CaCl_2$-KCl-NaCl and ~1,8 for $BaCl_2$-KCl. If the composition of acidic cation is different from that of melts described in the previous section the value pI_I in [21.3.21] can be corrected as follows:

$$pI_{I_l} = pI_I + \log \frac{N_{Me^{n+},I_l}}{N_{Me^{n+},I}} \qquad [21.3.22]$$

where:

pN_{Me^{n+},I_l}, $N_{Me^{n+},I}$ molar fractions of the most acidic cation in non-studied and the studied melts, respectively.

21.3.4.3 The estimation of effect of temperature

The pP value obtained according the above equations can be corrected for temperature if it differs from 700°C. It has been shown that at relatively small temperature changes oxide solubility is close to value predicted by the Shreder's equation.[37] This allows one to estimate the solubility products at different temperatures using the following equation:

$$pP_{T_2} = pP_{T^*} - \frac{5.2T_{mp}(T^* - T_2)}{(T^* + T_2)} \qquad [21.3.23]$$

where:

T^*	temperature at which pP_{T^*} is known
T_2	temperature at which pP should be estimated
T_{mp}	melting point of the oxide

21.3.5 CONCLUSIONS

The existing data allow

- to estimate level of contamination of melts by oxide containing impurities
- to predict oxide solubility in molten salts having different anion composition and acidic properties

It should be emphasized, however, that there are problems which require further work:

- quantitative estimation of surface effect on oxide solubility
- the removal of oxide ion admixtures by the their conversion to oxide deposit.

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21.4 ALTERNATIVE CLEANING TECHNOLOGIES/DRYCLEANING INSTALLATIONS

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21.4.1 DRYCLEANING WITH LIQUID CARBON DIOXIDE (LCD)

21.4.1.1 Basics

The use of compressed CO_2 for dissolving oils and fats from different substrates under industrial conditions has been published in German journals since 1982 (Quirin, KW; FSA 84; 460-468).

The activity of surfactants under pressure and the formulation of reverse micelles has been published by Johnston, Lemert and McFann in Am. Chem. Soc. Ser. 406 (1989).

The structure of reverse micelle and microemulsion phases in near critical and supercritical fluid as determined from dynamic light scattering studies has been published by Johnston and Penninger in: Supercritical Fluid Science and Technology, ACS Symp. Ser. Washington DC, 1989.

The use of perfluoropolyether microemulsions in liquid and supercritical CO_2 has been published by Chittofrati, Lenti, Sanguinetti, Visca, Gambi, Senatra and Zhou in Progr. Colloid & Polym. Sci., 79, 218-225 (1989).

A process for cleaning or washing of clothing in liquid and supercritical CO_2 is the issue of the German Patent DP 39 04 514 A1 by Schollmeyer and Knittel of 23.08.1990.

CO_2 is a slightly toxic, colorless gas with a pungent, acid smell. It will not burn or support combustion. The gas is 1.4 times heavier than air and sublimes at atmospheric pressure at minus 78°C. CO_2 is not corrosive to steel, as long as it is free of water. With water it reacts to H_2CO_3, which can cause rapid corrosion to steel. Chromesteel or aluminum should be used if contact with water is unavoidable. CO_2 will react violently with strong bases, ammonia and amines.

The critical data of CO_2 are:

pressure	73.81 bar
temperature	31.3°C
volume	0,096 l
density	0.468 g/ml

Above T_{crit}, CO_2 cannot be liquefied not even under highest pressure. Above critical data substances are in supercritical condition. (Supercritical CO_2 = ScCD).

At 20°C and 55.4 bar CO_2 is liquid (LCD). The physical properties are:

density	0.77 g/ml
viscosity	0.1 mPas
surface tension	5 mN/m
solvent power	about 20 (K.B.)

LCD is a solvent for apolar substances. Its activity can be widened by combination with surfactants. Micro-emulsions in LCD can be created with different surfactants (AOT/F-Surf.) and water.

CO_2 is a natural resource, non-flammable, non-smog producing, physically stable. LCD can be stored and transported under pressure without harm. Containers must be treated

in accordance to the national regulations (in Germany Druckbehälter Verordnung certification). Tanks and/or containers for LCD have three to four times the weight of their net capacity.

21.4.1.2 State of the art

The stability of textiles, textile dyes, buttons, zips, interlinings under influence of high pressure in LCD and ScCD was tested at DTNW, Krefeld, DWI/TH Aachen. Both, LCD and ScCD, if they are pure, do not harm textiles and dyes. After treatment in ScCD buttons and plastic zips are destroyed, when the decompression of CO_2 runs fast.

LCD and ScCD are able to penetrate into apolar polymers such as polyester and polyamide, and plasticize the material so that dispersed substances can migrate into them. This behavior is used for dyeing processes with dispersion dyestuffs in ScCD, which allows textile dyeing without waste. The same procedure can cause greying in drycleaning, if resolved pigments are dispersed in LCD cleaning fluids.

In Journal of Supercritical Fluids, (1990), 3, 51-65 Consani and Smith of Battelle Pacific Northwest Laboratories report the Observation on the Solubility of Surfactants and Related Molecules in Carbon Dioxide at 50°C. Nearly all known surfactants are classified.

In US patent 5,467,492 Hughes Aircraft Company claims a dry cleaning in LCD with the distinguishing feature of a non moving basket together with jet agitation to the load by current circulation of the LCD cleaning fluid. In order to reach this aim, the pressure vessel contains a cylindrical perforated basket to take the load. After the pressure vessel is totally filled with LCD, the load is then set into motion and agitated by high velocity fluid jets. A dry cleaning machine presented at Las Vegas in 1997 was equipped with a 135 l pressure cylinder and the capability to clean a load of textiles of about 10 kg.

At the same exhibition Miccel, Technologies, Inc.; North Carolina State University presented the MiCARE Garment Cleaning Fluid System, which consists of LCD together with patented surfactants as cleaning fluid and a dry cleaning machine for LCD, equipped with a moving basket, creating agitation in the conventional manner.

In Science, Feb. 1996, E. Goldbaum published a report on the development of a team of scientists of the University of Texas, the University of Nottingham and the University of Colorado, using water in CO_2 microemulsions with fluorinated surfactants in place of conventional solvents, such as chlorinated hydrocarbons or hydrocarbons. This research was funded by a Department of Energy grant of the US.

The Research Institute Hohenstein together with other German Research Institutes and industrial Partners (Kreussler) are working on a basic research project, to define the interactions between LCD, textiles, surfactants, dissolved, emulsified and/or dispersed matter in this system.

The Dutch Research Institute TNO, Delft works together with industrial partners on a project to develop the complete background for textile cleaning in LCD under practical conditions. As part of this project Kreussler is responsible for the research and development of detergents and the cleaning process.

21.4.1.3 Process technology

Outer garments - apparel - in average of European countries contain about 15 g/kg soiling, when they are brought to dry cleaning. This “soiling” contains:

50% pigments	aerosols, carbon black, iron oxides, dust;
30% water soluble	perspiration, salt, body excrements;

10% polymers	albumin (blood, milk), starch (food);
10% solvent soluble	oils, fat, wax, grease.

The main problem in dry cleaning is the removal of pigments, water soluble material and polymers. Apolar solvents as perc, hydrocarbons or LCD are not able to achieve this.

Drycleaning detergents (DD) will widen the activity of the drycleaning process in removing pigments and polar substances. In order to gain a maximal benefit from DD, the process technology must meet the special requirements. DD's offer dispersing and emulsifying activity to solvents, they activate water additions into micro-emulsions in order to achieve removal of polar matter in apolar solvent. To optimize this action, a multi bath process is used, which works under the conditions of extraction from high to low contaminated cleaning fluids. Regeneration of cleaning fluids is realized by filtration and distillation. For filtration a drum-pump-filter-drum circuit is used. For distillation a distilling vessel, condensing equipment and clean solvent tank are necessary. The dimensions must be constructed with regard to the requirements of the quantity of removed "soil" during a full working day, which means with a 10 kg machine 750 g pigments, 600 g "salts" and polymers, 100 g oils and fats, 1000 g DD and about 10 l of water. In order to save costs, the cleaning baths are as short as possible, which means, about 3 l of solvent per kg load, so that per process one full bath can be distilled. In order to separate clean, average and high contaminated cleaning fluid, most drycleaning machines are equipped with 3 tanks, a filter and a distilling vessel with the capacity of the biggest tank.

In order to build less expensive machines, sometimes drycleaning machines are offered which are equipped with insufficient size for distilling and less than 3 tanks. In this case the possible cleaning result will not meet the necessary hygienic and esthetic requirements of customers.

The same rules apply to LCD as to conventional solvents. A one tank machine and distilling from tank to tank instead from cage to clean tank, combined with an insufficient filter size, cannot meet the minimum requirements, even if the solvent is LCD.

21.4.1.4 Risks

The solubility of water in LCD is low (0.1%); the solubility of CO_2 in water is high; at 4 bar and 20°C 1 l of water dissolves 4 l of CO_2 gas, of which about 0.1 % reacts to H_2CO_3, a corrosive substance to iron and steel.

Up to now the interaction in the system LCD, surfactants, water and textiles together with solved and dispersed contaminants has not yet been studied under practical conditions. The influence of surfactants on the equilibrium of water in the system of high pressure without airspace (free water, water in LCD emulsion, water adsorbed on textiles) is not yet known. In order to achieve the removal of polar substances from textiles, in conventional cleaning systems a desorption of moisture from textiles is necessary. If this method is compatible with LCD is not yet known.

The low risk of shrinkage on natural textiles in dry cleaning is due to the fact, that the adsorption of moisture is reduced, after fibers are soaked with apolar solvent beyond condensation conditions of water. In presence of moisture within condensation conditions natural textiles will shrink in dry cleaning more than in aqueous processes. The LCD cleaning process works completely within condensation conditions of water. This means, that LCD cleaning can bear a high risk of shrinkage, in particular, when water additions are used in order to remove apolar soiling.

The material and manufacturing costs of LCD machines are more expensive than normal drycleaning machines, and substantially more expensive than wet cleaning machines. The operating costs depend on the expenses of the distribution of LCD, which seems to need a total new network. With costs of about DM 2.50 per kg ($US 1.20/kg), LCD is more expensive than perc and similar to HCS. At the same time the consumption of LCD seems to be four times larger than perc and eight times larger than HCS. Not to mention water in wet cleaning.

Present Care Labeling considers perc, HCS and water, no LCD. If any textile damage will occur, it will be the user's responsibility.

The investment climate in drycleaning is very weak, so that there is no tendency to invest into an unknown technology.

21.4.1.5 Competition

LCD stands in competition to dry cleaning in TCE and in HCS as well as to wet cleaning.

The following comparison is done under the supposition of a capacity of 20 kg/h for investment costs and a quantity of 100 kg for consumption costs (Table 21.4.1). All costs in DEM.

The result of this comparison is very clear: most competitive is Wet Cleaning, followed by HCS dry cleaning. In order to avoid garment risks on sensitive textiles in wet cleaning, a combined installation with 70% wet cleaning and 30% HCS cleaning would be the optimum.

In order to make LCD competitive, solvent costs must be reduced rapidly and basic research work has to be done in order to increase garment safety, cleaning results and the technical reliability.

Table 21.4.1. Cost comparison of textile cleaning methods

Costs/Properties	TCE	HCS	Wet Clean	LCD
Machine	120,000.00	80,000.00	40,000.00	160,000.00
Space, m^3	2.20	2.50	1.80	5.00
Solvent	5.40	5.80	2.00	30.00
Additives	12.00	8.00	16.00	12.00
Energy	23.80	21.40	11.20	15.00
Waste	12.50	8.00	0.00	4.00
Consumables total	53.70	43.20	29.20	61.00
Reliability	good	sufficient	very good	high risk
Maintenance	good	good	very good	not known
Cleaning results	good	sufficient	very good	not known
Garment risks	low	very low	sufficient	not known
Environment	high risk	low risk	no risk	no risk

Figure 21.4.1. Miele System Kreussler washing machine and dryer.

21.4.2 WET CLEANING

The new technique results from intensive research work of Kreussler. The processing methods and in particular their translation into production-ready machine technology was developed in co-operation of Kreussler with Miele of Gütersloh.

What does this new textile cleaning system look like, what prospects does it offer, what are its limitations and how it can be integrated into the practical operations of a textile cleaning company?

21.4.2.1 Kreussler textile cleaning system

For achieving drycleaning with water it is essential to use a washing machine with at least 80 cm drum diameter, centrifugal acceleration of 0.9 g-force in the wash cycle and 450 g-force during spinning (at least 1000 rpm), appropriate drum and lifter rib design, and accurate regulation of temperature and liquor flow, as well as precise control of mechanical action and dosing.

Also necessary is a large-capacity tumble dryer, with drum at least 100 cm in diameter, having precisely controlled centrifugal acceleration; horizontally directed air flow, parallel to the drum axle; and precision electronics to regulate temperature and residual moisture level.

These requirements, comprising washer-extractor and tumble dryer together with other important know-how, are provided by the “Miele System Kreussler”.

Miele System Kreussler

The washer-extractor (Miele WS 5220 TR), with a drum volume of 220 litres, has a loading capacity of 8-10 kg for delicate outerwear, 12-15 kg of ordinary outerwear and 20-22 kg of normal textiles designated washable by the care label. The special outerwear cleaning is carried out using the LANADOL process, for which approx. 140 litres of water are used per load. Cycle time is about 25 minutes.

The dryer (Miele 6559 TR) has a drum diameter of 110 cm, with a 550 litre volume. The drying air flows through the load horizontally - parallel to the drum axle - from the rear towards the door, thus achieving optimum evaporation level with a short drying time. The necessary temperature progression and precise residual moisture is ensured with precision electronics.

A significant aspect is that not only the LANADOL process but all other wash programs can be carried out in the Miele System Kreussler machines, providing comprehensive textile cleaning facilities.

LANADOL processing technique

Most textiles offered to drycleaners for processing can be handled with three basic processes:

- Extra: Garments without wash symbol
- Normal: Garments with 30/40°C wash symbol
- Proofing: Poplin and sportswear

Figure 21.4.2. (left) Polyester/wool trousers after drying.(right) Dosing method for polyester/wool trousers after drying LANADOL AKTIV and LANADOL APRET.

Figure 21.4.3. Knitwear and silk, unfinished after drying.

Within each of these processing groups, the work should be sorted into light/medium/heavy weight, the best load combination consisting of items with the same or similar drying characteristics. It would be preferable, too, to differentiate roughly between light and dark colors.

Heavily soiled or grease stained areas should be pre-treated by simple pre-spotting with LANADOL AVANT, using PRENETT A-B-C for special staining. Where non-color-fastness is suspected, a dye-fastness check (seam test) should be made with a damp white cotton cloth.

After the relevant program is selected, the process runs fully automatically. The exact amount required of the special cleaning and fibre protection agent LANADOL AKTIV is added automatically at precisely the right time.

A fibre protection agent, providing retexturing and antistatic finish for drying, is also added automatically.

Following spin-drying, woollen textiles have a particularly low residual moisture content of about 30%. After selection of the program suitable for the

Figure 21.4.4 Down-filled anoraks and ski clothing, washed... ... and impregnated.

load make-up, the tumbler will dry to the pre-determined residual moisture level within 15 - 25 minutes.

With garments structured in several layers - such as men's jackets, ladies' suit jackets and coats - further drying at room temperature or in a drying cabinet is beneficial, before finishing on a hot air - steam garment former. All other garments can be finished normally.

21.4.2.2 Possibilities

We will not dwell here on the possibilities for processing textiles which are washable according to their care labels. On removal from the dryer, the items are quite smooth, needing little effort to finish. Treatment of washable outerwear with the LANADOL process is so problem-free, so simple and rapid, the work is so clean, bright and fresh, with such a pleasant handle and freedom from static, that one would not wish to handle this classification in any other way. One immediately realizes that conventional drycleaning would be just second best for such textiles. Customers will also come to appreciate this. Even more interesting, however, is the use of the LANADOL process for textiles which are not washable according to their care label.

According to current processing knowledge, the progression from “ideal” to “difficult” garments can be listed as follows:

Silk, knitwear, cotton, wool, viscose, linen and structured garments (jackets). “Difficult” in this context refers mainly to finishing requirements. It can be quite possible that a man’s jacket, of which the interlining has shrunk, could in addition to treatment on the garment former, need additional hand ironing for up to 10 minutes for perfect results. Usually, however, suit jackets can be processed without problems, although not particularly fast. Without doubt, men’s and ladies’ jackets can be drycleaned faster, simpler and with fewer problems. After the LANADOL process, however, they will be fresher, cleaner and nicer to wear.

Other classifications which are not indicated by the care label to be suitable for domestic washing can generally be treated without problems by the LANADOL process, with which processing risks can in most cases be assessed as less than for drycleaning.

Of special interest is treatment by the LANADOL process of textiles which are problematic for drycleaning. Down-filled anoraks, raincoats, impregnated goods - and also covers for rheumatism sufferers, bulky textiles and glittery items. The LANADOL process is

ideal for these - quick and safe with excellent results. Wet proofing is just in a class of its own. Bulky textiles without sweals, without perc residues, without peculiar odors but clean, fresh, fluffy and soft, and all after a short process demonstrate particularly well LANADOL processing's superiority for this group of classifications.

21.4.2.3 Limitations

Where there is light, there is also shadow. To evaluate the new system, coming to terms with the shadowy side is vital. There are darker aspects to the method in the high demands it places on operators and the limits, often not obvious, to its care possibilities for certain textiles.

System limits

The compromise necessary to achieve low textile shrinkage, good cleaning results and reasonable processing time implies a process-technology tightrope walk where even small deviations from the norm can lead to a fall. For this, read damaged textiles. It is essential, therefore, to adhere to all the specified parameters. This involves not only the equipment together with the types and amounts of chemicals used, but also application of the correct process for the classification to be treated. At the moment, we will not risk even a transfer of the process to other machine sizes of the same make.

Skill limits

To sort work into classifications for the appropriate process methods, personnel with knowledge of textiles gained after comprehensive training in textile cleaning are required. Furthermore, experienced finishing personnel are needed, particularly if textiles not washable according to their care labels are to be treated with the LANADOL process, even more so if jackets are to be cleaned.

Limits set by textiles

The main problem item, the jacket, has already been mentioned several times. Problems can be caused by:

- Seam shrinkage
- Interlining shrinkage
- Lining shrinkage

In most cases seam shrinkage can be remedied by expert finishing methods. Remedying shrunk interlining can be simple or very difficult. The amount of finishing work required will vary considerably, according to the adhesive and fabric construction used. Pure viscose lining material can shrink considerably in some cases. If the prescribed residual moisture level was kept to precisely during the drying process, this shrinkage can be remedied. However, if there was over-drying then recovery is frequently impossible.

If all three eventualities have occurred on the same jacket, then it is a goner. On the other hand, this really happens very rarely. The limits outlined here accurately reflect experiences to date. With wider use, the catalogue might possibly grow more extensive - but so also would the experience to deal with such problems.

21.4.2.4 Adapting to working practices

The LANADOL process is ideal to supplement an existing drycleaning process, so that one can readily envisage the proportion growing a step at a time. With increasing confidence in this processing method, soon not only those textiles which are washable according to their care label will be cleaned in water, but also more general outerwear. It is then only a question of time in a textile care company before most work will be cleaned with water and the

smaller part, comprising articles requiring more complicated treatment, will be treated with solvent.

Not ideal, but nevertheless possible, is a situation where an attractive plant location uses the LANADOL process exclusively, should local conditions prohibit use of solvent equipment or permit it only with great difficulty. In this case, with a well equipped finishing department and qualified operators, a drycleaner's complete service range is feasible, with possibly just very few exceptions.

21.4.3 FUTURE

Dry cleaning with TCR is at the end of its development. HCS dry cleaning at present is in a phase of consolidation. Wet cleaning is in its early beginnings and LCD cleaning isn't in practice yet.

TCE will probably soon be rendered a "knock out property" by its environmental behavior. Also the operating costs will increase rapidly because of more specific regulations with regard to storage and handling as well as to the waste removal of TCE. Today 80% of dry cleaning is done in TCE. Possibly more than 90% of existing TCE machines will be replaced by other systems within the next 10 years.

HCS has no probable "knock out property". Possible new developments may reduce the solvent consumption and increase the cleaning results. Because of low operating costs HCS will be the most important replacement for perc machines in the near future.

Wet Cleaning has no "knock out property". New developments will reduce the garment risks, the finishing work and the operating speed. Minimizing the water consumption is already solved technically though these technologies have not been put to use due to the low cost availability of water resources. New services to customers and the revitalization of professional textile care will move on with Wet Cleaning. Most of the new operations will be installed with wet cleaning equipment only or with a combination of wet- and HCS cleaning.

LCD bears the risk of three "knock out properties": reliability, cleaning result, and garment damage. In order to solve the problems connected with the removal of polar "soiling" and the prevention against greying on synthetic fibers and shrinking of natural fibers, a lot of basic research has to be done. Additionally a lot of developmental work has to be done in order to make LCD economically competitive to existing processes. That means not only a reduction of LCD consumption without increasing the process time and the use of energy, but also build up of a simple distribution of this solvent.