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Recent developments in thermodynamics and thermophysics of non-aqueous mixtures containing ionic liquids. A review

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Abstract

Mixtures of ionic liquids with organic solvents exhibit a most interesting research area in thermodynamics. The increasing utilization of ionic liquids in chemical processes and separation processes requires reliable and systematic data of thermodynamic and thermophysical properties such as activity coefficients, VLE and LLE data, heats of mixing as well as gas solubility data, densities and transport properties like viscosity, electric conductivity and mutual diffusion coefficients. This review presents an survey of the most recent data material including current developments and aspects of research activities needed in the future.

Keywords: Ionic liquids; Mixtures; Thermodynamic mixture properties; Transport properties; Review

1. Introduction

The term "ionic liquid" (IL) is used for a modern class of substances belonging to molten salts which consist of large organic cations like quaternary ammonium, imidazolium or pyridinium ions combined with anions of smaller size and more symmetrical shape such as Cl^-, Br^-, I^-, $AlCl_4^-$, BF_4^-, PF_6^-, $ROSO_3^-$, NTf_2^- (bis (trifluoromethylsulfonyl)imide), triflate (trifluoromethanesulfonate) and others. Many of the possible combinations of these ions exist as liquids at room temperature and below and some of them have turned out to be stable at temperatures up to 500 K.

During the last years the interest in ionic liquids has increased dramatically for several reasons.

- The most striking property of ILs is their non detectable vapour pressure. This suggests the utilization of ILs as ideal solvents replacing conventional solvents in frame of a "green chemistry".
- Due to their highly polar character caused by coulomb forces acting between the ions in the liquid state ILs open new ways for chemical reactions in homogeneous as well as biphasic catalysis including biocatalysis.
- Some of the ILs show selective solubilities for particular components in fluid mixtures. These ILs are most interesting candidates for separation processes where they could serve as extraction media.
- Other fields of possible applications are the utilisation of ILs as lubricants, thermofluids, plastizisers and electrically conductive liquids in electrochemistry.

While the majority of research work has been focussed on organic synthesis of ILs and on the study of chemical reactions in ILs systematic investigations of thermodynamic and thermophysical properties of ILs and in particular of mixtures containing ILs are still

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TABLE 1
Selection of modern inonic liquids

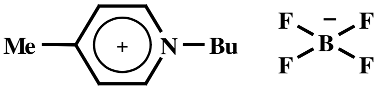
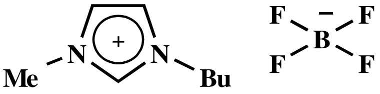
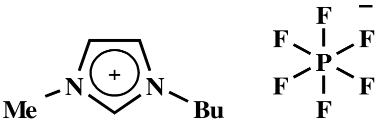
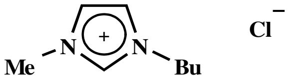
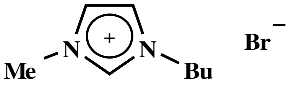
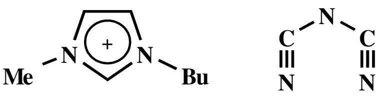
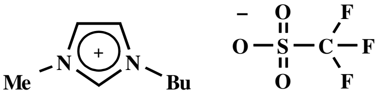
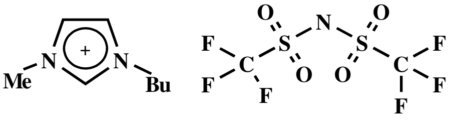
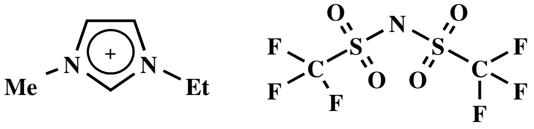
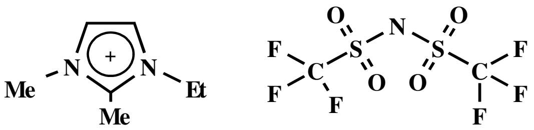
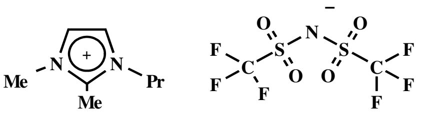
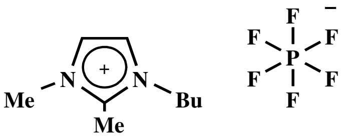
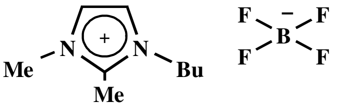
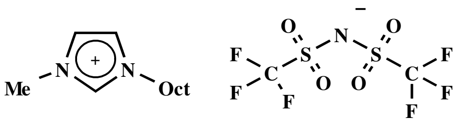
Compound	Structure	Abbreviation
4-*n*-Butyl-pyridiniumtetrafluoroborate		[4-*n*BPyr][BF_4]
1-*n*-Butyl-3-methylimidazolium tetrafluoroborate		[BMIM][BF_4]
1-*n*-Butyl-3-methylimidazolium hexafluorophosphate		[BMIM][PF6]
1-*n*-Butyl-3-methylimidazolium chloride		[BMIM][Cl]
1-*n*-Butyl-3-methylimidazolium bromide		[BMIM][Br]
1-*n*-Butyl-3-methylimidazolium dicyanamide		[BMIM][dca]
1-*n*-Butyl-3-methylimidazolium trifluoromethanesulfonate		[BMIM][triflate]
1-*n*-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide		[BMIM][NTf_2]
1-*n*-Ethyl-3-methylimidazolium- bis(trifluoromethylsulfonyl)imide		[EMIM][NTf_2]
2,3-Dimethyl-1-ethylimidazolium bis(trifluoromethylsulfonyl)imide		[EMMIM][NTf_2]

TABLE 1 (*continued*)

Compound	Structure	Abbreviation
2,3-Dimethyl-1-propylimidazolium bis(trifluoromethylsulfonyl)imide		[PMMIM][NTf$_2$]
1-*n*-Butyl-2,3-dimethylimidazolium hexafluorophosphate		[BMMIM][PF$_6$]
1-*n*-Butyl-2,3-dimethylimidazolium tetrafluoroborate		[BMMIM] [BF$_4$]
1-*n*-Octyl-3-methyl-imidazolium bis-(trifluoromethylsulfonyl)imide		[OMIM][NTf$_2$]

rare. On the other side data of these properties are of considerable importance for selecting appropriate ILs and their mixtures in different applications of chemical engineering as mentioned above.

Several articles on ILs describing general chemical aspects of their application have already been published in the literature [1–9] in particular [3] contains also valuable information on physico-chemical properties of ILs. This review summarizes the most recent developments of thermodynamic and thermophysical studies of IL + non-aqueous solvent mixtures including an overview on the data material available today. The presentation is restricted to systems which seem to have the most promising chance to be used successfully in the different fields of chemistry and chemical engineering.

The literature covering studies on the molecular structure of ILs, molecular simulation results, *ab initio* calculations of ion pairs is not discussed in this review.

Chemical structure and names of modern ILs are listed in table 1.

2. Activity coefficients in ionic liquid mixtures

Thermodynamic activity coefficients are a measure for the deviation of ideal behavior in liquid mixtures. If the pure liquid is the reference state activities a_i and corresponding activity coefficients γ_i of component i in a liquid mixture are defined by

$$a_i = x_i\gamma_i, \tag{1}$$

where x_i is the mole fraction of component i in the mixture. The dependence of γ_i on temperature is given by

$$R \cdot \left(\frac{\partial \ln \gamma_i}{\partial 1/T}\right)_p = H_i^{\mathrm{E}}, \tag{2}$$

where H_i^{E} is the partial molar excess enthalpy which is the difference of the partial molar enthalpy H_i in the solution and H_i^0, the molar enthalpy of the pure liquid component i. Often the state of infinitely diluted solution of i in the liquid system is of interest, connected with Henry's constant K_{H}:

$$K_{\mathrm{H}} = \lim_{\substack{x_i\to 0\\ p_i\to 0}} \frac{p_i}{x_i} = \varphi_{i0} \cdot p_{i0} \cdot \gamma_i^{\infty}, \tag{3}$$

γ_i^{∞} is the activity coefficient of i in the infinitely diluted solution, p_i is its partial pressure, φ_{i0} and p_{i0} are the fugacity coefficients in the gaseous phase and saturation pressure in the pure liquid state of component i, respectively. The distribution coefficient $K_{\mathrm{AB},i}$ of a solute i is defined as the limiting ratio of mole fraction $x_{\mathrm{A},i}$ and $x_{\mathrm{B},i}$ of i distributed between the two liquid phases A and B:

$$K_{\mathrm{AB},i} = \lim_{x_{\mathrm{A},i} x_B \to 0} \frac{x_{\mathrm{A}i}}{x_{\mathrm{B}i}} = \gamma_{\mathrm{B},i}^{\infty}/\gamma_{\mathrm{A},i}^{\infty}. \tag{4}$$

If phase A is the substance i or j itself in the gaseous state with partial pressures p_i or p_j in the limit $p_i, p_j \to 0$, the ideal gaseous state exists in this phase and $\gamma_{i,\mathrm{A}}^{\infty} = \gamma_{j,\mathrm{A}}^{\infty} = 1$. Then the ratio of equation (4) for i and j becomes

TABLE 2
References of γ_i^∞ of different classes of solvents in ionic liquids

Solvents ILs	C_1OH–C_6OH	Alkenes, alkynes	Chloromethanes	Acetone	Acetonitrile	MTBE	TAME	Aromatics benzene Toluene	Cyclohexane	*n*-Alkanes
[MBPy][BF_4]	[12]		[12]	[12]	[12]	[12]	[12]	[10]	[10]	[10]
[MMIM][NTf_2]								[23,18]	[23,18]	[18]
[EMIM][NTf_2]	[14,12]	[17]	[12]	[12,18]	[12]	[12]	[12]	[23,14]	[23,12]	[12,18]
[E_2MIM][NTf_2]	[18]							[12,18]		
[EMIM][$C_2H_5OSO_3$]		[18]						[23,18]	[23,18]	[18]
[BMIM][NTf_2]	[21]	[18,21]		[24]	[24]			[18]	[18]	[18,24]
[OMIM][Cl]		[14]						[13]		[13]
[N-EPyr][NTf_2]	[19]	[19]	[19]	[19]		[19]	[19]	[19]	[19]	[19]
[MMIM][$(CH_3)_2PO_4$]				[19][a]				[19]	[19]	[19]
[HPyr][$CH_3OC_2H_2SO_4$]	[19][b]							[19]	[19]	[19]
[OMIM][BF_4]	[24]	[24]						[24]		[24]
[HMIM][NTf_2]	[29]	[28]	[28]					[28]		[28]
[BMIM][Oc-O-SO_3]	[29]	[29]	[29]					[29]		[29]

[a] Contains also THF.
[b] With Butanon and Pentanon.

$$\frac{K_{AB,i}}{K_{AB,j}} = S_{ij}^\infty = \gamma_i^\infty/\gamma_j^\infty, \tag{5}$$

where γ_i^∞ and γ_j^∞ are the values of γ for i and j, respectively, in infinite dilution of i and j in the liquid phase B, *e.g.*, the ionic liquid. S_{ij}^∞ in equation (5) is called the selectivity.

Activity coefficients γ_i^∞ of organic solutes in ILs have been reported in the literature during the last years. In most cases a special technique based on the gaschromatographic determination of the solute retention time in packed or capillary columns filled with the IL as stationary phase has been used [10–16,24–30]. An alternative method is the "dilutor technique" [8,9] or the procedure to determine γ_i^∞ by extrapolating VLE data to infinite dilution [20]. A method for correlating and predicting values of γ_i^∞ in ILs and their temperature dependence using the experimental material available until 2004 has been published recently [31].

Table 2 summarizes the systems where experimental data of γ_i^∞ in ILs are available. The list contains references published until early 2005. Figures 1–3 show some typical results which are representative for the general behavior of γ_i^∞ in ILs classified into strong polar solvents (example: alcohols), polarizable non-polar solvents (example: aromatics), and inert and weakly polarizable solvents (example: saturated hydrocarbons).

Not unexpected γ_i^∞ values are small for small polar solvents indicating a considerable or complete solubility in ILs, γ_i^∞ values increase for non-polar and polarizable solvents such as benzene associated with a distinctly worse solubility in ILs compared to polar compounds. High values of γ_i^∞ and very small solubilities are found for saturated hydrocarbons which are almost insoluble in ILs. Within each of these classes γ_i^∞ increases with the chainlength of the alkylrest of the solvent reflecting the increasing non-polar character.

The most interesting effect concerning applications in separation processes is the remarkable difference in γ_i^∞

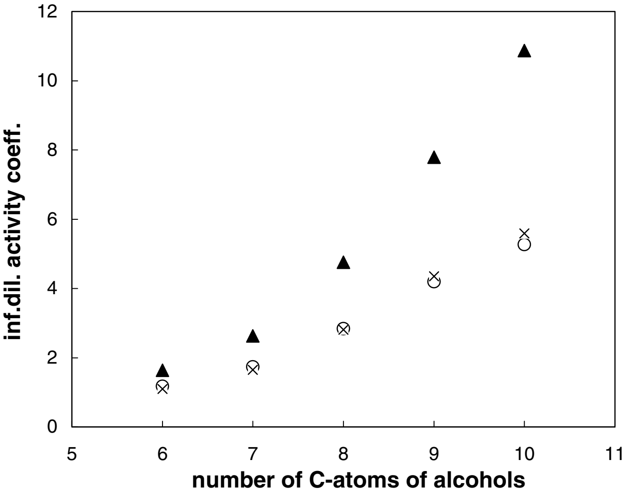


FIGURE 1. Limiting activity coefficients γ_i^∞ of methanol (1) to hexanol (6) at 313 K in ▲, [4-*n*BPyr][BF_4]; ○, [EMIM][NTf_2]; ×, [EMMIM][NTf_2].

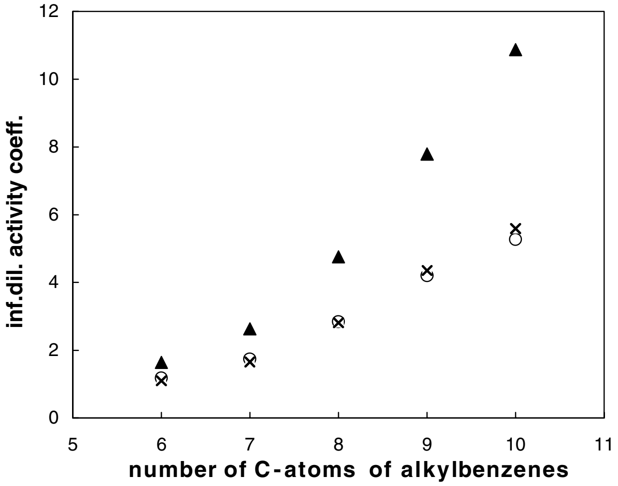


FIGURE 2. Limiting activity coefficients γ_i^∞ of benzene (6), toluene (7), ethylbenzene (8), iso-propylbenzene (9), *t*-butylbenzene (10) at 313 K in ▲, [4-*n*BPyr][BF_4]; ○, [EMIM][NTf_2]; ×, [EMMIM][NTf_2].

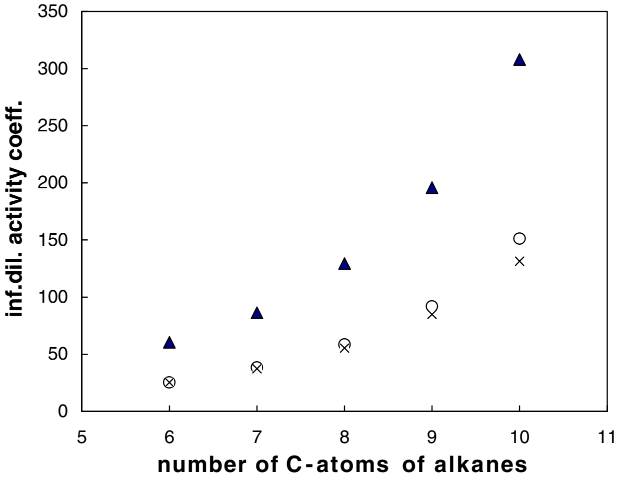


FIGURE 3. Limiting activity coefficients γ_i^∞ of *n*-hexane (6) to *n*-decane (10) at 313 K in ▲, [4-*n*BPyr][BF$_4$]; ○, [EMIM][NTf$_2$]; ×, [EMMIM][NTf$_2$].

values between aromatic and aliphatic compounds. The low solubility of saturated hydrocarbons compared to aromatics suggests the idea to use ILs as extraction solvents for separating mixtures of aromatic and aliphatic components. Applications for patents exist already in the literature [32].

A suitable measure for the separation potential of an IL is the selectivity S_{ij}^∞ defined by equation (5). Some results for the key system hexane + benzene are presented in table 3 for a series of ILs in comparison with three conventional extraction fluids. The data show, that some of the ILs even exceed the selectivity of the best conventional extraction liquid sulfolane. With respect to the non detectable vapour pressure of the ILs this result indicates the possible superiority of ILs serving as effective extraction fluids for separating aromatic/aliphatic mixtures.

TABLE 3
Selectivities S_{ij}^∞ at infinite dilution of various solvents for the hexane/benzene separation ($S_{ij}^\infty = \gamma_i^\infty/\gamma_j^{\infty a}$ at 298.15 K)

Solvent	S_{ij}^∞
Sulfolane	30.5
Dimethylsulfoxide	22.7
N-Methyl-2-pyrrolidinone	12.5
[HMIM][PF$_6$]	21.6
[HMIM][BF$_4$]	23.1
[OMIM][Cl]	8.7
[EMIM][EtOSO$_3$]	41.4
[EMIM][(CF$_3$SO$_2$)$_2$N]	24.4
[BMIM][(CF$_3$SO$_2$)$_2$N]	16.7
[BMIM][MDEGSO$_4$]	39.7
[BMIM][OcOSO$_3$]	5.1

[a] From [29].

TABLE 4
Limiting partial molar excess enthalpies $H_i^{E\infty}$ of organic solutes obtained calorimetrically and by gas-liquid chromatography (GC) at 298 K in [EMIM][NTf$_2$]

Solute	$H_i^{E\infty}$/J mol^{-1}	
	Calorimetric	From γ_i^∞ (GC)
Methanol	5639 ± 50	7787
t-Butanol	7039 ± 50	7240
1-Hexanol	10076 ± 600	10812
Chloroform	−3255 ± 20	−1722
Toluene	−1018 ± 10	−684

The majority of systems listed in table 2 has been studied at different temperatures in the range of 298 K to 353 K and equation (2) has been used to derive partial molar excess enthalpies $H_i^{E,\infty}$ from the temperature dependence of γ_i^∞. However, comparison with directly measured values of $H_i^{E,\infty}$ using precision calorimetry [33] reveals, that the agreement is not always completely satisfying as shown in table 4. This indicates limitations of the indirect method which arise mainly from the small slope of $\ln\gamma_i^\infty$ *vs.* $1/T$ plots. Therefore experimental errors of the gaschromatographic or dilutor method should not be underestimated.

First systematic attempts for describing and predicting γ_i^∞ of solutes in ILs on a molecular basis have been performed using the COSMO-RS model [34]. 38 solutes + IL systems have been investigated by comparing predicted values of γ_i^∞ with experimental data taken from [10–12]. The results look promising, in some cases, however, distinct deviations from experimental results have also been observed. A certain problem using COSMO-RS in ionic systems is the fact, that this theory does not describe the Debye–Hückel limiting law.

Data of activity coefficients covering the whole range of liquid composition of IL + organic mixtures have been reported in the literature more recently obtained from VLE data using a static measuring technique. VLE data of the ILs [EMIM][NTf$_2$], [BMIM][NTf$_2$], [EMIM][C$_2$H$_5$OSO$_3$] and [PyrH][C$_2$H$_5$OC$_2$H$_4$OSO$_3$] mixed with cyclohexane, cyclohexene, benzene and toluene show strong positive deviations of vapor pressures from the ideal behavior and (liquid + liquid) immiscibility gaps have been found in all cases in the temperature range 303 to 353 K [23]. In contrast to these data mixtures of [BMIM][NTf$_2$] + alcohols (methanol, ethanol, propanol) are completely miscible and the evaluation of experimental VLE data even show values of γ_i below unity for the methanol system at lower mole fractions of methanol [20]. VLE of mixtures containing low volatile solvents and ILs are difficult to study due to the low vapor pressures of these mixtures. VLE data have been obtained using the transpiration technique which has proved to give reliable results in such cases where the vapor pressure of the mixture does not exceed (200 to 300) Pa. [EMIM][NTf$_2$] mixed with higher aldehydes, ketones, ethers and diols have been studied using this method [21,22]. All these low volatile polar solvents are completely miscible with [BMIM][NTf_2] at temperatures above 298 K.

VLE of [BMIM][Br] and [BMIM][BF_4] + trifluoroethanol (TFE) binary mixtures have also been studied [25]. Strong negative deviations from ideality have been observed with activity coefficients $\gamma_{TFE} < 1$.

The first ternary systems for which VLE have been measured are the mixtures [EMIM] [NTf_2] + acetone + 2-propanol, and [EMIM][NTf_2] + 2-propanol + water as well as [BMIM][NTf_2] + acetone + 2-propanol, and [BMIM][NTf_2] + 2-propanol + water [26].

3. (Liquid + liquid) and (solid + liquid) equilibria

The literature reporting on LLE containing ILs has increased recently and some of these data allow to construct a certain pattern how parameters of the chemical structure of ILs can possibly be correlated with properties of the solvent such as molecular size and polarity. Beside of the study of LLE of [BMIM][PF_6], [BMIM][BF_4] [35–38] and [EMIM][PF_6] [36] mixed with water, non-aqueous systems investigated contain in most cases alcohols. Binary systems studied are: [EMIM][NTf_2] + propan-1-ol, +butan-1-ol, +pentan-1-ol [39], [RMIM][PF_6] + butan-1-ol with R = butyl, pentyl, hexyl, heptyl and octyl [40], [BMIM][NTf_2] + 2-methylpropanol [41], [HMIM][BF_4] + propan-1-ol, +butan-1-ol, +butan-2-ol, +pentan-1-ol, +pentan-2-ol, +hexan-1-ol [42,43],[EMIM][NTf_2] + propan-1-ol, +butan-1-ol, +pentan-1-ol and [BMIM][NTf_2] + cyclohexanol [44], [EMIM][PF_6] + different alcohols [45], [OMIM][BF_4] + butan-1-ol, +pentan-1-ol [46].

A certain systematics of the LLE behavior of IL + alcohol mixtures has already been discussed in ref [48] where also new data of LLE are reported for the systems [BMIM][BF_4] + propanol, +butanol, +hexanol including isomeric alcohols, [BMIM][NTf_2] + butan-1-ol, +hexan-1-ol, [HMIM][BF_4] + octan-1-ol and [BMIM][triflate] + dodecan-1-ol. An analysis including the most recent results is illustrated in figure 4.

All mixtures with alcohols show an upper critical solution temperature (UCST), which depends in systematic way on (i) the chainlength of the alkylgroup of the imidazolium cation (ii) the chainlength of the alcohol and (iii) the kind of anion. In figure 4 the UCST is plotted *vs.* the chainlength of the alcohols for different types of ILs. The critical composition w_c (mass fraction) is not a suitable measure for the characterization since the critical region of the LLE coexistence curve is usually flat and correct values of w_c are difficult to determine precisely enough. figure 4 reveals: (i) decreasing values of the UCST with the chainlength of IL at given alcohol and kind of anion, (ii) increasing values of UCST with the carbon number of alcohols and fixed anion in the IL at fixed alkylchain decreasing UCST in the order of anion [PF_6] > [BF_4] > [NTf_2] at fixed type of imidazolium cation.

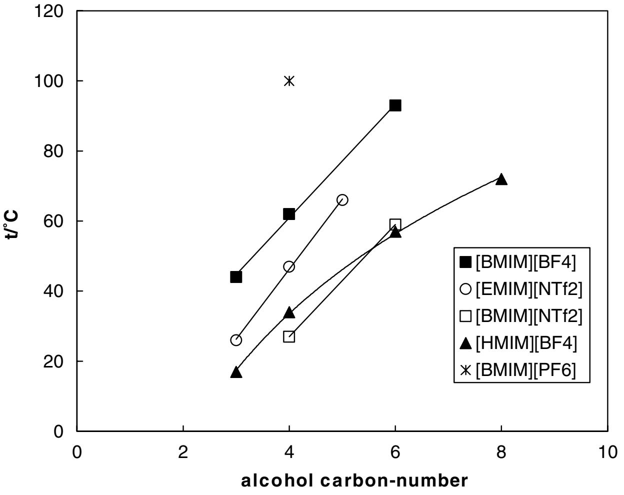


FIGURE 4. Upper critical solution temperatures (UCST) in (liquid + liquid) equilibria of alcohol + IL mixtures *vs.* the carbon number of linear alcohols.

The presentation in figure 4 allows to make tentative predictions of UCST-values for systems which have not been studied experimentally. For example, the UCST is ca. 80 °C for [EMIM][NTf_2] + hexanol, the UCST is ca. 43 °C for [BMIM][NTf_2] + pentanol.

In a comprehensive study binary LLE data of the ILs [1-hexyl-oxymethyl-MIM][BF_4] and [1-hexyl-oxymethyl-MIM][NTf_2] each mixed with aliphatic hydrocarbons (C_5 to C_8), aromatics (benzene, toluene, ethylbenzene, xylenes) have been published just recently [47]. These results indicate, that mixing gaps are broader and higher than those observed with alcohols and in most cases the UCST cannot be determined directly. For example, the experimentally determined UCST of the mixture [$C_6H_{13}OCH_2MIM$][NTf_2] + benzene is 352 K while the system [$C_6H_{13}OCH_2MIM$][BF_4] + benzene has an UCST of approximately 644 K estimated from fitting the NRTL equation to LLE data at lower temperatures. UCST points of alkanes are still higher. Typical for IL + hydrocarbon mixtures is the assymmetric shape of the mixing gap. At ambient conditions the solubility of the IL in the hydrocarbon phase *i* close to zero ($w'_{IL} \approx 0$) while the phase rich in IL contains considerable amounts of hydrocarbons. The situation resembles that of IL + CO_2 systems (see next section). Solubilities are higher for aromatics than for saturated hydrocarbons. Similar results have been obtained from VLE data of imidazolium based ILs + hydrocarbons where mixing gaps could be determined quantitatively detected by the pressure independence of the total liquid composition inside the gap [20–23].

Ternary LLE systems consisting of volatile solvents and an ionic liquid have been studied the first time for the system [EMIM][I_3] + toluene + heptane and [BMIM][I_3] + toluene + heptane [49] focussing on the use of ionic liquids for extracting aromatic hydrocarbons from mixtures of aromatic and aliphatic hydrocarbons. High separation factors in the range 50 to 100 according to equation (4) have been observed reflecting the preferred solubility of toluene in the IL phase. LLE of the ternary systems 1-hexene + ethanol + [HMIM]-[PF_6] or [HMIM][BF_4] have also been studied indicating that these ILs are suitable solvents for the (liquid + liquid) extraction of ethanol from olefines [50]. The problem of separating ethanol from ethers in ether synthesis reactions has been treated by using ILs as extraction fluid and it has been found that [BMIM][CF_3OSO_3] is a suitable agent for that purpose as the ternary LLE data of this IL with ethanol + *t*-amylethylether (TAME) indicate [51].

Experimental data on (solid + liquid) equilibria (SLE) of mixtures containing ILs also exist in the literature and have been studied in a systematic way with [C_{12} MIM][Cl] [52]. Solubilities of this IL in alcohols (C_2 to C_{12}) decrease with the increase of molecular weight starting from hexanol. For the lower alcohols the dependence on the carbon number is not significant. Eutectic points have been observed for mixtures with *t*-butanol, 1-decanol and 1-dodecanol and the data have been correlated with the Wilson, UNIQUAC-ASM and NRTL1 equations [53].

4. Gas solubilities in ionic liquids

So far most attention has been paid to the solubility of CO_2 in ILs. First systematic investigations have been carried out with CO_2 + [BMIM][PF_6][54], +[OMIM][PF_6], +[OMIM][BF_4] and +[BMIM]-[NO_3][55]. The phase behavior of these binary systems is quite unusual. Large amounts of CO_2 are soluble in these ILs at moderate pressures. The mole fraction of CO_2 in the mixture x_{CO_2} reaches 0.7 at 100 bar, above this pressure, however, the solubility can be enhanced only insignificantly by applying substantially higher pressures. Most striking is the fact, that the compressed gaseous phase contains no detectable traces of dissolved IL in CO_2. As a consequence the two phase region is extended on the CO_2 rich side of the phase diagram to high pressures without indication of a mixture critical point. This behavior seems to be the rule with IL + CO_2 mixtures and has been confirmed by a series of detailed studies of the systems [EMIM][PF_6] + CO_2 [56], [HMIM][BF_4] + CO_2 [57], [EMIM][BF_4] + CO_2 [58] and [HMIM][BF_4] + CO_2 [59] at pressures up to 900 bar. As an example figure 5 shows results taken from [58]. The solubility curve resembles an adsorption process of CO_2 molecules at some kind of "inner surface" of the IL rather than a solution process as expected for normal systems where the solubility of the gas is smaller at lower pressure and increases with higher pressures leading to an opposite curvature as observed for CO_2 + IL systems. It is demonstrated in figure 5, that the solubility curve of CO_2 in ILs can indeed be fitted well by a simple Langmuir adsorption isotherm

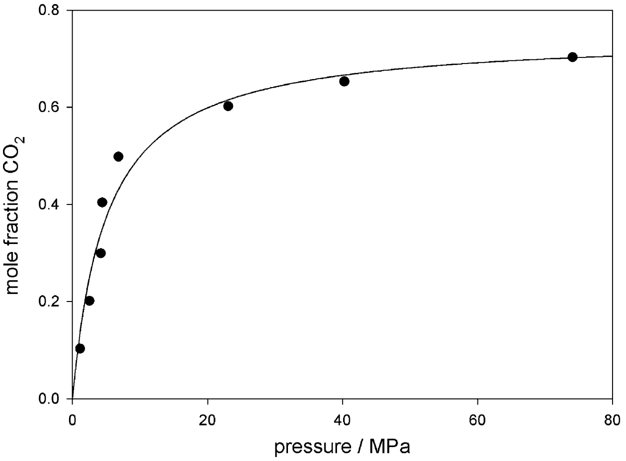


FIGURE 5. Solubility of CO_2 in [HMIM][BF_4] at $T = 330$ K as function of pressure experiments from [58], — equation (6) with $a = 0.7497$ MPa and $b = 5.044$ MPa.

$$x_{CO_2} = \frac{a \cdot p}{b + p}. \tag{6}$$

Other experimental isotherms available in the literature [54–59] can be described by equation (6) with comparable quality [60]. An alternative approach using an irregular ionic lattice model for CO_2 solubilities in ILs has recently been suggested [61] and is based on similar assumptions as discussed here. The interpretation agrees with molecular simulation results [62], where it has been suggested, that the CO_2 molecule is preferably attached to the anion (PF_6, BF_4 and especially NTf_2) localized possibly in the free volume space between the large cations. This is also in agreement with the remarkable fact, that the volume of the absorbing IL-phase increases only moderately with respect to the pure IL even though the mixture contains more than double as much CO_2 than IL molecules [54,55]. Experiments using an interesting, completely different technique has lead to similar results [63]. Light absorption of solvatochromic dyes attached preferentially to the IL molecules decreases when the pressure and the mole fraction of CO_2 in the IL phase increases due to the dilution of the dye in the expanding system. The spectroscopic results indicate clearly that in case of [BMIM][PF_6] + CO_2 the volume expands only by 30% to 40% at 250 bar while the mole fraction of CO_2 exceeds 0.7.

Several authors also report that the viscosity of the ILs studied decreases dramatically with increasing mole fraction of CO_2 and increasing pressure [64,65]. The CO_2 molecules seem to act as a kind of lubricant between the ions of the IL. This effect and the fact that no IL is dissolved in the compressed CO_2 phase is of large importance for technical application in separation processes. Already in an early state of thermodynamic investigations on ILs it has been suggested to use ILs as non-volatile solvents for extracting and recovering substances of environmental, pharmaceutical or other significant importance using supercritical CO_2 [54,65]. Solubility of other gases including CO_2 in ILs have also been measured at different temperatures in the pressure range up to 13 bar or close to ambient pressures and it turned out that C_2H_4, C_2H_6, CH_4, Ar in [BMIM][PF_6] are distinctly less soluble than CO_2 [66]. Similar results obtained in [BMIM][PF_6] at pressures up to 97 bar have been reported [67]. Henry's constants of CO_2 and O_2 in [BMIM][BF_4] have determined at atmospheric pressure [68].

In order to test a modified regular solution theory for describing gas solubilities values of Henry's constants of CO_2 and C_2H_4 have also been determined at 303 K in [EMIM][NTf_2], [EMIM][CF_3SO_3], [EMIM][dca], [BMIM][PF_6] [69,70].

The considerable difference in the solubilities of gases in ILs suggest to use ILs as supported liquid membranes in gas separation or pervaporation processes [71]. The physico-chemical basis of treating such processes in frame of simple or more extended versions of the solution diffusion model is described, *e.g.*, in [72].

5. Densities, transport properties and critical phenomena

There exists a considerable amount of density data of pure ILs in the literature. Densities of [BMIM][PF_6], [OMIM][PF_6], [OMIM][BF_4] and [NBuPy][BF_4] have been obtained in the pressure range 1 bar to 2070 bar at temperatures between 298 K and 343 K from which thermal expansivities and isothermal compressibilities have been derived [73]. Densities of 13 further ILs have been measured at ambient pressure in the temperature range 293 K to 360 K [74]. Compared to this considerable information on PVT-properties of pure ILs the situation for mixtures containing ILs is less satisfying. Beside of some systematic work done on IL + CO_2 mixtures mentioned already above [54,55], there exist very few reliable data of liquid densities or excess volumes V^E in the literature. Data of densities and V^E of [BMIM][BF_4] + H_2O at 313 K and 353 K are reported in [75]. V^E is positive over the whole range of composition. [4-Methyl-*N*-butyl-pyridinium][BF_4] + methanol has also been studied [76] and negative V^E-values have been obtained, *e.g.*, V^E is -0.8 cm^3/mol at a weight fraction of 0.4 of methanol at 323 K. Densities with positive excess volumes for the binary system [EMIM][BF_4] + H_2O are reported, *e.g.*, $V^E = +0.21$ at $x_{H_2O} = 0.5$ and 298 K [77] and interestingly V^E increases with temperature for this system. [OMIM][BF_4] + butan-1-ol shows a S-shaped V^E curve, V^E is positive at $x_{\text{butanol}} < 0.5$ and negative at $x_{\text{butanol}} > 0.5$ [46]. [OMIM][BF_4] + 1-pentanol behaves similarly but the region $V^E < 0$ is restricted to $0.85 < x_{\text{pentanol}} < 1$ [46]. Apparent molar volumens of the IL [EMIM][CH_3 CH_2-O-SO_3] in aqueous solution have been measured from which partial molar volumens $\bar{V}_{IL}$ are derived [78]. Decreasing values of $\bar{V}_{IL}$ with increasing concentration in water, *e.g.*, from $\bar{V}_{IL} = 192.9\ \text{cm}^3 \cdot \text{mol}^{-1}$ at $0.2224\ \text{mol} \cdot \text{kg}^{-1}$ to $\bar{V}_{IL} = 189.3\ \text{cm}^3 \cdot \text{mol}^{-1}$ at $3.044\ \text{mol} \cdot \text{kg}^{-1}$ and 298 K, indicate also positive excess volume for this IL + H_2O system.

It is difficult to draw general conclusions from the scarce results of excess volumens of IL + solvent mixtures available in the literature. It seems that aqueous solutions of ILs have positive excess volumens while mixtures with ILs with polar organic compounds show a tendency to exhibit negative V^E values. Whether there is any regular pattern of this kind of behavior in IL mixtures requires more and systematic measurements of densities of IL + solvent mixtures.

Transport properties play an important role in chemical reaction processes and separation problems. This concerns in the first place the viscosity coefficient and the mutual diffusion coefficient in mixtures. While there exist quite extensive data material for the viscosity of pure ILs [79] it is surprising, that viscosity measurements in IL + solvent mixtures are rarely available in the literature and data of mutual diffusion coefficients seem to exist only for the system [BMIM][PF_6] + methanol until now [80]. First reliable data of viscosities of IL + solvent mixtures have not been published before 1996. The mixture [EMIM][$AlCl_4$] + benzene was studied showing the typical steep decrease of viscosity with increasing concentration of the solvent [81]. Other authors [75] reported results of the viscosity of [BMIM][BF_4] + H_2O where a remarkable decrease of η from ca. 150 mPa s in the pure IL to ca. 18 mPa s in a mixture containing 10 weight percent H_2O was observed. Similar results have been obtained for the system [4-methyl-butyl-pyridinium][BF_4] + methanol where the observed values for η are ca. 100 mPa s for the pure IL and ca. 10 mPa s at ca. 10 weight percent of methanol in the mixture [76]. At higher concentrations of H_2O or methanol the change in viscosity is much less dramatic. Viscosities of the binary mixtures of [Allyl MIM][Cl] with water and ethanol have recently been published [82].

Further binary systems where viscosity data are available are: [BMIM][BF_4] with acetonitrile, dichloromethane, 2-butanone, N,N-dimethylformamide [83]. Also viscosity data of the ternary system [BMIM][PF_6] + H_2O + acetone are available [84]. No principal new aspects of the behavior of viscosities in IL + organic solvent mixtures have been discovered in these studies.

Most interesting for applications in electrochemistry are data of electrical conductivities of IL + solvent mixtures. For pure Alkylimidazolium salts electric conductivities have been measured as function of temperature [84–88], also some data on mixtures can be found in the literature [82–84,87]. The first study on mixtures of $[NBu_4][PF_6]$ in acetone, acetonitrile, dichloromethane was published in 2001 [89]. The typical result of these investigation is an increase of the electrical conductivity with the concentration of the solvent due to the strongly decreasing viscosity [87]. Only at lower concentrations of the IL the electrical conductivity passes a maximum reaching finally low values due to the lower concentration of the charge carrying ions.

Heat conductivity and heat capacity measurements exist only for pure ILs so far and have been performed with respect to possible applications of ILs as heat transfer fluids [90,91].

A review on thermodynamics of ionic liquid mixtures should include the interesting phenomena occuring close to the (liquid + liquid) critical point of ionic solutions. The Ising like behavior observed usually at critical points of non electrolyte mixtures seems to overlap in case of ionic systems with a mean field behavior concerning critical exponents close to the critical point [92,93]. This unusual phenomenon can best be studied under convenient conditions with IL + solvent mixtures exhibiting an UCST point close to room temperature and ambient pressure and has recently stimulated experimental as well as theoretical work on criticality of ionic liquids in mixtures [94,95].

6. Conclusions

The increasing interest in ionic liquids has lead to more research activities concerning thermodynamic and thermophysical properties of mixtures containing ionic liquids during the last few years. While data on activity coefficients, VLE and LLE date are now available for a number of binary and a few ternary systems, the situation is still not satisfying with respect of a systematic knowledge of these properties and further research work has to fill the remaining gaps. More results of gas solubilities at ambient and elevated pressures are also desirable due to the promising possibilities of supercritical extraction processes using ionic liquids. Two task groups sponsored by the IUPAC have now been established to improve the situation working on a data collection project and initiating experimental work on key systems of IL + solvent mixtures.

In spite of their practical importance there is a considerable lack of data on transport properties in IL + solvent mixtures such as viscosity, heat and electrical conductivity, and diffusion coefficients. Data of other properties like surface and interphase tension are completely missing and deserve much more attention in future research projects.

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References

[1] T. Welton, Chem. Rev. 99 (1999) 2071.
[2] P. Wasserscheid, W. Keim, Angew. Chem. Int. Ed. 39 (2000) 3772.
[3] P. Wasserscheid, T. Welton (Eds.), Ionic Liquids in Synthesis, Wiley-VCH, Weinheim, 2003.
[4] Hua Zhao, Phys. Chem. Liq. 41 (2003) 545.
[5] F. Endres, J. Phys. Chem 218 (2004) 255.
[6] K.N. Marsh, J.A. Boxall, R.N. Lichtenthaler, Fluid Phase Equilib. 219 (2004) 93.
[7] R.D. Rogers, K.R. Seddon (Eds.), Ionic Liquids: Industrial Application for Green Chemistry, ACS Symposium Series 818, American Chemical Society, Washington DC, 2002.
[8] R.D. Rogers, K.R. Seddon (Eds.), Ionic Liquids as Green Solvents: Progress and Prospects, ACS Symposium Series 856, American Chemical Society, Washington DC, 2003.
[9] K.N. Marsh, A. Deev, A.C. Wu, E. Trau, A. Klamt, Korean J. Chem. Eng. 47 (2002) 357–362.
[10] A. Heintz, D.V. Kulikov, S.P. Verevkin, J. Chem. Eng. Data 46 (2001) 1526–1529.
[11] A. Heintz, D.V. Kulikov, S.P. Verevkin, J. Chem. Eng. Data 47 (2002) 894–899.
[12] A. Heintz, D.V. Kulikov, S.P. Verevkin, J. Chem. Thermodyn. 34 (2002) 1341–1347.
[13] A. Heintz, J.K. Lehmann, S.P. Verevkin, in: R.D. Rogers, K.R. Seddon (Eds.), Ionic Liquids as Green Solvents: Progress and Prospects, ACS Symposium Series 856, American Chemical Society, Washington DC, 2002, pp. 134–150 (Chapter 12).
[14] W. David, T.M. Letcher, D. Ramjugernath, J.P. Raal, J. Chem. Thermodyn. 35 (2003) 1335–1341.
[15] T.M. Letcher, N. Deenadayalu, B. Soko, D. Ramjugernath, A. Nevines, P.K. Naicker, J. Chem. Eng. Data 48 (2003) 708–711.
[16] T.M. Letcher, B. Soko, P. Reddy, N. Deenadayalu, J. Chem. Eng. Data 48 (2003) 1587–1590.
[17] N. Deenadayalu, T.M. Letcher, P. Reddy, J. Chem. Eng. Data 50 (2005) 105–108.
[18] M. Krummen, P. Wasserscheid, J. Gmehling, J. Chem. Eng. Data 47 (2002) 1411–1417.
[19] R. Kato, J. Gmehling, Fluid Phase Equilib. 226 (2004) 37–44.
[20] S.P. Verevkin, J. Safarov, E. Bich, E. Hassel, A. Heintz, Fluid Phase Equil. (2005) in press.
[21] T.V. Vasiltsova, S.P. Verevkin, E. Bich, A. Heintz, R. Lukasik, U. Domanska, J. Chem. Eng. Data 50 (2005) 142–148.
[22] S.P. Verevkin, T.V. Vasiltsova, E. Bich, A. Heintz, Fluid Phase Equilib. 218 (2004) 165–175.
[23] R. Kato, M. Krummen, J. Gmehling, Fluid Phase Equilib. 224 (2004) 47–54.
[24] A. Heintz, L. Marinez Casás, I.A. Nesterov, V.N. Emel'yanenko, S.P. Verevkin, J. Chem. Eng. Data (2005) in press.

[25] K.S. Kim, B.K. Shin, H. Lee, F. Ziegler, Fluid Phase Equilib. 218 (2004) 215–220.
[26] M. Döker, J. Gmehling, Fluid Phase Equilib. 227 (2005) 255–266.
[27] A. Heintz, S.P. Verevkin, J. Chem. Eng. Data (2005) in press.
[28] T.M. Letcher, A. Marciniak, M. Marciniak, U. Domanska, J. Chem. Thermodyn., in press.
[29] T.M. Letcher, A. Marciniak, M. Marciniak, U. Domanska, J. Chem. Eng. Data, in press.
[30] A. Heintz, S.P. Verevkin, J. Chem. Eng. Data (2005), in press.
[31] D.M. Eike, J.F. Brennecke, E.J. Maginn, Ind. Eng. Chem. Res. 43 (2004) 1039–1048.
[32] J. Gmehling, M. Krummen, DE Patent, 2001 – 10154052.
[33] W. Marczak, S.P. Verevkin, A. Heintz, J. Sol. Chem. 32 (2003) 519–526.
[34] M. Diedenhofen, F. Eckert, A. Klamt, J. Chem. Eng. Data 48 (2003) 475–479.
[35] J.L. Anthony, E.J. Maginn, J.F. Brennecke, J. Phys. Chem. 105 (2001) 10942–10949.
[36] D.S.H. Wong, J.P. Chen, J.M. Chang, C.H. Chou, Fluid Phase Equilib. 194–197 (2002) 1089–1095.
[37] L.P.N. Rebelo, V. Najdanovic-Visak, Z.P. Visak, M. Nunes da Ponte, J. Szydlowski, C.A. Cordeiriña, J. Troncoso, L. Romani, J.M.S.S. Esperanca, H.J.R. Guedes, H.C. de Sousa, Green Chem. 6 (2004) 369–381.
[38] V. Najdanovic-Visak, J.M.S.S. Esperanca, L.P.N. Rebelo, M. Nunes da Ponte, H.J.R. Guedes, K.R. Seddon, J. Szydlowski, Phys. Chem. Chem. Phys. 4 (2002) 1701–1703.
[39] A. Heintz, J.K. Lehmann, C. Wertz, J. Chem. Eng. Data 48 (2003) 472–474.
[40] C.T. Wu, K.N. Marsh, A.V. Deev, J.A. Boxall, J. Chem. Eng. Data 48 (2003) 486–491.
[41] V. Najdanovic-Visak, J.M.S.S. Esperanca, L.P.N. Rebelo, M. Nunes da Ponte, H.J.R. Guedes, K.R. Seddon, H.C. de Sousa, J. Szydlowski, J. Phys. Chem. B 107 (2003) 12797–12807.
[42] M. Wagner, O. Stanga, W. Schröer, Phys. Chem. Chem. Phys. 5 (2003) 3943–3950.
[43] M. Wagner, O. Stanga, W. Schröer, Phys. Chem. Chem. Phys. 6 (2004) 4421–4431.
[44] A. Heintz, J.K. Lehmann, C. Wertz, J. Jacquemin, J. Chem. Eng. Data (2005) in press.
[45] U. Domanska, A. Marciniak, J. Phys. Chem. B 108 (16) (2004) 5113–5119.
[46] A. Heintz, D. Klasen, J.K. Lehmann, C. Wertz, J. Sol. Chem. (2005) in press.
[47] U. Domanska, A. Marciniak, J. Chem. Thermodyn. (2005) in press.
[48] J.M. Crosthwaite, S.N.V.K. Aki, E.J. Maginn, J.F. Brennecke, J. Phys. Chem. 108 (16) (2004) 5113–5119.
[49] M.S. Selvan, M.D. McKinley, R.H. Dubois, J.L. Atwood, J. Chem. Eng. Data 45 (2000) 841–845.
[50] T.M. Letcher, P. Reddy, Fluid Phase Equilib. 219 (2004) 107–112.
[51] A. Arce, O. Rodriguez, A. Soto, Ind. Eng. Res. 43 (26) (2004) 8323–8327.
[52] U. Domanska, E. Bogel-Lukasik, R. Bogel-Lukasik, J. Phys. Chem. B 107 (2003) 1858–1863.
[53] U. Domanska, E. Bogel-Lukasik, Ind. Eng. Chem. Res. 42 (2003) 6986–6992.
[54] L.A. Blanchard, D. Hancu, E.J. Beckman, J.F. Brennecke, Nature 28 (1999) 399.
[55] L.A. Blanchard, Z. Gu, J.F. Brennecke, J. Phys. Chem. B 105 (2001) 2437–2444.
[56] A. Shariati, C.J. Peters, Supercrit. Fluids 25 (2003) 43–48.
[57] A. Shariati, C.J. Peters, Supercrit. Fluids 30 (2004) 139–144.
[58] M. Costantini, V.A. Toussaint, A. Shariati, C.J. Peters, I. Kikic, J. Chem. Eng. Data 50 (2005) 52–55.
[59] M.C. Kroon, A. Shariati, M. Costantini, J. van Spronsen, G.J. Witkamp, R.A. Sheldon, C.J. Peters, J. Chem. Eng. Data 50 (2005) 173–176.
[60] A. Heintz and E. Bich, unpublished results.
[61] M.R. Ally, J. Braunstein, R.E. Baltus, S. Dai, D.W. DePaoli, J.M. Simonson, Ind. Eng. Chem. Res. 43 (2004) 1296–1301.
[62] C. Cardena, J.L. Anthony, J.K. Shah, T.I. Morrow, J.F. Brennecke, E.J. Maginn, J. Am. Chem. Soc. 126 (2004) 5300–5308.
[63] J. Lu, C.L. Liotta, C.A. Eckert, J. Phys. Chem. A 107 (2003) 3995–4000.
[64] Z. Liu, W. Wu, B. Han, Z. Dong, G. Zhao, J. Wang, T. Jiang, G. Yang, Chem. Eur. J. 9 (2003) 3897–3903.
[65] L. Blanchard, J.F. Brennecke, Ind. Chem. Res. 40 (2001 /sb:date> 287–292.
[66] J.L. Anthony, E.J. Maginn, J.F. Brennecke, J. Phys. Chem. B 106 (2002) 7315–7320.
[67] A.P.-S. Kamps, D. Tuma, J. Xia, G. Maurer, J. Chem. Eng. Data 48 (2003) 746–749.
[68] P. Husson-Borg, V. Majer, M.F. Costa Gomes, J. Chem. Eng. Data 48 (2003) 480–485.
[69] D. Camper, P. Scovazzo, C. Koval, R. Noble, Ind. Eng. Chem. Res. 43 (2004) 3049–3054.
[70] P. Scovazzo, D. Camper, J. Kieft, J. Poshusta, C. Koval, R. Noble, Ind. Eng. Chem. Res. 43 (2004) 6855–6860.
[71] J.F. Brennecke, J.L. Anthony, E.J. Maginn, in: P. Wasserscheid, T. Welton (Eds.), Ionic Liquids in Synthesis, Wiley-VCH, Weinheim, 2003, pp. 81–93 (Chapter 3.4).
[72] A. Heintz, R.N. Lichtenthaler, in: T.M. Letcher (Ed.), Chemical Thermodynamics, A Chemistry for the 21st Century Monograph, Blackwell Science, 1999.
[73] Z. Gu, J.F. Brennecke, J. Chem. Eng. Data 47 (2002) 339–345.
[74] C.P. Fredlake, J.M. Crosthwaite, D.G. Hert, S.N.V.K. Aki, J.F. Brennecke, J. Chem. Eng. Data 49 (2004) 954–964.
[75] K.R. Seddon, A. Stark, M.J. Torres, Pure Appl. Chem. 72 (12) (2000) 2275–2287.
[76] A. Heintz, D. Klasen, J.K. Lehmann, J. Sol. Chem. 31 (6) (2002) 467–476.
[77] S. Zhang, X. Li, H. Chen, J. Wang, J. Zhang, M. Zhang, J. Chem. Eng. Data 49 (2004) 760–764.
[78] X. Lu, W.G. Xu, J.S. Gui, H.W. Li, J.Z. Yang, J. Chem. Thermodyn. 37 (2005) 13–19.
[79] R.A. Mantz, P.C. Trulove, in: P. Wasserscheid, T. Welton (Eds.), Ionic Liquids in Synthesis, Wiley-VCH, Weinheim, 2003, pp. 56–68 (Chapter 3.2).
[80] J. Richter, A. Leuchter, G. Palmer, in: P. Wasserscheid, T. Welton (Eds.), Ionic Liquids in Synthesis, Wiley-VCH, Weinheim, 2003, pp. 162–167 (Chapter 4.4).
[81] Q. Liao, C.L. Hussey, J. Chem. Eng. Data 41 (1996) 1126–1130.
[82] H. Xu, D. Zhao, P. Xu, F. Liu, G. Gao, J. Chem. Eng. Data 50 (2005) 133–135.
[83] J.J. Wang, Y. Tian, Y. Zhao, K.L. Zhuo, Green Chem. 5 (2003) 618–622.
[84] J. Zhang, W. Wu, T. Jiang, H. Gao, Z. Liu, J. He, B. Han, J. Chem. Eng. Data 48 (2003) 1315–1317.
[85] H. Ohno, M. Yoshizawa, Solid State Ionics 154 (2002) 303–309.
[86] T. Nishida, Y. Tashiro, M. Yamamoto, J. Fluorine Chem. 120 (2003) 135–141.
[87] P.C. Trulove, R.A. Mantz, in: P. Wasserscheid, T. Welton (Eds.), Ionic Liquids in Synthesis, Wiley-VCH, Weinheim, 2003, pp. 103–126 (Chapter 3.6).
[88] K. Ito, N. Nishina, H. Ohno, Electrochim. Acta 45 (2000) 1295–1298.
[89] D.L. Goldfarb, M.P. Longinotti, H.R. Corti, J. Sol. Chem. 30 (2001) 307–322.

[90] M.E. van Valkenburg, R.L. Vaughn, M. Williams, J.S. Wilkes, Thermochim. Acta 425 (2005) 181–188.
[91] J.D. Holbrey, W.M. Reichert, R.G. Reddy, R.D. Rogers, in: R.D. Rogers, K.R. Seddon (Eds.), Ionic Liquids as Green Solvents: Progress and Prospects, ACS Symposium Series 856, American Chemical Society, Washington DC, 2002, pp. 121–133 (Chapter 11).
[92] H. Weingärtner, W. Schröer, in: I. Prigogine, S.A. Rice (Eds.), Advances in Chemistry and Physics, 116 ed., John Wiley & Sons, Inc., New York, 2001.
[93] W. Schröer, H. Weingärtner, in: J. Samios, V.A. Durov (Eds.), Novel Approaches to the Structure and Dynamics of Liquids: Experiments, Theory and Simulations, Kluwer Academic Publishers, 2004.
[94] W. Schröer, H. Weingärtner, Pure Appl. Chem. 76 (2004) 19–27.
[95] W. Schröer, in: D. Henderson (Ed.), Ionic Matter, Modern Trends in Theory and Applications: Experiments, Theories and Simulations, NATO ASI-Series, Kluwer Academic Publishers, 2004.

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