RESEARCH PAPER

www.rsc.org/pccp

Thermomorphic phase separation in ionic liquid–organic liquid systems—conductivity and spectroscopic characterization

Anders Riisager, *^{*ab*} Rasmus Fehrmann,^{*a*} Rolf W. Berg,^{*a*} Roy van Hal^{+*bc*} and Peter Wasserscheid^{**c*}

^a Department of Chemistry and Interdisciplinary Research Center for Catalysis (ICAT), Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark. E-mail: ar@kemi.dtu.dk; Fax: (+45) 45252235; Tel: (+45) 45252233

^b Institut für Technische Chemie und Makromolekulare Chemie, RWTH-Aachen, Worringer Weg 1, D-52074 Aachen, Germany

^c Lehrstuhl für Chemische Reaktionstechnik, Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058 Erlangen, Germany. E-mail: peter.wasserscheid@crt.cbi.uni-erlangen.de; Fax: (+49) 9131 8527421; Tel: (+49) 9131 8527420

Received 21st April 2005, Accepted 29th June 2005 First published as an Advance Article on the web 21st July 2005

Electrical conductivity, FT-Raman and NMR measurements are demonstrated as useful tools to probe and determine phase behavior of thermomorphic ionic liquid–organic liquid systems. To illustrate the methods, consecutive conductivity measurements of a thermomorphic methoxyethoxyethyl-imidazolium ionic liquid/ 1-hexanol system are performed in the temperature interval 25–80 °C using a specially constructed doubleelectrode cell. In addition, FT-Raman and ¹H-NMR spectroscopic studies performed on the phase-separable system in the same temperature interval confirm the mutual solubility of the components in the system, the liquid–liquid equilibrium phase diagram of the binary mixture, and signify the importance of hydrogen bonding between the ionic liquid and the hydroxyl group of the alcohol.

Introduction

10.1039/b505588

ö

In recent years, several concepts applying ionic liquids have been developed for phase-separable catalytic applications¹ and separation technology,² by using the unique properties of ionic liquids^{3,4} in comparison to traditional liquid reaction media, *e.g.* non-volatility, polar but yet non-coordinating nature,⁵ high thermal stability and large liquidus range.⁶ Some of the more recent catalytic developments include the use of transition metal catalyzed two-phase^{7–9} and analogous "heterogenized" supported ionic liquid phase (SILP)^{10,11} systems as well as scCO₂-ionic liquid systems.¹² For selective separations recent developments include the use of task specific ionic liquids (TSILs) for, *e.g.* aqueous coordinative extraction of heavy metals with polyether-modified ionic liquids,^{13,14} removal of hetero-aromatics from fuel and diesel fractions^{7,15} and adsorptive desulfurization of flue gas.¹⁶

In search for alternative methodologies to perform organic liquid phase-separable catalytic reactions using ionic liquid technology, we have been attracted by an approach involving thermomorphic ionic liquid–organic systems, *i.e.* composite systems which change their phase behavior with temperature. Such systems can eliminate mass-transfer limitations prevailing in interfacial catalytic reactions (like in biphasic and possibly also in SILP approaches), if the systems consist of a homogeneous phase at reaction conditions (*e.g.* elevated temperatures) but of separated ionic liquid catalyst phase and organic phase at lower temperatures. Thermo-regulated transition metal catalysts are well-known from, *e.g.* fluorous phase-organic liquid systems¹⁷ and for aqueous-organic systems using catalysts based on nonionic polyether-functionalized phos-

† Present address: Solvent Innovation GmbH, Nattermannallee 1, D-50829 Cologne, Germany.

phine ligands.^{18–21} Also, aqueous-organic systems exhibiting temperature-dependent reversible phase separation due to preferential water-solubility of products are known.²²

Ionic liquids are entirely composed of ions which facilitate their study by conductivity measurements. This has previously been used extensively for phase equilibria studies of solid/ liquid vanadium alkali pyrosulfate molten melts (i.e. hightemperature ionic liquids) to determine phase diagrams of the mixtures.²³ In addition, ionic liquids are polar²⁴ highly ordered hydrogen-bonded fluids.²⁵⁻²⁷ As a consequence, a solvent used to dissolve an ionic liquid in a system possessing thermomorphic phase behavior must be quite polar and have a comparatively high permittivity (dielectric constant), since the ability of a solute to form hydrogen bonds or other possible relatively strong interactions with a solvent is an important feature of this behavior. Thus, it must be a good insulator to lower the attraction between the ions in the ionic liquid. In addition, the ionic liquid may interact with the species of the other phase in competition with the intermolecular forces of the molecules in that phase and thereby facilitate phase miscibility. A common class of solvents which possesses such characteristics is alcohols. Alcohols are composed of structured molecular entities associated via hydrogen bonding, which is clearly reflected by their relatively high boiling points compared to hydrocarbons having comparable molecular weight and structure.

Liquid–liquid equilibria (LLE) in binary mixtures of common [1-alkyl-3-methylimidazolium][X] ionic liquids (X = $[PF_6]^-$, $[BF_4]^-$, $[(CF_3SO_2)_2N]^-$, $[(CN)_2N]^-$ and $CF_3SO_3^-$) and 1-butanol²⁸ or other linear and branched alcohols with various chain lengths^{25,29} have previously been examined using visual cloud point determinations. In all cases, typically LLE behavior of partially miscible two-component systems with an upper critical solution temperature (UCST) was observed, with

3052 Phys. Chem. Chem. Phys., 2005, 7, 3052–3058 This journal is © The Owner Societies 2005



Scheme 1 Preparation of 1,3-bis-[2-(2-methoxyalkoxy)ethyl]imidazolium bis-trifluoromethylsulfonylamide ionic liquids.

relatively low solubility of the ionic liquid in the alcohol but high solubility of the alcohol in the ionic liquid (sometimes more than 50 mol%). Moreover, the alcohol solubility in the ionic liquids followed the order of alcohol branching, *i.e.* tertiary > secondary > primary alcohols, which correlates with the relative basicity of the alcohols (*i.e.* hydrogen bond acceptor capability).²⁹ In addition, a longer alkyl chain of the alcohol resulted in an increase in the UCST due to less interaction with the ionic liquid through, *e.g.* hydrogen-bonding, while an increase in the length of the alkyl chain on the imidazolium cation resulted in higher mutual solubility, *i.e.* decrease in UCST.

In order to exemplify the methodology of using electrical conductivity as a probe of thermomorphic behavior, we have measured the conductivity in a binary liquid system composed of the ionic liquid 1,3-bis[2-(2-methoxyethoxy)ethyl]imidazolium bis-trifluoromethylsulfonylamide, **3** (Scheme 1 with n = 1) and 1-hexanol, as a representative system. More generally, this ionic liquid-alcohol system belongs to a series of thermomorphic composite systems containing various linear and branched C_4 – C_{12} alcohols and the di-substituted imidazolium ionic liquid, which may be prepared by stepwise alkylation of imidazole with methanesulfonic acid 2-(2-alkoxyethoxy)ethyl esters 1 via mono-substituted 1-[2-(2-methoxyalkoxy)ethyl]imidazole compounds 2 (Scheme 1). Using a similar synthetic strategy we have also prepared [1-(2-(2-methoxyalkoxy)ethyl)-3-alkylimidazolium][X] ionic liquids (where X = alkyl sulfate, dialkyl phosphate or [(CF₃SO₂)₂N]⁻ after additional anion exchange) by alkylations using the corresponding methyl and ethyl compounds. More details on these ionic liquids will be reported elsewhere.

Analogous bis-alkoxymethyl substituted³⁰ and 1,3-bis-alkoxymethyl-2-alkyl substituted imidazolium ionic liquids³¹ containing Cl⁻, [BF₄]⁻, [PF₆]⁻ or [(CF₃SO₂)₂N]⁻ anions have previously been prepared by imidazole alkylation using halogenmethyl alkyl ethers followed by anion metathesis. Also, closely related 1-methyl-3-alkoxyethyl substituted imidazolium ionic liquids based on the same anions³² or on more hydrophobic perfluoroalkyltrifluoroborate anions³³ (*i.e.* $[R_FBF_3]^-$), respectively, have previously been reported by similar procedures and examined with respect to their physicochemical properties including, e.g. visual solubility characteristics and ionic conductivity. Notably, it was here realized that the presence of ether functional alkyl groups in the imidazolium ionic liquids considerably modified their solubility compared to the similar alkyl-substituted compounds, while altering of the anion did not have any significant influence.³² In addition, also more hydrophilic 1-alkyl-3-poly(ethyleneglycol)imidazolium ionic liquids with [BF4]⁻, [PF6]⁻ or [(CF3SO2)2N]⁻ anions have been prepared by microwave mediated alkylation of alkyl-imidazolium with chloropolyethoxy-ethanol compounds followed by anion exchange reactions.³⁴ Importantly, however, so far none of the previous studies involving the hydroxyl- or ether-modified imidazolium ionic liquids have included examination of thermomorphic phase-separable properties.

In the present study, we apply primarily conductivity as a quantitative method for measuring the phase separation temperatures rather than the more qualitative visual method of cloud point determination.

Experimental

General comments

All solvents and reagents used for syntheses were purchased from commercial sources in high quality and used without further purification. For the conductivity measurements the double electrode cell with the gold electrodes (described below in detail) was cleaned before use by 4 M HNO₃, water and ethanol and finally oven dried (110 °C). Moreover, 1-hexanol (Fluka, $\geq 99\%$) was dried with 4 Å molecular sieves before use. All NMR spectra were measured on a Varian Mercury 300 MHz spectrometer at 25 °C unless otherwise specified. The density of the ionic liquid **3** was determined using a pycnometer (V = 5.0 ml), the water content determined by Karl–Fisher titration (Hydranal-Coulomat AG anolyte, Riedel-de Haën), and the melting point (T_m) and decomposition temperature (T_d) by thermal analysis (Perkin Elmer PYRIS diamond DSC, temperature ramp: 5 °C min⁻¹).

Methanesulfonic acid 2-(2-methoxyethoxy)ethyl ester, 1 (n = 1)

To an ice-cooled solution of 93.7 ml 2-(2-methoxyethoxy)ethanol (95.52 g, 0.795 mol) and 110.2 ml triethylamine (80.45 g, 0.795 mol) in 1.5 l anhydrous diethyl ether was 61.7 ml methanesulfonyl chloride (91.07 g, 0.795 mol) slowly added over approximately 2 h under vigorous stirring. After continuous stirring overnight, the precipitated triethylammonium chloride was removed by filtration and the diethyl ether removed under reduced pressure with a rotation evaporator. The crude liquid ester product was then re-dissolved in dichloromethane, washed with water and finally isolated by removing the solvent under reduced pressure again. Yield = 152.43 g (97%).

¹H-NMR (300 MHz), CDCl₃/TMS: δ /ppm = 2.876 (3H, s, – OCH₃), 3.155 (3H, s, –SCH₃), 3.337 (2H, t, *J* = 4.5 Hz, CH₃O–CH₂–CH₂–), 3.453 (2H, t, *J* = 4.5 Hz, CH₃O–CH₂–CH₂–), 3.556 (2H, t, *J* = 4.5 Hz, –SO₃–CH₂–CH₂–), 4.162 (2H, t, *J* = 4.5 Hz, –SO₃–CH₂–CH₂–), 4.162 (2H, t, *J* = 4.5 Hz, –SO₃–CH₂–CH₂–), 4.162 (2H, t, *J* = 4.5 Hz, SO₃–CH₂–CH₂–). ¹³C-NMR (75.34 MHz), CDCl₃/TMS: δ /ppm = 37.54 (–OCH₃), 58.93 (–SCH₃), 69.11 (CH₃O–CH₂–CH₂–), 69.83 (CH₃O–CH₂–CH₂–), 70.60 (–SO₃–CH₂–CH₂–), 71.94 (–SO₃–CH₂–CH₂–).

1-[2-(2-Methoxy)ethyl]imidazole, 2 (n = 1)

Under stirring and cooling in an ice-water bath 238.5 g sodium hydroxide (5.96 mol) was added to a solution of 4.90 g tetraethylammonium bromide (0.023 mol) in 300 ml water. After most of the base was dissolved, 52.35 g imidazole (0.769 mol) was added to the suspension followed by 152.43 g methanesulfonic acid 2-(2-methoxyethoxy)ethyl ester (1, n = 1) (0.769 mol). The mixture was then reacted by stirring overnight at room temperature, where the mixture was allowed to gradually warm up by melting of the ice in the cooling bath. Finally, the product was separated from the reaction mixture by extraction with dichloromethane four times, where after the liquid, monoalkylated product was isolated by removal of the dichloromethane under reduced pressure. Yield = 64.4 g (49%).

¹H-NMR (300 MHz), CD₃CN/TMS: δ /ppm = 3.328 (3H, s, -OCH₃), 3.472 (2H, t, J = 4.5 Hz, CH₃O- CH_2 - CH_2 -), 3.554 (2H, t, J = 4.5 Hz, CH₃O- CH_2 - CH_2 -), 3.714 (2H, t, J = 5.2 Hz, -N- CH_2 - CH_2 -), 4.115 (2H, t, J = 5.2 Hz, -N- CH_2 - CH_2 -), 6.949 (1H, broad s, -N-CH=CH-N), 7.093 (1H, broad s, -N-CH=CH-N), 7.530 (1H, s, -N=CH-N-). ¹³C-NMR (75.34 MHz), CD₃CN/TMS: δ /ppm = 46.14 (-OCH₃), 57.64 (CH₃O- CH_2 - CH_2 -), 69.64 (CH₃O- CH_2 - CH_2 -), 71.18 (-N- CH_2 - CH_2 -),

117.10 (-N-*C*H₂-CH₂-), 119.21 (-N-*C*H=CH-N-), 128.11 (-N-CH=*C*H-N-), 137.22 (-N=*C*H-N-).

1,3-bis-[2-(2-Methoxyethoxy)ethyl]imidazolium bis-trifluoromethylsulfonylamide, 3 (n = 1)

A mixture of 7.56 g 1-[2-(2-methoxyethoxy)ethyl]imidazole (2, n = 1) (44.4 mmol) and 8.80 g methanesulfonic acid 2-(2methoxyethoxy)ethyl ester (1, n = 1) (44.4. mmol) was heated at 60 °C for approximately 100 h under argon atmosphere until all imidazole was quaternized (determined by ¹H-NMR of samples taken during the reaction). Then, a solution of 12.91 g lithium bis-trifluoromethylsulfonylamide (45.0 mmol) in 50 ml water was added to the reaction mixture along with 50 ml dichloromethane. After stirring the two-phase mixture vigorously for 2 h the aqueous phase was separated from the organic product phase, washed twice with dichloromethane and discharged. The dichloromethane washing phases were then combined with the organic reaction phase where after the volatile solvent was removed under reduced pressure. Finally, the non-volatile ionic liquid product left behind was further dried *in vacuo* (1 mbar, 50 °C, 6 h). Yield = 21.3 g (87%). ρ (22 °C) = 1.330 g cm⁻³, [H₂O] = 7.7 mM (104 ppm), $T_{\rm m} <$ $-60 \,^{\circ}\mathrm{C}, \, T_{\mathrm{d}} = 344 \,^{\circ}\mathrm{C}.$

¹H-NMR (300 MHz), CDCl₃/TMS: δ /ppm = 3.305 (6H, s, -OCH₃), 3.468 (4H, t, J = 4.2 Hz, CH₃O-CH₂-CH₂-), 3.587 (4H, t, J = 4.2 Hz, CH₃O-CH₂-CH₂-), 3.781 (4H, t, J = 4.5 Hz, -N-CH₂-CH₂-), 4.301 (4H, t, J = 4.6 Hz, -N-CH₂-CH₂-), 4.301 (4H, t, J = 4.6 Hz, -N-CH₂-CH₂-), 7.419 (2H, s, -N-CH=CH-N-), 8.709 (1H, s, -N=CH-N-). ¹³C-NMR (75.45 MHz), CDCl₃/TMS: δ /ppm = 49.96 (-OCH₃), 59.02 (-N-CH₂-CH₂-O-), 68.66 (-N-CH₂-CH₂-O-), 70.42 (CH₃O-CH₂-CH₂), 71.70 (CH₃O-CH₂-CH₂), 122.92 (-N-CH=CH-N-), 123.08 (-N=CH-N-), 136.34 (-SO₂-CF₃). ¹⁹F-NMR (282.33 MHz), CDCl₃/TMS: δ /ppm = -79.52 (-SO₂-CF₃).

Conductivity measurements

The conductivity (L) was measured on the binary 3/1-hexanol system using a Radiometer CDM230 conductivity meter and a compact Pyrex glass cell ($d_{inner} = 16 \text{ mm}, l = 100 \text{ mm}, V \approx 11$ cm³) equipped with two sets of gold electrodes penetrating a gas tight (sealed by Viton O-ring) and electrically insulating polyetheretherketone (PEEK) polymer top and a Rotulex cap connected by tightening screws (Fig. 1). The vertically adjustable gold electrode pairs (8 \times 12.5 \times 2 mm Au plate, 1 mm Au wire) were fixed and made gas tight (Viton O-rings around the electrodes) by tightening the screws between the top and the cap during measurements. To maintain the relative position of the electrode plates during measurements, the electrode wires were penetrating a PEEK positioning plate placed between the upper electrode pair and the cell cap. Furthermore, in order to perform conductivity measurements with the lower electrode plates only, the gold wires were partly coated (from 3 mm above the electrode plate to 20 mm from the top of the wire) with a non-conducting PTFE-like layer (ca. 50 µm Accofal 2G54 layer, Accoat Coating, Denmark) possessing a high penetration resistance for liquids and high physico-chemical and thermal (-240 to 250 °C) stability. Moreover, a stainless steel cannula injection tube fitted with a septum positioned in the PEEK top allowed successive alcohol addition without manipulation of the cell during measurement series.

To perform the conductivity measurements the cell containing a magnetic stirring bar was placed in a stirred (700–1000 rpm) and thermostatic silicon oil bath (Heidolph MR3003 magnetic stirrer with Pt100 thermo element regulation). The actual cell temperature during the measurements was measured with an external Pt100 thermo element connected to an Omega DP460 control unit (± 0.1 °C) positioned at the outer wall of the glass cell. Cell conductivity constants *K* (about 0.5 cm⁻¹ depending on the actual position of the electrodes for each



Fig. 1 Double-electrode pair conductivity cell. (a) Stainless steel cannula injection tube, (b) PEEK Rotulex top with tightening screws, (c) PEEK Rotulex cap, (d) Pyrex glass tube (l = 100 mm), (e) vertical adjustable Accofal-coated gold electrode (d = 1 mm), (f) PEEK positioning plate, (g) gold electrode plate ($8 \times 12.5 \times 2 \text{ mm}$), (h) magnetic stirring bar.

electrode pair in the cell) used to obtain the specific conductivities κ (in mS cm⁻¹ with $\kappa = LK$) was calculated as the mean value of cell constants determined from measuring the conductivity of a 0.1 D KCl solution before and after each series of measurements on the ionic liquid-alcohol system, as described in the literature.³⁵

Each series of conductivity measurements was started by measuring on heated (about 80 °C), monophasic systems after allowing the system to equilibrate to constant conductivity without stirring. Subsequently, the following measurements were done at gradually decreased temperatures after similar equilibration periods. Consecutive measurements were performed on mixed systems with increasingly molar ratios of 1-hexanol, *i.e.* X(1-hexanol) from 0 to 1, by injecting known amounts of the alcohol directly through the cannula injection tube into the ionic liquid contained in the cell. The specific conductivities could be measured within $\pm 0.1\%$.

Spectroscopic measurements

The ionic liquid **3**, 1-hexanol and a mixture thereof were studied by FT-Raman spectroscopy at 25 °C (Bruker IF S66 FRA-106 FT-spectrometer, 1064 nm NIR Nd-YAG laser, 100 mW, liquid nitrogen cooled Ge-diode detector) and by ¹H-NMR spectroscopy in the temperature interval 20–70 °C. The variable temperature NMR measurements were performed on the liquids (without spinning) in dried NMR capillary tubes containing a sealed capillary tube with d⁶-DMSO for signal locking and as internal chemical shift reference, after rigorous mixing, temperature equilibration and phase separation (if present). The temperature of the NMR probe was precalibrated to ± 0.1 °C by measuring on an ethyleneglycol standard. Chemical shifts are determined to ± 0.01 ppm and the integrated peaks to $\pm 2\%$.

Results and discussion

Consecutive conductivity was measured on the binary 3/ 1-hexanol system at 13 different compositions in the full

Composition no.	Molar ratio 1-hexanol/3	X(1-hexanol)	CST (°C
1	0.0000	0.0000	
2	0.055(4)	0.052(5)	< 20
3	0.095(1)	0.086(9)	< 20
4	0.188(1)	0.158(3)	<20
5	0.443(7)	0.307(3)	<20
6	0.922(0)	0.479(7)	<20
7	1.805(8)	0.643(6)	< 20
8	2.354(4)	0.701(9)	40
9	3.189(7)	0.761(3)	48
10	3.578(0)	0.781(6)	51
11	7.207(2)	0.878(2)	52
12	14.062(7)	0.933(4)	51
13		1.0000	—

^{*a*} Inaccuracies in compositions are indicated by the numbers in parentheses. ^{*b*} CSTs (critical solution temperatures) determined by differentiation of the conductivity equations (see text for more details).

composition range (see Table 1 for details) and in the temperature range of 25–80 °C with a double electrode glass cell. In Fig. 2 representative results are shown for the measured specific conductivities (on a logarithmic scale) *versus* temperature in both phases of a system having a composition corresponding to X(1-hexanol) = 0.878(2) and of the ionic liquid alone.

The specific conductivities measured with the two sets of electrode pairs in the 3/1-hexanol mixture were lower and different than the values for the pure ionic liquid, as a result of a large difference in concentration of the charge carrying species. When heated from room temperature to a CST of 52 °C specific conductivities progressively approached the same values for the lower ionic liquid-rich and upper alcohol-rich phase, respectively (Fig. 2). In contrast, significantly lowerbut identical-specific conductivity was measured with the two electrode pairs in the cell above the CST when the mixture became homogeneous. This observation strongly indicated that phase miscibility was accompanied by a significant change in mobility of the conducting species as a result of intermolecular interactions between the ionic liquid and alcohol species. This was further supported by complementary ¹H-NMR spectroscopic examinations (vide infra). For the examined alcoholrich systems with compositions X(1-hexanol) > 0.643(6)a similar phase separation was observed as above, with



Fig. 2 Specific conductivity as function of the temperature of the ionic liquid **3** (×) and of the upper phase (\odot) and lower phase (\bigcirc), respectively, of a 3/1-hexanol mixture with mole fraction *X*(1-hexanol) = 0.878(2).

CSTs of 40 to 52 (± 0.5) °C depending on the composition (see Table 1).

In the examined temperature interval the conductivity of the alcohol-rich phase was increased by a factor of ca. 10^3 compared to the non-ionic pure alcohol, as a result of a significant solubility of strong ionic liquid electrolyte in the very weak alcohol electrolyte. The presence of ionic liquid in the alcoholrich phase at room temperature was confirmed by the existence of the characteristic FT-Raman band at 742 cm⁻¹ assigned to normal modes of coupled S-N and C-S stretching bands (and perhaps CF₃ deformation) of the [(CF₃SO₂)₂N]⁻ anion (in accordance with the literature³⁶), by comparison to the corresponding solid lithium-salt (Fig. 3, see Table 2 for further assignments of the observed FT-Raman bands to the species present). Similarly, an increase in the relative intensity of FT-Raman bands at, e.g. 2900 cm⁻¹ (assigned to CH₂ and CH₃ stretching), indicated a considerable content of alcohol in the ionic liquid-rich phase at room temperature. For this phase, however, a less pronounced change in conductivity was observed compared to the alcohol-rich phase despite the dissolution, indicating only minor interference of the alcohol with the ion pairing in the ionic liquid at ambient temperature.

Assuming that only ionic liquid species are charge carrying in the binary system and that the activity coefficients of the species remain unchanged with temperature, the relative concentration of the ionic liquid (C_{rel}) in the system can be estimated, as function of the temperature, from the ratio between the measured specific conductivities of the ionic liquid alone and the two phases, as shown in Fig. 4.

Here, it can be seen that $C_{\rm rel}$ in the alcohol-rich and ionic liquid-rich phases changed linearly with temperature from initially 0.33 and 0.66 at room temperature, respectively, *i.e.* concentration of the ionic liquid in the ionic liquid-rich phase was twice the concentration in the alcohol-rich phase, to being essentially equal at 0.50 above the CST (as expected for one single phase).



Fig. 3 Normalized FT-Raman spectra recorded at 25 °C of solid Li[(CF₃SO₂)₂N] salt, 1-hexanol, ionic liquid **3**, and the upper and lower phase of a **3**/1-hexanol system having X(1-hexanol) = 0.878(2) (arrows indicate characteristic FT-Raman bands of 1-hexanol and **3**, respectively).

 Table 2
 Observed FT-Raman bands^a and their assignment^b

1-Hexanol	Ionic liquid 3	Li[(CF ₃ SO ₂) ₂ N] (solid)	Assignment
	3173 w, 3112 vw		Cation
2955 w sh, 2928 w sh	2963 vs, 2928 vw		CH_x str
2900 vs	2886 vs, 2831 s		CH_x str
2874 vs, 2732 w	2774 vw, 2728 vw		CH_x str
	1569 w, 1473 vw sh		Cation
	1451 m, 1425 m		Cation
1450 m			1-Hexanol
		1359 vw	Anion
	1340 m	1345 w, 1319 m	Anion
1303 m. 1223 vw			1-Hexanol
	1294 w		Cation
	1243 s	1248 s	Anion
	1218 vw br	1212 w 1229 w	Anion
	1210 111 01	1153 w	Anion
	1137 m	1100 11	Cation
	1107 11	1131 w	Anion
1188 vw 1119 w			1-Hexanol
1077 w 1061 w			1-Hexanol
1077 10, 1001 10	1108 w 1031 m		Cation
1027 w 996 vw	1100 w, 1051 m		1-Hexanol
1027 w, 990 vw	962 w 918 vw br		Cation
953 VIV 919 VIV	502 w, 510 vw 61		1-Hevanol
888 m 866 yw 854 yw			1-Hevanol
000 m, 000 vw, 004 vw	848 m		Cation
	817 w br	811 vay br	Anion
	742 vs	748 vs	Anion
820 m. 754 mm	/42 /3	748 VS	1 Havanal
820 w, 734 vw	659 100	660 w	Anion
	632 vw	605 w	Anion
	508 m	600 m	Anion
	578 m	572 ch	Anion
	572 111	575 81	Amon
455	554 m	360 W, 333 W	Anion
455 VW		129 1	I-Hexanol
	402	428 W Dr	Anion
100 2(2	403 m		
409 vw, 363 w		200	I-Hexanol
	220 h	389 m 246 m -h	Anion
	339 w sh	346 w sh	Anion
217	328 m	333 s, 317 w	Anion
31 / VW	212		I-Hexanol
	312 m	200	Cation
	280 s	280 s	Anion

^{*a*} Intensity codes: w = weak, m = medium, s = strong, sh = shoulder, v = very, br = broad. Calibration with cyclohexane lines to a precision of 1 cm⁻¹. ^{*b*} Assignments of Raman bands to group vibrations are difficult because couplings are intense. However, the bis-trifluoromethylsulfonyl-amide anion vibrations have previously been studied³⁶ and those in 1,3-dialkylimidazolium cation systems also recently.³⁷ Cation = 1,3-bis-[2-(2-methoxyethoxy)ethyl]imidazolium, anion = bis-trifluoromethylsulfonylamide.

The specific conductivities measured at temperatures between 20 and 80 °C (*i.e.* including data below and above the UCSTs) in the ionic liquid-rich phase of 3/1-hexanol mixtures having different compositions can be well fitted to empirical equations of the type $\kappa(T) = aT^5 + bT^4 + cT^3 + dT^2 + eT + f$ (R² factors ≥ 0.996). The equations obtained can further be used to calculate conductivities at specific temperatures as function of the alcohol molar ratio. In Fig. 5 calculated isothermal curves using this method are shown.

In order to get further information on the composition and the effect of the various interactions present in the mixture of 1-hexanol and **3** undergoing phase change, ¹H-NMR spectra obtained in the temperature interval 20–70 °C of the pure alcohol and of the lower, ionic liquid-rich phase (or homogeneous mixture at higher temperatures) in a system having an initial composition X(1-hexanol) = 0.807(0) were analyzed. The measurements of ¹H chemical shifts (δ_{H}) and comparison of the integrals of clearly separated proton signals of the alcohol and the ionic liquid, respectively, allowed determination of the temperature and composition dependant change of



Fig. 4 Relative concentration (C_{rel}) of the ionic liquid **3** as function of the temperature in the upper phase (\odot) and lower phase (\bigcirc), respectively, of a **3**/1-hexanol mixture with mole fraction X(1-hexanol) = 0.878(2) (dotted line indicate the CST determined for the mixture).



Fig. 5 Specific conductivities as function of 1-hexanol mole fractions in lower ionic liquid-rich phases of 3/1-hexanol mixtures calculated at isothermal temperatures of (from bottom to top): 20 °C (\Box), 30 °C (\diamond), 40 °C (Δ), 50 °C (\times), 55 °C (*), 60 °C (-), 70 °C (\bigcirc) and 80 °C (+).

 $\delta_{\rm H}$. Hence, in Fig. 6, representative compositions determined as the molar 1-hexanol/3 ratios and the alcohol mole fractions as function of the temperature calculated from the integral ratios of the alcohol-CH₃ protons and the 3-NCH=CHN, 3-NCH₂CH₂O or 3-OCH₃ protons, respectively, are shown.

From the proton integrals an excellent agreement was found between the three selected signals, revealing an increased amount of alcohol in the saturated ionic liquid-rich phase, corresponding to mole fractions of 1-hexanol between 0.53 and 0.79, when the mixture was heated from room temperature to a CST estimated to be 51.5 °C (Fig. 6). This CST value was nearly the same as that found by conductivity measurements for mixtures having related compositions (*vide supra*), and confirmed a very high alcohol content in the ionic liquid-rich phase, as also suggested by the relative ionic liquid concentrations determined from the conductivity (see Fig. 4). Above the CST, the mixture became homogeneous and, accordingly, the composition remained unchanged in good agreement with the initial value of X(1-hexanol) = 0.807(0) of the mixture.

Combined, the CSTs determined from the conductivity and the NMR examinations together with the phase saturation temperatures found by the NMR experiment, allowed the



Fig. 7 Liquid–liquid equilibrium phase diagram showing upper critical solution temperatures (UCSTs) above 20 °C determined for the 3/ 1-hexanol binary system by conductivity (±0.5 °C) (\bullet) and ¹H-NMR (±1.0 °C) (\bigcirc) measurements, respectively, as function of the 1-hexanol mole fraction (dotted line represents extrapolation).

construction of a LLE phase diagram of the 3/1-hexanol system from temperatures above 20 °C, as illustrated in Fig. 7.

The determined phase diagram disclosed good consistency between the complementary measurements, and revealed a marked phase miscibility gap in the binary system. Notably, all ionic liquid-rich compositions of the mixture had CSTs below room temperature due to the very high alcohol solubility in the ionic liquid already at room temperature (almost 50 mol%), as also previously observed for some related alcohol/ 1,3-dialkyl-imidazolium ionic liquid systems.²⁹

The temperature dependence of $\delta_{\rm H}$ on the alcohol-OH proton ($\Delta \delta_{\rm OH}$), where $\Delta \delta_{\rm OH} = \delta_{\rm OH}(20 \,^{\circ}{\rm C}) - \delta_{\rm OH}(T)$, was also determined for the system having a composition corresponding to X(1-hexanol) = 0.807(0) (Fig. 8).

For the pure alcohol $\Delta \delta_{OH}$ was positive and changed almost linearly upon heating, as a consequence of a gradual up-field shift of δ_{OH} related to a steady structural change caused by a progressive breaking of hydrogen bonds in the liquid at higher temperatures (Fig. 8). Hence, at a temperature of 51.5 °C, corresponding to the CST for the mixture, the $\Delta \delta_{OH}$ value was 0.47 ppm for the pure alcohol. In comparison, all other alcohol protons were only shifted slightly down-field in the same temperature interval, due to increased thermally molecular



Fig. 6 Composition of the lower phase of 3/1-hexanol system with X(1-hexanol) = 0.807(0) as function of the temperature determined by ¹H-NMR spectroscopy from comparison of alcohol-CH₃ integral with integrals of 3-NCH = CHN (\Box), 3-NCH₂CH₂O (Δ) and 3-OCH₃ (\bigcirc), respectively (dotted line indicate the CST determined by conductivity).

0.9 0.7 ∆∂он (ррт) 0.5 0.3 0.1 -0.1 10 20 30 40 50 60 70 80 T (°C)

Fig. 8 Temperature dependence of the chemical shift of the alcohol proton $(\Delta \delta_{OH})$ in pure 1-hexanol (\bigcirc) and in the lower phase of a 3/1-hexanol system with X(1-hexanol) = 0.807(0) (\bigcirc) (dotted line indicates the CST determined for the mixture from the conductivity measurements).

In contrast to the situation in the pure alcohol, the variation in the measured $\Delta \delta_{\rm OH}$ for the mixtures levelled off in the temperature interval from 30 °C to the CST, reaching a much lower value of $\Delta \delta_{\rm OH} = 0.30$ ppm (36% lower) at CST. At temperatures above the CST $\Delta \delta_{OH}$ increased practically linearly again with essentially the same slope as for the pure alcohol, however, with a $\Delta \delta_{OH}$ value corresponding to a shift of approximately 10 °C when compared to the pure alcohol. Combined, these observations clearly demonstrated that the alcohol intra-molecular hydrogen bonding structure was not preserved when the alcohol dissolved in the ionic liquid-rich phase at intermediate temperatures below the CST. Most likely, this can be attributed to competitive hydrogen bonding of the alcohol to the ionic liquid anion or to the polyether alkyl groups in the ionic liquid imidazolium cation. This also suggests that mutual phase miscibilities are accompanied by a notable change in mobility of the conducting ionic liquid species, as previously indicated by the complementary conductivity measurements.

Conclusion

In this work we have demonstrated the use of conductivity measurements as a simple technique for investigating thermomorphic behavior of binary ionic liquid-organic liquid systems, exemplified by measurements on a binary methoxyethoxyethylimidazolium ionic liquid/1-hexanol system. Moreover, we have shown how temperature dependent ¹H-NMR and FT-Raman measurements combined with the conductivity examinations can provide (i) information about miscibility, (ii) be used as complimentary methods for determining critical solution temperatures (CSTs) as function of composition and the phase diagram, and (iii) provide information about structural changes occurring for the compounds upon mixing.

In perspective, we believe that the introduced conductivity methodology can be implemented to monitor reactions in biphasic ionic liquid catalysis, and as an analytical tool for determining cross contamination in extraction and separation technology based on ionic liquids. Furthermore, we envisage that thermomorphic ionic liquid-organic liquid binary systems may have application for important catalytic processes where catalyst-product/reactant separation is problematic. Such possible reactions will be explored in future work.

Acknowledgements

This work was supported by the ConNeCat project "Smart ligands-smart solvents" financed by the German Federal Ministry for Education and Research (BMBF), and the Danish Technical Research Council regarding part of the work carried out at the Technical University of Denmark. The authors thank Bodil Holten and Charlotte H. Gotfredsen (Department of Chemistry, Technical University of Denmark), and Lykke Ryelund (Department of Chemistry, University of Copenhagen) for technical assistance.

References

- C. C. Tzschucke, C. Markert, W. Bannwarth, S. Roller, A. Hebel 1 and R. Haag, Angew. Chem., Int. Ed., 2002, 41, 3964-4000.
- Ionic Liquids in Synthesis, ed. P. Wasserscheid and T. Welton, VCH-Wiley, Weinheim, 1st edn., 2003.

- 3 J. S. Wilkes, J. Mol. Catal. A: Chem., 2004, 214, 11-17.
- K. N. Marsh, J. A. Boxall and R. Lichtenthaler, Fluid Phase 4 Equilib., 2004, 219, 93–98.
- 5 M. J. Muldoon, C. M. Gordon and I. R. Dunkin, J. Chem. Soc., Perkin Trans. 2, 2001, 433-435.
- 6 J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker and R. D. Rogers, Green Chem., 2001, 3, 156-164.
- 7 J. Esser, P. Wasserscheid and A. Jess, Green Chem., 2004, 6, 316-322.
- H. Olivier-Bourbigou and L. Magna, J. Mol. Catal. A: Chem., 2002, 182-183, 419-437.
- 9 J. Dupont, R. F. de Souza and P. A. Z. Suarez, Chem. Rev., 2002, 102, 3667-3692.
- 10 A. Riisager, R. Fehrmann, S. Flicker, R. van Hal, M. Haumann and P. Wasserscheid, Angew. Chem., Int. Ed., 2005, 44, 815-819. C. P. Mehnert, Chem.-Eur. J., 2005, 11, 50-56. 11
- 12
- S. V. Dzyuba and R. A. Bartsch, Angew. Chem., Int. Ed., 2003, 42, 148-150, and cited references.
- A. E. Visser, R. P. Swatloski, W. M. Reichert, R. Mayton, S. 13 Sheff, A. Wierzbicki, J. H. Davis Jr. and R. D. Rogers, Chem. Commun., 2001, 135-136.
- 14 J. D. Holbrey, A. E. Visser, S. K. Spear, W. M. Reichert, R. P. Swatloski, G. A. Broker and R. D. Rogers, Green Chem., 2003, 5, 129-135.
- 15 A. Bösmann, L. Datsevich, A. Jess, A. Lauter, C. Schmitz and P. Wasserscheid, Chem. Commun., 2001, 2494-2495.
- 16 W. Wu, B. Han, H. Gao, Z. Liu, T. Jiang and J. Huang, Angew. Chem., Int. Ed., 2004, 43, 2415-2417.
- 17 D. J. Brauer, K. W. Kottsieper, C. Liek, O. Stelzer, H. Waffenschmidt and P. Wasserscheid, J. Organomet. Chem., 2001, 630, 177 - 184.
- 18 X. Zheng, J. Jiang, X. Liu and Z. Jin, Catal. Today, 1998, 44, 175 - 182.
- 19 J. Jiang, Y. Wang, C. Liu, F. Han and Z. Jin, J. Mol. Catal. A: Chem., 1999, 147, 131-136.
- J. Jiang, Y. Wang, C. Liu, Q. Xiao and Z. Jin, J. Mol. Catal. A: 20 Chem., 2001, 171, 85-89.
- Y. Wang, J. Jiang, Q. Miao, X. Wu and Z. Jin, Catal. Today, 2002, 21 74, 85-90.
- 22 P. J. Dyson, D. J. Ellis and T. Welton, Can. J. Chem., 2001, 79, 705-708.
- 23 S. B. Rasmussen, H. Hamma, O. B. Lapina, D. F. Khabibulin, K. M. Eriksen, R. W. Berg, G. Hatem and R. Fehrmann, J. Phys. Chem. B, 2003, 107, 13823-13830, and cited references.
- S. N. V. K. Aki, J. F. Brennecke and A. Samanta, Chem. 24 Commun., 2001, 413-414.
- 25 U. Domanska and A. Marciniak, J. Phys. Chem. B. 2004, 108. 2376-2382
- 26 S. A. Katsyuba, P. J. Dyson, E. E. Vandyukova, A. V. Chernova and A. Vidis, Helv. Chim. Acta, 2004, 87, 2556-2565.
- J.-F. Huang, P.-Y. Chen, I.-W. Sun and S. P. Wang, Inorg. Chim. 27 Acta, 2001, **320**, 7–11.
- 28 C.-T. Wu, K. N. Marsh, A. V. Deev and J. A. Boxall, J. Chem. Eng. Data, 2003, 48, 486-491.
- 29 J. M. Crosthwaite, S. N. V. K. Aki, E. J. Maginn and J. F. Brennecke, J. Phys. Chem. B, 2004, 108, 5113-5119.
- 30 J. Pernak, K. Sobaszkiewicz and J. Foksowicz-Flaczyk, Chem.-Eur. J., 2004, 10, 3479-3485.
- J. Pernak, A. Olszowka and R. Olszewski, Pol. J. Chem., 2003, 77, 31 179 - 187
- L. C. Branco, J. N. Rosa, J. J. Moura Ramos and C. A. M. 32 Afonso, Chem.-Eur. J., 2002, 8, 3671-3677.
- 33 Z.-B. Zhou, H. Matsumoto and K. Tatsumi, Chem.-Eur. J., 2004, 10, 6581-6591.
- 34 J. Fraga-Dubreuil, M.-H. Famelart and J. P. Bazureau, Org. Proc. Res. Dev., 2002, 6, 374-378.
- 35 G. Jones and B. C. Bradshaw, J. Am. Chem. Soc., 1933, 55, 1780-1800.
- 36 D. Brouillette, D. E. Irish, N. J. Taylor, G. Perron, M. Odziemkowski and J. E. Desnoyers, Phys. Chem. Chem. Phys., 2002, 4, 6063-6071.
- 37 R. W. Berg, M. Deetlefs, K. R. Seddon, I. Shim and J. M. Thompson, J. Phys. Chem. B, submitted.