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Conductivities of Binary Mixtures of Ionic Liquids with Polar Solvents[†]

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Data for the conductivity, κ, of selected binary mixtures of the ionic liquids [emim][BF_4], [bmim][BF_4], [bmim][PF_6], [bmim][DCA], and [hmim][BF_4] with polar solvents (water, propylene carbonate, dimethylsulfoxide, methanol, dichloromethane) at 25 °C are reported. Additionally, mixture densities, ρ, were determined to convert κ into molar conductivity, Λ. The obtained results were fitted by appropriate interpolation formulas. Where possible, data were compared with information from the literature. Electrode polarization and sample purity, including [BF_4^-] hydrolysis, were considered as possible sources of errors in κ. The effect of viscosity on the accuracy of ρ and thus Λ was checked.

Introduction

Room-temperature ionic liquids (RTILs) are salts with a melting point around or below ambient temperature. Generally formed by bulky and asymmetric cations and/or anions, they exhibit a variety of interesting properties, like negligible vapor pressure, that can be tuned by appropriate choice of anion and cation. This possibility to design (at least in principle) task specific RTILs stimulated the search for applications in chemistry and chemical engineering.[1−4]

Among the large variety of conceivable or already available ionic liquids, those based on substituted imidazolium cations are probably the most intensively studied. This is reflected by a growing number of reviews dealing with the physicochemical properties of such RTILs in the pure state and of their mixtures with cosolvents.[5−7] Surprisingly, systematic studies of the transport properties of binary mixtures of RTILs and polar solvents, like their conductivity, κ, are scarce. Only for aqueous mixtures, a fair number of investigations was published recently.[8−12]

In this paper, we report precise measurements of the conductivity, κ, of several imidazolium-based ionic liquids and their mixtures with polar solvents over the entire miscibility range at 25 °C. Additionally, mixture densities, ρ, were determined to calculate molar concentrations, c, and molar conductivities, Λ, of the investigated samples.

The following systems were studied: 1-*N*-ethyl-3-*N*-methylimidazolium tetrafluoroborate ([emim][BF_4]) + water (W) or + acetonitrile (AN); 1-*N*-butyl-3-*N*-methylimidazolium tetrafluoroborate ([bmim][BF_4]) + W, + AN, + methanol (MeOH), + propylene carbonate (PC), + dimethyl sulfoxide (DMSO), and + dichloromethane (DCM); 1-*N*-butyl-3-*N*-methylimidazolium hexafluorophosphate ([bmim][PF_6]) + AN; 1-*N*-butyl-3-*N*-methylimidazolium dicyanamide ([bmim][DCA]) + W and + AN; and 1-*N*-hexyl-3-*N*-methylimidazolium tetrafluoroborate ([hmim][BF_4]) + W and + AN. The results were compared with available literature data.

As possible reasons for the observed differences between literature data for κ and the present results, effects of electrode polarization and sample purity are discussed. To quantify the latter, measurements of AN mixtures prepared with a commercial batch of [emim][BF_4], further on designated as [emim][BF_4]#1, and with material synthesized after a newly developed procedure, [emim][BF_4]#2, were compared. Additionally, the impact of [BF_4^-] hydrolysis was studied. The effect of sample viscosity on the accuracy of ρ (and thus c and Λ) determined by vibrating-tube densimetry is considered.

Experimental Section

Materials. The following chemicals were used for preparing the RTILs: 1-methylimidazole (MI, Merck & Carl Roth 99 %) was distilled over KOH under reduced pressure, stored over 4 Å molecular sieves, and redistilled under reduced pressure prior to use. 1-Bromoethane (Merck ≥ 99 %), 1-chlorobutane (Merck ≥ 99 %), 1-bromobutane (Merck ≥ 98 %), and 1-chlorohexane (Merck ≥ 99 %) were distilled prior to use. The salts $AgBF_4$ (fluorochem, 99 %), $NaBF_4$ (VWR Prolabo 98.6 %), and KPF_6 (fluorochem, 99 %) were dried but otherwise used as received, whereas sodium dicyanamide ([Na][DCA], Fluka ≥ 96 %) was recrystallized from methanol.

High-purity solvents were used throughout. Water was purified with a Millipore MILLI-Q purification unit, yielding batches with specific resistivity $\geq 18\ \mathrm{M\Omega \cdot cm^{-1}}$. AN (Merck ≥ 99.9 %) was distilled over CaH_2 and stored over 4 Å molecular sieves. The GC purity of the used product was > 99.99 %, and coulometric Karl Fischer titration (Mitsubishi Moisturemeter MCI CA-02) yielded mass fraction $H_2O < 50 \cdot 10^{-6}$. MeOH (Merck ≥ 99.9 %) was distilled over Mg/I_2 yielding GC purity > 99.99 % and mass fraction $H_2O < 20 \cdot 10^{-6}$. PC (Merck 99.5 %), DMSO (Merck 99.5 %), and DCM (Acros 99.9 %) were stored over 4 Å molecular sieves. Prior to use, these solvents had GC purities > 99.94 % for PC and > 99.99 % for DMSO and DCM. Their water mass fractions were $< 20 \cdot 10^{-6}$.

The sample [emim][BF_4]#1 purchased from IoLiTec had a stated purity of > 98 %. It was dried and stored like the other RTILs (see below) but otherwise used as received.

Synthesis. All RTILs were synthesized from MI via appropriate halides (see below). Except for [emim][BF_4], previously published routes were followed.[13−15]

[emim][Br], [bmim][Cl], [bmim][Br], and [hmim][Cl] were obtained by adding a slight molar excess, $n_{\mathrm{RHal}} \approx 1.1 n_{\mathrm{MI}}$, of

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Table 1. Conductivities, κ, of the Investigated Neat Ionic Liquids at 25 °C[a]

	$\kappa/\mathrm{S \cdot m^{-1}}$				
	[emim][BF_4]	[bmim][BF_4]	[bmim][PF_6]	[bmim][DCA]	[hmim][BF_4]
this work	1.553 ± 0.008^{b}	0.353 ± 0.002	0.1469 ± 0.0007	1.139 ± 0.006	0.1228 ± 0.0006
literature	1.63 ± 0.08^{8} 1.39^{9} 1.4^{26} 1.5^{28} 1.4^{30} 1.571 ± 0.2^{32}	0.194 ± 0.002^{25} 0.35^{26} 0.36^{27} 0.46^{28}	0.146 ± 0.003^{22} 0.144 ± 0.004^{23} 0.159 ± 0.002^{24} 0.157 ± 0.002^{25} 0.15^{27}	1.1^{31}	0.16^{28}

[a] Standard uncertainties are given where available. [b] Sample [emim][BF_4]#2.

Table 2. Investigated Mole Fractions, x_{IL}, Corresponding Molar Concentrations, c_{IL}, Densities, ρ, Conductivities, κ, and Molar Conductivities, Λ, of [bmim][BF_4] + Acetonitrile Mixtures at 25 °C[a]

x_{IL}	$\frac{10^{-3}c_{IL}}{\mathrm{mol \cdot m^{-3}}}$	$\frac{10^{-3}c_{IL}{}^{b}}{\mathrm{mol \cdot m^{-3}}}$	$\frac{\rho}{\mathrm{kg \cdot m^{-3}}}$	$\frac{\rho^{b}}{\mathrm{kg \cdot m^{-3}}}$	$\frac{\kappa}{\mathrm{S \cdot m^{-1}}}$	$\frac{10^{4}\Lambda}{\mathrm{S\ m^{2} \cdot mol^{-1}}}$	$\frac{10^{4}\Lambda^{b}}{\mathrm{S\ m^{2} \cdot mol^{-1}}}$
0.009414	0.1744	0.1744	792.87	792.87	1.629	93.4	93.4
0.01981	0.3588	0.3588	809.82	809.81	2.71	75.4	75.4
0.03142	0.5545	0.5545	827.13	827.12	3.51	63.3	63.3
0.04389	0.7538	0.7538	844.54	844.54	4.12	54.7	54.7
0.07179	1.162	1.162	879.61	879.61	4.88	42.0	42.0
0.1077	1.622	1.622	918.10	918.10	5.19	32.0	32.0
0.1538	2.123	2.123	959.09	959.08	5.04	23.8	23.8
0.2149	2.666	2.666	1002.40	1002.38	4.50	16.89	16.89
0.2966	3.239	3.239	1047.32	1047.29	3.62	11.16	11.16
0.3900	3.741	3.741	1085.90	1085.85	2.72	7.27	7.27
0.6126	4.549	4.548	1146.22	1146.07	1.285	2.82	2.82
0.7544	4.893	4.892	1171.38	1171.11	0.802	1.639	1.640
0.8943	5.157	5.155	1190.63	1190.20	0.500	0.970	0.970
1	5.319	5.316	1202.19	1201.64	0.353	0.664	0.664

[a] The standard uncertainty of ρ is 0.05 $\mathrm{kg \cdot m^{-3}}$; the relative standard uncertainty of κ and Λ is 0.5 %. [b] Corrected for the damping effect in vibrating tube density measurements.

the appropriate alkyl halide (1-bromoethane, 1-chlorobutane, 1-bromobutane, or 1-chlorohexane) to a stirred solution (~ 40 % v/v) of MI in AN under an atmosphere of dry nitrogen. The formed 1-*N*-alkyl-3-*N*-methylimidazolium halides [emim][Br], [bmim][Cl], and [bmim][Br] were recrystallized at least four times from AN to give colorless products, whereas [hmim][Cl] was washed twice with ethyl acetate (Merck p.a.).

[emim][BF_4] was obtained via anion metathesis from equimolar amounts of [emim][Br] and $NaBF_4$ dissolved in acetonitrile. After evaporation of the solvent at a vacuum line, dichloromethane was added in excess. The precipitated NaBr was separated by filtration, and DCM was subsequently removed by distillation. This procedure yielded [emim][BF_4] with a Br^- mass fraction of 0.016. By adding equimolar amounts of $AgBF_4$ dissolved in MeOH, the excess Br^- was precipitated as AgBr and removed by filtration. Then, the mixture was kept overnight at ca. −18 °C leading to phase separation into a yellowish methanol phase and a colorless RTIL-rich phase, which was isolated.

[bmim][BF_4], [bmim][PF_6], and [hmim][BF_4] were obtained via anion metathesis from equimolar amounts of the corresponding 1-*N*-alkyl-3-*N*-methylimidazolium halides dissolved in DCM and metal salts ($NaBF_4$, KPF_6 as aqueous solution). The aqueous phase was extracted three times with DCM to collect the RTILs in the organic phase, which was subsequently washed thrice with small amounts of water to remove traces of metal halides (NaCl, NaBr, KCl) before distilling off the solvent. All preparation steps involving aqueous phases were performed rapidly with materials cooled to ≈ 0 °C prior to use to minimize the hydrolysis of [BF_4^-] and [PF_6^-].

[bmim][DCA] was obtained by stirring equimolar amounts of [bmim][Cl] and [Na][DCA] at ≈ 35 °C overnight. To separate the ionic liquid, an excess of DCM was added and the precipitating NaCl filtered off. After removal of the solvent at a vacuum line, this procedure was repeated, yielding a slightly yellowish product.

Sample Preparation. All RTILs were dried at a high-vacuum line ($p < 10^{-8}$ bar) for 7 days at ≈ 40 °C prior to use. Water mass fractions were always $< 50 \cdot 10^{-6}$. Potentiometric titration of RTIL samples in aqueous solution against a standard solution of $AgNO_3$ (Carl Roth) yielded halide mass fractions $< 20 \cdot 10^{-6}$ for [bmim][BF_4], [bmim][PF_6], and [hmim][BF_4], as well as < 0.5 % for [bmim][DCA]. Halide impurities could neither be detected for the commercial nor for the synthesized sample of [emim][BF_4]. Except for [emim][BF_4]#1, where a signal arising from an acidic proton (≈ 0.01 mol fraction of impurity) was observed at a chemical shift of $\approx 6.5 \cdot 10^{-6}$, no contaminations were detected with ^{1}H NMR and ^{19}F NMR (where applicable).

All dried RTILs were stored in an N_2-filled glovebox. N_2-protection was also maintained when preparing the mixtures and during all subsequent steps of sample handling, including the measurements. Mixtures were prepared immediately before use on an analytical balance without buoyancy correction and thus have a standard uncertainty of about ± 0.2 %.

Conductivity. Measurements were performed with the equipment described by Barthel and co-workers,[16,17] consisting of a home-built precision thermostat stable to < 0.003 K in combination with a cold source (Lauda Kryomat K 90 SW), a manually balanced high-precision conductivity bridge, and a set of five two-electrode capillary cells. The cells with cell constants C in the range of (25 to 360) $\mathrm{cm^{-1}}$ were calibrated with aqueous KCl.[18]

All measurements were carried out at (25 ± 0.01) (NIST traceable Pt sensor and bridge, ASL) by recording the cell resistance as a function of AC frequency, ν, between 120 Hz and 10 kHz. To eliminate electrode polarization, the conductivity, κ, of each sample was obtained as $\kappa = C/R_\infty$ from the extrapolation $R_\infty = \lim_{\nu\to\infty} R(\nu)$ using the empirical function $R(\nu) = R_\infty + A/\nu^a$; A is specific to the cell and $a \approx 0.5$.[19]

Measurements of selected samples with different cells agreed within 0.5 %. Thus, this value may be taken as a good estimate for the relative uncertainty of the present κ and the derived molar conductivities, $\Lambda = \kappa/c_{\mathrm{IL}}$.

Density. To convert RTIL mole fractions, x_{IL}, into molar concentrations, c_{IL}, the densities, ρ, of the mixtures were determined at (25 ± 0.02) °C with a vibrating tube densimeter (Anton Paar DMA 60, DMA 601HT). The instrument was calibrated with degassed water and purified nitrogen at atmospheric pressure, assuming densities from standard sources.[20] The precision of the measurements was ± 0.001 $\mathrm{kg \cdot m^{-3}}$. Taking into account the sources of error (calibration, measurement, purity of materials), we estimate the uncertainty of ρ to be within ± 0.05 $\mathrm{kg \cdot m^{-3}}$.

Results and Discussion

Conductivities of Neat Ionic Liquids. Table 1 summarizes the measured κ together with available literature data for the investigated ionic liquids. Where possible, published uncertainties were included. The conductivity of a sample depends on the charge density (which is high in RTILs) and on the mobility of the ions, which is coupled to viscosity via the Stokes–Einstein relation.[21] As a consequence of their large viscosity, pure RTILs generally exhibit only moderate values of κ compared to their binary mixtures with polar solvents (see below).

The literature survey reveals a considerable scatter of the available κ for the pure RTILs. For each studied RTIL, our data are usually in reasonable agreement with some of the published values. Especially for [bmim][$\mathrm{PF_6}$], which is easily accessible in high purity, our value is—within the claimed errors—in quantitative agreement with the data of Widegren et al.[22] and Kanakubo et al.,[23] but it is significantly smaller than those published by Li et al.[24,25] For [emim][$\mathrm{BF_4}$], larger deviations of up to 10 % may reflect the more demanding synthesis of this RTIL, but differences of 30 % for [hmim][$\mathrm{BF_4}$] and even 45 % for [bmim][$\mathrm{BF_4}$] are surprising as the purification of these RTILs is straightforward.

One might think that the obvious discrepancies appearing in Table 1 reflect the purity of the samples used by the various groups. However, the published contents of water and halide impurities are generally small.[9,22−28] Measurement of our first [bmim][$\mathrm{BF_4}$] sample, which was prepared via the [bmim][Br] route and contained $1.5 \cdot 10^{-4}$ mass fraction $\mathrm{Br^-}$ yielded $\kappa = 0.360\ \mathrm{S \cdot m^{-1}}$, whereas subsequent batches, prepared via [bmim][Cl] and containing $< 20 \cdot 10^{-6}$ mass fraction $\mathrm{Cl^-}$, had $\kappa = 0.353\ \mathrm{S \cdot m^{-1}}$. Thus, from the sample purities stated in the literature, a scatter of κ in the order of (2 to 3) % would be expected.

Further possible sources of error are sample handling and the measurement of conductivity itself. Generally, commercial instruments operating at a fixed AC frequency (usually 1 kHz) were used for the literature data of Table 1. However, it is well-known that the measured cell impedance depends on frequency due to the double-layer capacitance of the electrodes, so that precise determinations of κ require correction for this systematic error.[19] In addition to comparable sample purity, the correction for electrode polarization applied by the groups of Widegren et al.,[22] Kanakubo et al.,[23] and by us is certainly the major reason for the excellent agreement of the corresponding κ values. However, perusal of our data revealed that conductivities corrected to $\nu^{-1} \to 0$ differed from κ determined at 1 kHz by 1 % at most. Thus, electrode polarization cannot explain the large deviations noted from Table 1.

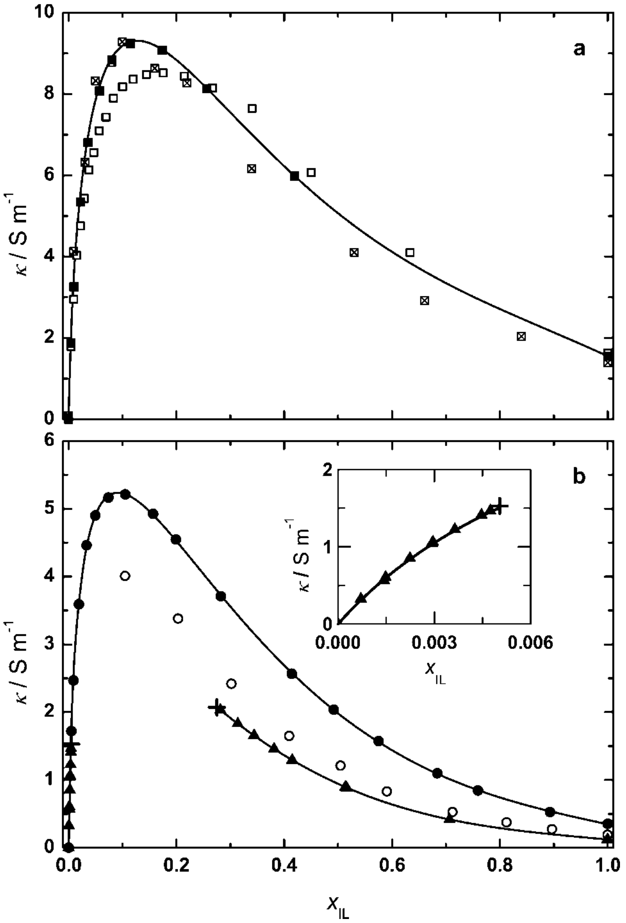

Figure 1. Conductivities, κ, of mixtures of (a) [emim][$\mathrm{BF_4}$]#2 (squares), (b) [bmim][$\mathrm{BF_4}$] (circles), and [hmim][$\mathrm{BF_4}$] (triangles) with water at 25 °C. Data represented by filled symbols were determined in this work, and lines represent fits with eq 2. Open symbols refer to the data of □, ref 8; square with an × in it, ref 9; ○, ref 25. The observed phase boundaries (+) for [hmim][$\mathrm{BF_4}$] + W are indicated.

It is well-known that the anions [$\mathrm{BF_4^-}$] and [$\mathrm{PF_6^-}$] are prone to hydrolysis[33−37] with one of the reaction products being HF, which may attack the conductivity cell. To study the effect of anion hydrolysis, κ was measured in a PTFE flask at 1 kHz as a function of time, t, for a [bmim][$\mathrm{BF_4}$] + W mixture of $x_{\mathrm{IL}} = 0.008604$ (see Supporting Information). Within six days, after which the experiment was stopped, κ rose from 2.41 $\mathrm{S \cdot m^{-1}}$ to 2.59 $\mathrm{S \cdot m^{-1}}$ approaching a plateau value ($\kappa(\infty) \approx 1.1\kappa(t_0)$) in a (probably pseudo-) first-order reaction with half-life $\tau \approx 1.2$ days. Elucidating the mechanism of [$\mathrm{BF_4^-}$] hydrolysis was beyond the scope of this study, but the rather moderate increase of κ suggests that some equilibrium is reached well before all [$\mathrm{BF_4^-}$] is decomposed. Thus, [$\mathrm{BF_4^-}$] and [$\mathrm{PF_6^-}$] hydrolysis may contribute to the scatter of κ values reported in Table 1 but also cannot explain the obvious outliers for [emim][$\mathrm{BF_4}$],[9] [bmim][$\mathrm{BF_4}$],[25,28] and [hmim][$\mathrm{BF_4}$][28] if we assume that these samples were sufficiently dry and properly stored.[29] In any case, with the measurement procedure followed in our experiments (see above), errors in κ associated with the hydrolysis of [$\mathrm{BF_4^-}$] and [$\mathrm{PF_6^-}$] remained well below 0.5 %.

Jarosik et al.[9] and Leys et al.[28] used impedance spectroscopy in combination with parallel-plate capacitor cells to determine κ. Possibly, such equipment is difficult to calibrate for high-precision conductivity measurements. Notable in the investigation of Li et al.[25] is the rather low density of 1182.2 $\text{kg}\cdot\text{m}^{-3}$ reported for [bmim][BF_4] at 25 °C, suggesting major contaminations of the sample. In contrast, our value of $\rho = 1202.19$ $\text{kg}\cdot\text{m}^{-3}$ is in good agreement with previously reported densities of 1201.420 $\text{kg}\cdot\text{m}^{-3}$,[38] 1202 $\text{kg}\cdot\text{m}^{-3}$,[27] 1201.34 $\text{kg}\cdot\text{m}^{-3}$,[39] (1201.29 and 1201.4) $\text{kg}\cdot\text{m}^{-3}$,[40] and 1202.298 $\text{kg}\cdot\text{m}^{-3}$.[41]

Conductivities of Binary Mixtures. The κ values for the investigated binary mixtures, covering the entire miscibility range, are listed in Tables 2 to 5. Selected results are displayed in Figures 1 to 3.

All investigated systems are completely miscible at 25 °C, except for [hmim][BF_4] + W. For this system, Wagner et al.[37] determined an upper critical solution temperature of $T_c = 58.16$ °C at the RTIL mass fraction of 0.4097 ($x_{IL} \approx 0.047$). At 25 °C, we obtained the phase boundaries for the RTIL-rich (indicated by superscript "IL"; $x_{IL}^{IL} = 0.2750$) and the W-rich phases (superscript "W"; $x_{IL}^{W} = 0.0050$) by comparing the conductivities of the saturated phases ($\kappa^{IL} = 2.07\ \text{S}\cdot\text{m}^{-1}$ and $\kappa^{W} = 1.53\ \text{S}\cdot\text{m}^{-1}$) with suitable extrapolations of $\kappa = f(x_{IL})$ from the corresponding homogeneous regions (Figure 1b).

The dependence of conductivity on RTIL concentration follows the typical pattern of concentrated electrolyte solutions: after a rapid initial rise at low x_{IL} due to the increasing number of charge carriers, κ passes through a pronounced maximum at $x_{IL} \approx 0.1$ to 0.25 (depending on the mixture) due to the counterbalancing effect of the rapidly rising viscosity on ion mobility.

To reproduce such a concentration dependence, the empirical Casteel-Amis[42] equation is widely used. Generally, data fitting is done on the molality scale, and obtained parameters are the maximum conductivity, κ_{max}, the corresponding concentration, and shape parameters, a and b. For the present systems, the Casteel-Amis equation can be reasonably applied in the mole-fraction scale, that is

$$\kappa = \kappa_{max}\left(\frac{x_{IL}}{x_{max}}\right)^{a} \exp\left[b(x_{IL} - x_{max})^2 - a\frac{x_{IL} - x_{max}}{x_{max}}\right] \qquad (1)$$

where x_{max} is the RTIL mole fraction at κ_{max}.

The obtained fit parameters are summarized in Table S1 of the Supporting Information together with the corresponding regression coefficients, r^2, and the standard deviations, σ, of the fits. Generally, the four-parameter description of $\kappa = f(x_{IL})$ with eq 1 is excellent, yielding $r^2 > 0.999$ and $\sigma < 4\cdot10^{-2}$ $\text{S}\cdot\text{m}^{-1}$ for most mixtures. Equation 1 can even be applied for [hmim][BF_4] + W, where the data sets on both sides of the miscibility gap can be well described with a single set of parameters (x_{max}, κ_{max}, a, b) albeit with x_{max} in the biphasic region. However, for several mixtures, systematic deviations around x_{max} are obvious (Figure S3 of the Supporting Information).

A significantly better interpolation of the present conductivity data can be obtained with the Padé (n, m) approximation

$$\kappa = x_{IL}(1 - x_{IL})\frac{\sum_{i=1}^{n} A_i(2x_{IL} - 1)^{i-1}}{1 + \sum_{j=1}^{m} B_j(2x_{IL} - 1)^{j}} + C_1 x_{IL} \qquad (2)$$

at the cost of an increased number of adjustable parameters. In eq 2, $\kappa = 0$ is assumed for the pure solvent (valid within our error limits for κ), whereas parameter C_1 represents the conductivity of the pure RTIL. In the fitting procedure, C_1 was adjusted but always found to be close to the measured data. The best results were obtained by using a seven-parameter fit with $n = 4$ and $m = 2$. The parameters A_i, B_i, and C_1 obtained by least-squares analysis are summarized in Table S2 of the Supporting Information, together with the corresponding standard deviations of the fits, σ ($r^2 > 0.999$ in all cases). The lines in Figures 1 to 3 represent such fits.

Table 3. Investigated Mole Fractions, x_{IL}, Corresponding Molar Concentrations, c_{IL}, Densities, ρ, Conductivities, κ, and Molar Conductivities, Λ, of Binary RTIL + Acetonitrile Mixtures at 25 °C[a]

x_{IL}	$10^{-3}c_{IL}$ / $\text{mol}\cdot\text{m}^{-3}$	ρ / $\text{kg}\cdot\text{m}^{-3}$	κ / $\text{S}\cdot\text{m}^{-1}$	$10^4\ \Lambda$ / $\text{S}\cdot\text{m}^2\cdot\text{mol}^{-1}$
[emim][BF_4]#1				
0.01082	0.2014	795.48	1.90	94.4
0.01646	0.3036	804.68	2.55	84.0
0.02252	0.4114	814.30	3.13	76.1
0.04929	0.8621	853.38	4.89	56.7
0.08059	1.342	893.87	6.03	44.9
0.1218	1.903	939.88	6.72	35.3
0.1736	2.513	988.57	6.92	27.6
0.2371	3.146	1038.16	6.65	21.2
0.3264	3.867	1093.25	5.90	15.26
0.4565	4.672	1153.25	4.64	9.94
0.6520	5.528	1215.55	3.10	5.61
0.8336	6.092	1255.87	2.11	3.46
1	6.484	1283.70	1.553	2.40
[emim][BF_4]#2				
0.008411	0.1571	791.26	1.585	100.9
0.01528	0.2823	802.59	2.46	87.1
0.02253	0.4113	813.87	3.14	76.4
0.04942	0.8649	854.17	4.94	57.2
0.1007	1.623	916.26	6.50	40.0
0.1433	2.165	960.07	6.94	32.0
0.2043	2.829	1012.50	6.91	24.4
0.2778	3.490	1063.36	6.41	18.36
0.3840	4.245	1120.11	5.41	12.75
0.4888	4.828	1163.04	4.44	9.21
0.6478	5.500	1211.72	3.20	5.81
0.7590	5.867	1237.95	2.54	4.33
0.8902	6.221	1263.01	1.95	3.13
1	6.468	1280.38	1.553	2.40
[bmim][PF_6]				
0.007571	0.1404	795.63	1.485	105.8
0.01576	0.2863	815.17	2.54	88.7
0.02489	0.4415	835.56	3.39	76.8
0.03448	0.5970	855.89	4.05	67.9
0.05838	0.9529	901.77	5.00	52.5
0.08779	1.338	950.71	5.39	40.3
0.1261	1.766	1004.47	5.27	29.8
0.1772	2.238	1062.70	4.68	20.9
0.2521	2.780	1128.61	3.63	13.04
0.3649	3.374	1199.71	2.30	6.82
0.5591	4.038	1278.14	0.995	2.47
0.7291	4.415	1321.97	0.469	1.062
0.8729	4.652	1349.76	0.253	0.543
1	4.815	1368.32	0.1469	0.305
[hmim][BF_4]				
0.004117	0.07700	784.24	0.838	108.8
0.008445	0.1560	791.63	1.442	92.5
0.01744	0.3142	806.26	2.35	74.7
0.03816	0.6489	836.42	3.51	54.2
0.06486	1.028	869.76	4.13	40.2
0.09763	0.1427	903.86	4.25	29.8
0.1399	1.855	939.67	3.96	21.4
0.1943	2.300	975.94	3.37	14.67
0.2712	2.785	1014.86	2.53	9.08
0.3907	3.322	1056.74	1.543	4.65
0.5902	3.894	1100.45	0.656	1.685
0.7435	4.183	1122.12	0.344	0.823
0.8889	4.287	1137.20	0.192	0.437
1	4.512	1146.34	0.1228	0.272

[a] The standard uncertainty of ρ is 0.05 $\text{kg}\cdot\text{m}^{-3}$; the relative standard uncertainty of κ and Λ is 0.5 %.

The effect of sample purity on conductivity was checked by comparing the commercial sample [emim][BF_4]#1 with material synthesized in our laboratory, [emim][BF_4]#2, in mixtures with

Table 4. Investigated Mole Fractions, x_{IL}, Corresponding Molar Concentrations, c_{IL}, Densitites, ρ, Conductivities, κ, and Molar Conductivities, Λ, of Binary RTIL + Water Mixtures at 25 °C[a]

x_{IL}	$10^{-3}c_{\mathrm{IL}}$ / $\mathrm{mol \cdot m^{-3}}$	ρ / $\mathrm{kg \cdot m^{-3}}$	κ / $\mathrm{S \cdot m^{-1}}$	$10^4\ \Lambda$ / $\mathrm{S \cdot m^2 \cdot mol^{-1}}$
		[emim][BF$_4$]#2		
0.004746	0.2534	1007.69	1.874	73.9
0.01001	0.5144	1018.31	3.26	63.4
0.02226	1.052	1040.22	5.35	50.9
0.03637	1.572	1061.36	6.81	43.3
0.05733	2.200	1087.31	8.08	36.7
0.08102	2.761	1110.93	8.84	32.0
0.1150	3.376	1136.45	9.24	27.4
0.1740	4.122	1168.60	9.08	22.0
0.2564	4.790	1198.61	8.13	16.98
0.4190	5.532	1233.28	5.99	10.82
1	6.484	1283.70	1.553	2.40
		[bmim][BF$_4$]		
0.005053	0.2669	1007.00	1.720	64.3
0.008751	0.4471	1013.47	2.47	55.2
0.01927	0.9018	1030.78	3.59	39.8
0.03304	1.391	1047.81	4.46	32.1
0.04969	1.867	1065.19	4.90	26.3
0.07385	2.400	1084.47	5.17	21.5
0.1053	2.910	1103.47	5.21	17.92
0.1566	3.482	1124.77	4.93	14.15
0.1991	3.810	1137.30	4.55	11.94
0.2824	4.247	1154.46	3.71	8.73
0.4140	4.656	1171.08	2.57	5.51
0.4919	4.815	1177.86	2.04	4.23
0.5749	4.946	1183.94	1.574	3.18
0.6838	5.078	1190.14	1.098	2.16
0.7594	5.150	1193.53	0.846	1.643
0.8931	5.253	1198.74	0.527	1.003
1	5.319	1202.19	0.353	0.664
		[bmim][DCA]		
0.009639	0.4879	1003.22	2.02	41.5
0.02791	1.214	1011.25	3.49	28.7
0.05432	1.965	1019.63	4.43	22.5
0.07995	2.485	1025.43	4.80	19.3
0.1112	2.952	1031.05	4.90	16.60
0.1933	3.708	1040.01	4.47	12.04
0.3214	4.304	1047.31	3.55	8.25
0.4686	4.661	1051.86	2.71	5.82
0.6386	4.898	1055.38	2.00	4.09
0.8742	5.092	1058.33	1.366	2.68
1	5.160	1059.12	1.139	2.21
		[hmim][BF$_4$]		
0.0007116	0.03906	998.06[b]	0.327	83.8
0.001428	0.07778	999.52	0.567	72.9
0.001482	0.08064	999.64[b]	0.608	75.4
0.002238	0.1208	1001.24[b]	0.854	70.7
0.002960	0.1568	1002.63	1.049	66.9
0.002960	0.1586	1002.70[b]	1.064	67.1
0.003642	0.1937	1003.94[b]	1.225	63.3
0.004470	0.2356	1005.24	1.411	59.9
0.004747	0.2495	1005.61[b]	1.466	58.8
0.2816	3.712	1113.63[b]	2.03	5.48
0.3140	3.806	1116.76	1.829	4.81
0.3441	3.881	1119.43[b]	1.655	4.27
0.3813	3.962	1122.43	1.456	3.68
0.4148	4.024	1124.75[b]	1.293	3.21
0.5139	4.170	1130.58	0.898	2.16
0.5161	4.173	1130.73[b]	0.885	2.12
0.7069	4.354	1138.70[b]	0.417	0.958
1	4.512	1146.34	0.1228	0.272

[a] The standard uncertainty of ρ is 0.05 $\mathrm{kg \cdot m^{-3}}$; the relative standard uncertainty of κ and Λ is 0.5 %. [b] Interpolated values.

Table 5. Investigated Mole Fractions, x_{IL}, Corresponding Molar Concentrations, c_{IL}, Densities, ρ, Conductivities, κ, and Molar Conductivities, Λ, of Binary [bmim][BF$_4$] + Polar Solvent Mixtures at 25 °C[a]

x_{IL}	$10^{-3}c_{\mathrm{IL}}$ / $\mathrm{mol \cdot m^{-3}}$	ρ / $\mathrm{kg \cdot m^{-3}}$	κ / $\mathrm{S \cdot m^{-1}}$	$10^4\ \Lambda$ / $\mathrm{S \cdot m^2 \cdot mol^{-1}}$
		MeOH		
0.007409	0.1776	802.48	0.867	48.8
0.01543	0.3603	818.28	1.451	40.2
0.02435	0.5526	834.29	1.97	35.6
0.03355	0.7396	849.76	2.40	32.4
0.05717	1.173	885.02	3.30	28.1
0.08589	1.624	921.13	3.81	23.4
0.1242	2.127	961.01	4.18	19.7
0.1755	2.662	1002.48	4.26	15.99
0.2480	3.237	1046.31	3.92	12.11
0.3624	3.877	1094.85	3.09	7.98
0.5583	4.556	1145.28	1.760	3.86
		PC		
0.02318	0.2653	1201.32	0.537	20.2
0.04836	0.5380	1202.51	0.873	16.22
0.1028	1.078	1204.30	1.230	11.41
0.1601	1.583	1205.43	1.346	8.51
0.2277	2.107	1206.17	1.332	6.32
0.3056	2.634	1206.51	1.229	4.67
0.4070	3.219	1206.44	1.055	3.28
0.5126	3.733	1206.03	0.875	2.34
0.6192	4.174	1205.48	0.715	1.713
0.7173	4.523	1204.39	0.593	1.310
0.8497	4.930	1203.39	0.463	0.939
		DMSO		
0.01925	0.2618	1101.56	0.687	26.2
0.03427	0.4556	1106.21	1.029	22.6
0.07837	0.9763	1117.80	1.558	15.96
0.1247	1.457	1128.31	1.715	11.77
0.1866	2.011	1139.50	1.672	8.31
0.2554	2.536	1150.71	1.502	5.92
0.3251	2.986	1159.40	1.310	4.39
0.4423	3.611	1171.71	1.015	2.81
0.5246	3.969	1178.20	0.854	2.15
0.6132	4.301	1184.27	0.711	1.653
0.7494	4.728	1192.13	0.543	1.149
		DCM		
0.007550	0.1156	1316.60	0.0602	5.21
0.01921	0.2883	1314.92	0.200	6.92
0.02714	0.4016	1313.40	0.310	7.72
0.03878	0.5627	1311.80	0.436	7.76
0.07987	1.083	1304.97	0.980	9.05
0.1395	1.726	1294.06	1.427	8.27
0.1940	2.219	1284.29	1.550	6.99
0.2674	2.773	1271.96	1.607	5.80
0.3355	3.199	1261.43	1.530	4.78
0.4787	3.902	1242.95	1.209	3.10
0.6019	4.360	1230.33	0.930	2.13
0.7730	4.846	1216.18	0.620	1.278
0.8496	5.024	1211.19	0.511	1.018
0.9107	5.152	1207.46	0.441	0.856
1	5.319	1202.19	0.353	0.664

[a] The standard uncertainty of ρ is 0.05 $\mathrm{kg \cdot m^{-3}}$; the relative standard uncertainty of κ and Λ is 0.5 %.

AN. The results are summarized in Figure 2c as relative deviations $\delta_{\mathrm{fit}} = (\kappa_{\mathrm{fit}} - \kappa)/\kappa_{\mathrm{fit}}$ of the experimental data, κ, from the interpolations, κ_{fit}, obtained from fitting the data set for [emim][BF$_4$]#2 with eq 2. For sample #2, the random scatter of κ around κ_{fit} was generally well below 0.5 % and thus below the claimed accuracy of our instrumentation. On the other hand, systematically smaller conductivities were observed for the commercial sample #1. This seems surprising in view of the acid-proton signal detected by NMR for this sample but may reflect a higher viscosity of batch #1.

Figure 1a compares the κ values obtained for [emim][BF$_4$]#2 + W in this study with results (κ_{lit}) published by Vila et al.[8] and by Jarosik et al.[9] At low RTIL contents, the agreement is fairly good, and the present values for x_{max} and κ_{max} are roughly consistent with those of Jarosik et al.[9] However, for $x_{\mathrm{IL}} > 0.1$ rather large relative deviations, up to $\delta_{\mathrm{lit}} = (\kappa - \kappa_{\mathrm{lit}})/\kappa \approx 0.2$,

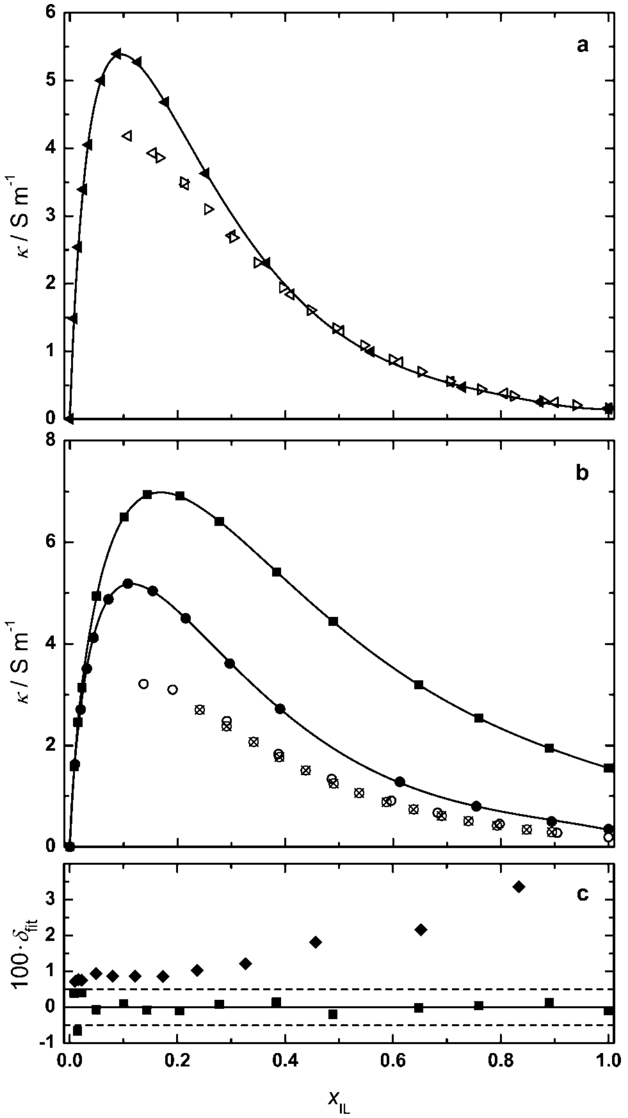

Figure 2. Conductivities, κ, of mixtures of (a) [bmim][PF$_6$] (triangles), (b) [bmim][BF$_4$] (circles), and [emim][BF$_4$]#2 (squares) with acetonitrile at 25 °C. Data represented by filled symbols were determined in this work, and lines represent fits with eq 2. Open symbols refer to: open triangle pointing right, ⊗, ref 24; open triangle pointing left, ○, ref 25. Panel (c) shows the relative deviations, δ_{fit}, of the experimental conductivities of samples ◆, [emim][BF$_4$]#1 and ■, [emim][BF$_4$]#2 from the fit of the latter data set with eq 2.

occur. As already discussed for the pure RTIL, these deviations are possibly connected to the technique used by these authors. The conductivity peak of Vila et al.[8] is significantly smaller and at a higher RTIL mole fraction so that at low x_{IL} the present κ exceed their data, whereas for RTIL-rich mixtures $\kappa < \kappa_{\mathrm{lit}}$. The only plausible explanation here is sample contamination well beyond the claimed purity.

For [bmim][BF$_4$] + W, a comparison with the data of Li et al.[24] (Figure 1b) is possible. Since already the conductivity of pure [bmim][BF$_4$] reported by these authors is significantly smaller than the value of this investigation (see above), it is not surprising that also for the mixtures $\kappa_{\mathrm{lit}} < \kappa$ with $0.2 \lesssim \delta_{\mathrm{lit}} \lesssim 0.5$. Similar deviations were observed for the systems [bmim][BF$_4$] + AN (Figure 2b) and [bmim][BF$_4$]/DCM (Figure 3).[24,25] On the other hand, for [bmim][PF$_6$] + AN (Figure 2a), the data of Li et al.[25,24] are in reasonable agreement with the present κ for $x_{\mathrm{IL}} > 0.4$ but deviate increasingly on further dilution.

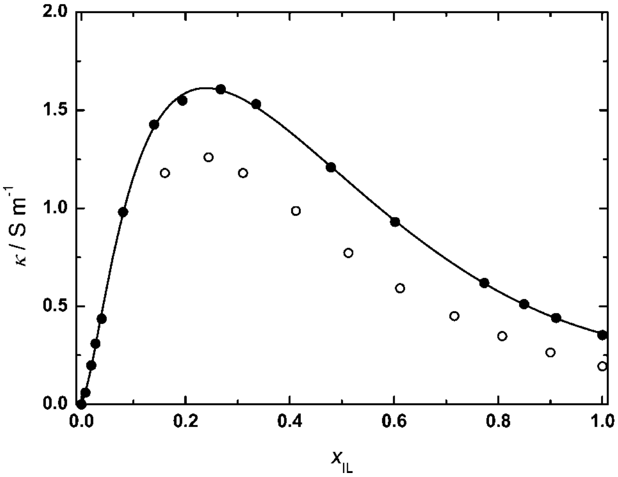

Figure 3. Conductivities, κ, of [bmim][BF$_4$] + DCM mixtures at 25 °C. Data represented by filled symbols were determined in this work, and the line shows the fit with eq 2. Open symbols refer to the data of ref 25.

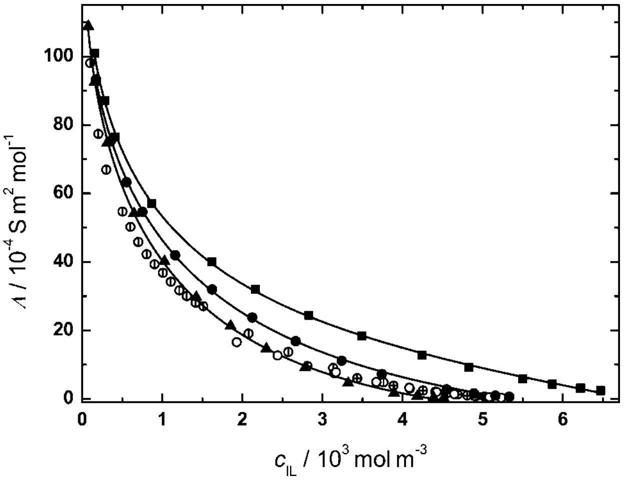

Figure 4. Molar conductivities, Λ, of mixtures of acetonitrile with ■, [emim][BF$_4$]#2; ●, [bmim][BF$_4$]; and ▲, [hmim][BF$_4$] at 25 °C. Lines represent fits with eq 3. Open symbols represent [bmim][BF$_4$] data from ⊕, ref 24; ○, ref 25; ⦶, ref 51.

Molar Conductivities of Binary Systems. Tables 2 to 5 include the molar conductivities, $\Lambda = \kappa/c_{\mathrm{IL}}$, of the investigated mixtures. Typical examples are shown in Figures 4 and 5. The data were fitted to the equation

$$\Lambda = D_1 - D_2\sqrt{c_{\mathrm{IL}}} + D_3 c_{\mathrm{IL}} \ln c_{\mathrm{IL}} + D_4 c_{\mathrm{IL}} \tag{3}$$

which corresponds to the truncated series expression derived for dilute electrolyte solutions from the theory of Onsager,[43,44] but without a theoretical meaning of the parameters D_i, $i = 1,..., 4$. The obtained parameters and the corresponding r^2 and σ values are summarized in Table S3 of the Supporting Information.

Reliable calculation of Λ requires accurate values for the molar electrolyte concentration, c_{IL}, and thus the density, ρ, of the solution. Vibrating-tube densimetry is very precise. However, the oscillation period of the vibrating tube depends on sample viscosity, η, leading to systematic errors in ρ.[45] Generally, this effect is small; however, pure RTILs are often very viscous, and Heintz et al. showed that here viscosity correction of the density data is worthwhile.[46]

Unfortunately, viscosity data for RTIL mixtures are scarce and published data—especially for the pure RTILs—often scatter considerably. Using the results of Wang et al.,[47] we checked

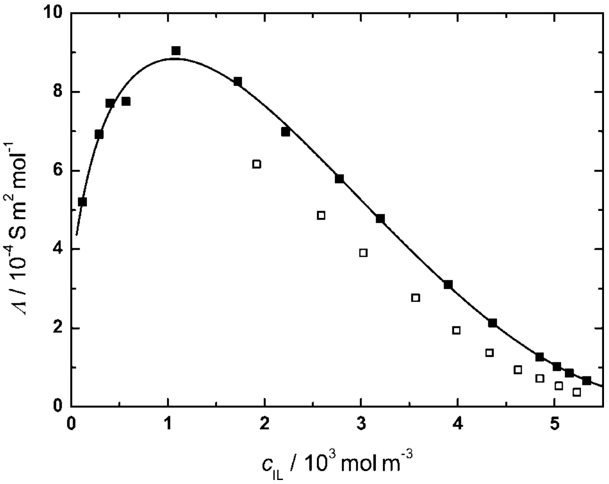

Figure 5. Molar conductivity, Λ, of [bmim][BF_4] + DCM mixtures at 25 °C. Lines represent fits with eq 3 with additional term D_5x^2. Filled symbols were determined in our laboratory, and open symbols refer to ref 25.

the magnitude of the viscosity correction suggested by Heintz et al.[46] on ρ, c, and Λ for [bmim][BF_4] + AN mixtures (Table 2). The used viscosities were considered reliable as the value given by the authors for the pure RTIL, $\eta = 0.110308$ Pa·s,[47] is in good agreement with those published by several other groups.[25,40,41,48] For the other investigated mixtures, a viscosity correction of ρ was not possible due to lacking $\eta(x_{IL})$.

Comparison of columns 4 and 5 of Table 2 indicates that for $\eta \gtrsim 6$ mPa·s, corresponding to $x_{IL} \gtrsim 0.4$, the effect of η on ρ is larger than the claimed accuracy ($\pm$ 0.05 kg·m^{-3}) of our density measurements. However, even for pure [bmim][BF_4], the systematic error in ρ and thus c_{IL} does not exceed 0.05 %. Since our accuracy in κ is only ± 0.5 %, viscosity correction of the reported molar conductivities is negligible. Obviously, this will not be true for a discussion of excess volumes and related quantities.

For the investigated mixtures, it was found that in general—[bmim][BF_4] + DCM being the only exception—Λ decreases continuously with increasing RTIL concentration (Tables 2 to 5, Figure 4). Probably, this reflects decreasing ion mobility induced by rising viscosity. Association effects may contribute, but dielectric relaxation studies suggest that the concentration of ion pairs in mixtures of RTILs with polar solvents is small.[49] This is probably different for [bmim][BF_4] + DCM, where a pronounced maximum is observed for Λ at $c_{IL} \approx 1 \cdot 10^3$ mol·m^{-3} ($x_{IL} \approx 0.08$) (see Figure 5). To fit the experimental data of this mixture, eq 3 was extended by the term D_5x^2 ($D_5 = 1.157 \cdot 10^{-10}$ S·m^8·mol^{-3}). For [bmim][BF_4] + DCM mixtures, strong ion association was observed with dielectric spectroscopy at low c_{IL}, but already at $x_{IL} \approx 0.3$ ($c_{IL} \approx 3 \cdot 10^3$ mol·m^{-3}) ion pairs are negligible.[50] The observed increase of Λ may thus indicate the redissociation of ion pairs as a consequence of increasing ion—ion interactions which is finally outweighed by decreasing ion mobility due to rising viscosity.

Not unexpectedly, comparison of the present Λ values with the limited number of literature data[8,24,25,28,51] reveals significant deviations (Figures 4 and 5). The possible reasons were already discussed above.

Conclusions

Conductivities, κ, densities, ρ, and molar conductivities, Λ, of selected binary mixtures of the ionic liquids [emim][BF_4], [bmim][BF_4], [bmim][PF_6], [bmim][DCA], and [hmim][BF_4] with polar solvents (water, propylene carbonate, DMSO, methanol, and dichloromethane) at 25 °C were reported. The data for κ and Λ were compared with literature values where possible. While our results for the pure RTILs conform excellently with *some* of the published data, the agreement with the limited number of mixture studies is poor.

As possible sources of error, electrode polarization and sample purity (as stated in the quoted literature) were considered. [BF_4^-] hydrolysis was discussed. The effect of viscosity on the accuracy of ρ and thus Λ was checked. It was found that these effects may explain some of the observed deviations of our results from the literature. However, they cannot account for the very large discrepancies seen in Figures 1 to 5. This suggests that some of the data found in the literature are flawed by major contaminations of the studied samples.

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Dedicated to Professor Robin H. Stokes on the occasion of his 90th birthday. The authors thank W. Kunz for access to laboratory facilities and R. Neueder for helpful discussions.

Supporting Information Available:

Graphs of the time-dependent conductivity of hydrolyzing [bmim][BF_4] + W and of representative fits with eq 1. Tables of the fit parameters for κ and Λ obtained with eqs 1 to 3. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Welton, T. Room-temperature ionic liquids. Solvents for synthesis and catalysis. *Chem. Rev.* **1999**, *99*, 2071–2083.
(2) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH: Weinheim, 2003.
(3) Endres, F.; El Abedin, S. Z. Air and water stable ionic liquids in physical chemistry. *Phys. Chem. Chem. Phys.* **2006**, *8*, 2101–2116.
(4) Pârvulescu, V. I.; Hardacre, C. Catalysis in ionic liquids. *Chem. Rev.* **2007**, *107*, 2615–2665.
(5) Marsh, K. N.; Boxall, J. A.; Lichtenthaler, R. Room temperature ionic liquids and their mixtures — a review. *Fluid Phase Equilib.* **2004**, *219*, 93–98.
(6) MacFarlane, D. R.; Seddon, K. R. Ionic liquids — progress on the fundamental issues. *Aust. J. Chem.* **2007**, *60*, 3–5.
(7) Weingärtner, H. Understanding ionic liquids at the molecular level: facts, problems, and controversies. *Angew. Chem., Int. Ed.* **2008**, *47*, 654–670.
(8) Vila, J.; Ginés, P.; Rilo, E.; Cabeza, O.; Varela, L. M. Great increase of the electrical conductivity of ionic liquids in aqueous solutions. *Fluid Phase Equilib.* **2006**, *247*, 32–39.
(9) Jarosik, A.; Krajewski, S. R.; Lewandowski, A.; Radzimski, P. Conductivity of ionic liquids in mixtures. *J. Mol. Liq.* **2006**, *123*, 43–50.
(10) Liu, W.; Zhao, T.; Zhang, Y.; Wang, H.; Yu, M. The physical properties of aqueous solutions of the ionic liquid [BMIM][BF_4]. *J. Solution Chem.* **2006**, *35*, 1337–1346.
(11) Comminges, C.; Barhdadi, R.; Laurent, M.; Troupel, M. Determination of viscosity, ionic conductivity, and diffusion coefficients in some binary systems: ionic liquids + molecular solvents. *J. Chem. Eng. Data* **2006**, *51*, 680–685.
(12) Widegren, J. A.; Magee, J. W. Density, viscosity, speed of sound, and electrolytic conductivity for the ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and its mixtures with water. *J. Chem. Eng. Data* **2007**, *52*, 2331–2338.
(13) Holbrey, J. D.; Seddon, K. R. The phase behaviour of 1-alkyl-3-methylimidazolium tetrafluoroborates; ionic liquids and ionic liquid crystals. *J. Chem. Soc., Dalton Trans.* **1999**, *13*, 2133–2139.
(14) Fredlake, C. P.; Crosthwaite, J. M.; Hert, D. G.; Aki, S. N.; Brennecke, J. F. Thermophysical properties of imidazolium-based ionic liquids. *J. Chem. Eng. Data* **2004**, *49*, 954–964.
(15) Cammarata, L.; Kazarian, S. G.; Salter, P. A.; Welton, T. Molecular states of water in room temperature ionic liquids. *Phys. Chem. Chem. Phys.* **2001**, *3*, 5192–5200.
(16) Barthel, J.; Wachter R.; Gores H.-J. Temperature dependence of conductance of electrolytes in nonaqueous solutions. *Modern Aspects of Electrochemistry*; Conway, B. E., Bockris, J. O'M., Eds.; 1979; Vol. 13, pp 1−79.

(17) Barthel, J.; Graml, H.; Neueder, R.; Turq, P.; Bernard, O. Electrolyte conductivity from infinite dilution to saturation. *Curr. Top. Solution Chem.* **1994**, *1*, 223–239.

(18) Barthel, J.; Feuerlein, F.; Neueder, R.; Wachter, R. Calibration of conductance cells at various temperatures. *J. Solution Chem.* **1980**, *9*, 209–219.

(19) Hoover, T. B. Conductance of potassium chloride in highly purified N-mehylpropionamide from 20 to 40 °. *J. Phys. Chem.* **1964**, *68*, 876–879.

(20) Lide, D. R. *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 2004.

(21) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*; Butterworths: London, 1959.

(22) Widegren, J. A.; Saurer, E. M.; Marsh, K. N.; Magee, J. W. Electrolytic conductivity of four imidazolium-based room-temperature ionic liquids and the effect of a water impurity. *J. Chem. Thermodyn.* **2005**, *37*, 569–575.

(23) Kanakubo, M.; Harris, K. R.; Tsuchihashi, N.; Ibuki, K.; Ueno, M. Effect of pressure on transport properties of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate. *J. Phys. Chem. B* **2007**, *111*, 2062–2069.

(24) Li, W.; Han, B.; Tao, R.; Zhang, Z.; Zhang, J. Measurement and correlation of the ionic conductivity of ionic liquid-molecular solvent solutions. *Chin. J. Chem.* **2007**, *25*, 1349–1356.

(25) Li, W.; Zhang, Z.; Han, B.; Hu, S.; Xie, Y.; Yang, G. Effect of water and organic solvents on the ionic dissociation of ionic liquids. *J. Phys. Chem. B* **2007**, *111*, 6452–6456.

(26) Nishida, T.; Tashiro, Y.; Yamamoto, M. Physical and electrochemical properties of 1-alkyl-3-methylimidazolium tetrafluoroborate for electrolyte. *J. Fluorine Chem.* **2003**, *120*, 135–141.

(27) Tokuda, H.; Tsuzuki, S.; Susan, M. A. B. H.; Hayamizu, K.; Watanabe, M. How ionic are room-temperature ionic liquids? An indicator of the physicochemical properties. *J. Phys. Chem. B* **2006**, *110*, 19593–19600.

(28) Leys, J.; Wübbenhorst, M.; Menon, C. P.; Rajesh, R.; Thoen, J.; Glorieux, C.; Nockemann, P.; Thijs, B.; Binnemans, K.; Longuemart, S. Temperature dependence of the electrical conductivity of imidazolium ionic liquids. *J. Chem. Phys.* **2008**, *128*, 064509.

(29) The situation seems to be different for wet samples stored in glass vessels. For a [bmim][BF$_4$] + W mixture with $x_{\mathrm{IL}} = 0.008604$, we observed a strong increase of κ after two days (Figure S2 of the Supporting Information).

(30) Fuller, J.; Carlin, R. T.; Osteryoung, R. A. The room temperature ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate: electrochemical couples and physical properties. *J. Electrochem. Soc.* **1997**, *144*, 3881–3886.

(31) Yoshida, Y.; Baba, O.; Saito, G. Ionic liquids based on dicyanamide anion: influence of structural variations in cationic structures on ionic conductivity. *J. Phys. Chem. B* **2007**, *111*, 4742–4749.

(32) Vila, J.; Ginés, P.; Pico, J. M.; Franjo, C.; Jiménez, E.; Varela, L. M.; Cabeza, O. Temperature dependence of the electrical conductivity in EMIM-based ionic liquids Evidence of Vogel-Tamman-Fulcher behavior. *Fluid Phase Equilib.* **2006**, *242*, 141–146.

(33) Villagrán, C.; Deetlefs, M.; Pitner, W. R.; Hardacre, C. Quantification of halide in ionic liquids using ion chromatography. *Anal. Chem.* **2004**, *76*, 2118–2123.

(34) Visser, A. E.; Swatloski, R. P.; Reichert, W. M.; Griffin, S. T.; Rogers, R. D. Traditional extractants in nontraditional solvents: groups 1 and 2 extraction by crown ethers in room-temperature ionic liquids. *Ind. Eng. Chem. Res.* **2000**, *39*, 3596–3604.

(35) Swatloski, R. P.; Holbrey, J. D.; Rogers, R. D. Ionic liquids are not always green: hydrolysis of 1-butyl-3-methylimidazolium hexafluorophosphate. *Green Chem.* **2003**, *5*, 361–363.

(36) Wasserscheid, P.; van Hal, R.; Boesmann, A. New, halogen-free ionic liquids — synthesis, properties, and applications. *Proc. Electrochem. Soc.* **2002**, *19*, 146–154.

(37) Wagner, M.; Stanga, O.; Schröer, W. Corresponding states analysis of the critical points in binary solutions of room temperature ionic liquids. *Phys. Chem. Chem. Phys.* **2003**, *5*, 3943–3950.

(38) Zafarani-Moattar, M. T.; Shekaari, H. Application of Prigogine-Flory-Patterson theory to excess molar volume and speed of sound of 1- *n* -butyl-3-methylimidazolium hexafluorophosphate or 1-*n*-butyl-3-methylimidazolium tetrafluoroborate in methanol and acetonitrile. *J. Chem. Thermodyn.* **2006**, *38*, 1377–1384.

(39) Iglesias-Otero, M. A.; Troncoso, J.; Carballo, E.; Romaní, L. Density and refractive index for binary systems of the ionic liquid [Bmim][BF$_4$] with methanol, 1,3-dichloropropane, and dimethyl carbonate. *J. Solution Chem.* **2007**, *36*, 1219–1230.

(40) Harris, K. R.; Kanakubo, M.; Woolf, L. A. Temperature and pressure dependence of the viscosity of the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate: viscosity and density relationships in ionic liquids. *J. Chem. Eng. Data* **2007**, *52*, 2425–2430.

(41) Sanmamed, Y. A.; Gonzalez-Salagado, D.; Troncoso, J.; Cerdeirina, C. A.; Romani, L. Viscosity-induced errors in the density determination of room temperature ionic liquids using vibrating tube densitometry. *Fluid Phase Equilib.* **2007**, *252*, 96–102.

(42) Casteel, J. F.; Amis, E. S. Specific conductance of concentrated solutions of magnesium salts in water-ethanol system. *J. Chem. Eng. Data* **1972**, *17*, 55–59.

(43) Onsager, L.; Fuoss, R. M. Irreversible processes in electrolytes. Diffusion, conductance and viscous flow in arbitrary mixtures of strong electrolytes. *J. Phys. Chem.* **1932**, *36*, 2689–2778.

(44) Barthel, J. M. G.; Krienke, H.; Kunz, W. *Physical Chemistry of Electrolyte Solutions - Modern Aspects*; Steinkopf: Darmstadt, Springer: New York, 1998.

(45) Kratky, O.; Leopold, H.; Stabinger, H. Density determination of liquids and gases to an accuracy of 10^{-6} g/cm^3, with a sample volume of only 0.6 cm^3. *Z. Angew. Phys.* **1969**, *27*, 273–277.

(46) Heintz, A.; Klasen, D.; Lehmann, J. K.; Wertz, C. Excess molar volumes and liquid-liquid equilibria of the ionic liquid 1-methyl-3-octyl-imidazolium tetrafluoroborate mixed with butan-1-ol and pentan-1-ol. *J. Solution Chem.* **2005**, *34*, 1135–1144.

(47) Wang, J.; Tian, Y.; Zhao, Y.; Zhuo, K. A volumetric and viscosity study for the mixtures of 1-n-butyl-3-methylimidazolium tetrafluoroborate ionic liquid with acetonitrile, dichloromethane, 2-butanone and N, N - dimethylformamide. *Green Chem.* **2003**, *5*, 618–622.

(48) Van Valkenburg, M. E.; Vaughn, R. L.; Williams, M.; Wilkes, J. S. Thermochemistry of ionic liquid heat-transfer fluids. *Thermochim. Acta* **2005**, *425*, 181–188.

(49) Stoppa, A.; Hunger, J. Hefter, G.; Buchner, R.,unpublished results.

(50) Hunger, J.; Stoppa, A.; Hefter, G.; Buchner, R. From ionic liquid to electrolyte solution: dynamics of binary 1-*N*-butyl-3-*N*-methylimidazolium tetrafluoroborate + dichloromethane mixtures. *J. Phys. Chem. B* **2008**, *112*, 12913–12919.

(51) Li, W.; Zhang, Z.; Zhang, J.; Han, B.; Wang, B.; Hou, M.; Xie, Y. Micropolarity and aggregation behavior in ionic liquid + organic solvent solutions. *Fluid Phase Equilib.* **2006**, *248*, 211–216.

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