J. Chem. Eng. Data **2010,** *55,* 1799–1803

Molar Conductivities and Association Constants of 1-Butyl-3-methylimidazolium Chloride and 1-Butyl-3-methylimidazolium Tetrafluoroborate in Methanol and DMSO[†]

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Molar conductivities, Λ, of dilute solutions of the ionic liquids 1-butyl-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium tetrafluoroborate in methanol and DMSO were determined as a function of temperature (methanol, $T = (273.15 \text{ to } 313.15)$ K; DMSO, $T = (293.15 \text{ to } 318.15)$ K). The data were analyzed with Barthel's low-concentration chemical model (lcCM) model to obtain the limiting molar conductivities, $\Lambda^\infty(T)$, and association constants, $K_A^\circ(T)$, of these electrolytes. From $\Lambda^\infty(T)$, the Eyring activation enthalpy of charge transport and (where possible) the ion conductivity of the cation, $\lambda^\infty([\text{bmim}]^+)$, were determined.

Introduction

Room-temperature ionic liquids (RTILs) are salts with a melting temperature around or below ambient temperature. Generally formed by bulky and asymmetric cations and/or anions, they exhibit a variety of interesting features like negligible vapor pressure. Since their properties can be tuned by appropriate choice of anion and cation, this possibility to design (at least in principle) task-specific RTILs has 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 have been 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, such as their conductivity, κ, are scarce. Only for aqueous mixtures, a fair number of investigations have been published recently.[8−12] The latest investigations on ion pair formation of some alkylimidazolium ionic liquids in water[13] and dichloromethane[14] at 25 °C revealed that the stability of the ion pair depends significantly on the alkyl-chain length of the cation and on the structure of the anion. However, almost nothing is known about the temperature dependence of transport properties of dilute RTIL solutions despite the importance of the infinite-dilution limit of such data as one of the two reference states (in addition to the pure RTIL) in mixture studies.

In this paper, we report precise measurements of the molar conductivity, Λ, of dilute solutions of the ionic liquids (ILs) 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF$_4$]) and the corresponding chloride ([bmim][Cl]), which is solid at room temperature, in methanol (MeOH) and dimethylsulfoxide (DMSO) over the temperature range of $T = (273.15 \text{ to } 313.15)$ K and (293.15 to 318.15) K, respectively. From the data association constants, K_A°, limiting molar conductivities at infinite dilution, Λ^∞, and, where possible, limiting ion conductivities, $\lambda^\infty([\text{bmim}]^+)$, of the cation were determined.

Experimental Section

Materials. The salts [bmim][Cl] and [bmim][BF$_4$] were synthesized and purified as described in detail previously.[15] Prior to use, the compounds were dried at a high-vacuum line ($p < 10^{-3}$ Pa) for 7 days at ≈313 K, yielding water mass fractions $<50 \cdot 10^{-6}$ with coulometric Karl Fischer titration. Potentiometric titration of [bmim][BF$_4$] samples in aqueous solution against a standard solution of AgNO$_3$ (Carl Roth) yielded a halide mass fraction of $<20 \cdot 10^{-6}$. No contaminations were detected with ^{1}H NMR and, where applicable, ^{19}F NMR. The dried ILs were stored in a 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.

Methanol (MeOH, Merck, p.a., > 99.9 %) and dimethylsulfoxide (DMSO, Merck, extra pure, > 99.9 %) were used as received. The conductivities, κ, of the solvents were in the range of $(2 \text{ to } 7) \cdot 10^{-7}$ S·cm^{-1}.

Stock solutions were prepared by mass from the IL and the solvent.

Density Measurements. The densities of the solutions were determined by the method of Kratky et al.[16] using a Paar densimeter (DMA 60, DMA 601 HT) at (298.15 ± 0.02) K. The instrument was calibrated with degassed water and purified nitrogen at atmospheric pressure, assuming densities from standard sources.[17] The precision of the measurements was ± 0.00001 kg·m^{-3}. Considering the possible sources of error (calibration, measurement, purity of materials), the estimated uncertainty of d is within ± 0.00005 kg·m^{-3}.

For the dilute solutions investigated, the solution density, d, increases linearly with increasing salt content

$$d = d_s + b \cdot m \qquad (1)$$

where d_s is the density of the solvent, given in Table 1, and m is the molality of the IL. The density gradients, b, of the studied

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[†] Part of the "Josef M. G. Barthel Festschrift".

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10.1021/je900531b

Table 1. Densities, d_s, Viscosities η, and Relative Permittivities, ε, of Methanol and DMSO as a Function of Temperature, T

T	d_s	$10^3 \cdot \eta$		d_s	$10^3 \cdot \eta$	
K	$kg \cdot dm^{-3}$	$Pa \cdot s$	ε	$kg \cdot dm^{-3}$	$Pa \cdot s$	ε
	MeOH[23]			DMSO[24]		
273.15	0.809772	0.7915	37.92			
278.15	0.805111	0.7305	36.78			
283.15	0.800446	0.6761	35.68			
288.15	0.795769	0.6273	34.63			
293.15	0.791080	0.5834	33.61	1.100424	2.2098	47.15
298.15	0.786373	0.5438	32.63	1.095448	1.9946	46.52
303.15	0.781646	0.5080	31.69	1.090467	1.8104	45.89
308.15	0.776894	0.4754	30.78	1.085481	1.6516	45.24
313.15	0.772114	0.4457	29.90	1.080490	1.5138	44.59
318.15				1.075493	1.3935	43.93

systems, which are assumed to be independent of temperature, are included in Tables 2 and 3.

Conductivity Measurements. Conductivity measurements were executed with a three-electrode flow cell connected to a mixing chamber and mounted in a lid for immersion in a temperature bath.[18,19] The cell was calibrated with potassium chloride solutions.[20] The computer-controlled measurement system, based on a high-precision thermostat (Lauda UB 40J, WK 1400) and an impedance analyzer (Agilent 4284A), was described previously.[21] This system allows automatic setting of each temperature of the measurement program with a reproducibility better than 0.003 K.

At the beginning of every measurement cycle, the cell was filled with a known mass of solvent under nitrogen atmosphere. After measurement of the solvent conductivity, $\kappa'(\nu)$, as a function of frequency, ν, in the range of (500 to 10 000) Hz in steps of 500 Hz for all chosen temperatures of the program, known masses of stock solution were subsequently added with a gastight syringe, and the temperature program was repeated.

The measurement procedure, which included correction for lead resistance and extrapolation of the recorded frequency-dependent conductivities, $\kappa'(\nu)$, to $1/\nu = 0$ to eliminate electrode polarization effects, was described in detail elsewhere.[21] The corrected conductivities, $\kappa = \lim_{1/\nu \to 0,} \kappa'(\nu)$, of all investigated systems, converted to molar conductivities, $\Lambda = \kappa/c$, are given in Tables 2 and 3 as a function of IL molality, m. The latter relates to the corresponding (temperature-dependent) molar concentration, c, via $c = m \cdot d/(1 + M_2 \cdot m)$, where M_2 is the molar mass of the solute (IL). Taking into account the sources of error (calibration, measurements, impurities), the values of κ and Λ are certain within 0.05 %.

Data Analysis

The present molar conductivities, $\Lambda(c)$ (Tables 2 and 3, Figures 1 and 2), were analyzed in the framework of the low-concentration chemical model (lcCM) of Barthel.[22] This approach uses the set of equations

$$\frac{\Lambda}{\alpha} = \Lambda^{\infty} - S\sqrt{\alpha c} + E\alpha c \ln(\alpha c) + J_1 \alpha c - J_2(\alpha c)^{3/2} \tag{2}$$

$$K_A^{\circ} = \frac{1 - \alpha}{\alpha^2 c (y'_{\pm})^2};\; y'_{\pm} = \exp\left(-\frac{\kappa_D q}{1 + \kappa_D R}\right);$$
$$\kappa_D^2 = 16\pi N_A q \alpha c;\; q = \frac{e^2}{8\pi\varepsilon_0 \varepsilon k_B T} \tag{3}$$

and

$$K_A^{\circ} = 4\pi N_A 10^3 \int_a^R r^2 \exp\left[\frac{2q}{r} - \frac{W_{\pm}^*}{k_B T}\right] dr \tag{4}$$

where Λ^{∞} is the molar conductivity at infinite dilution; $(1 - \alpha)$ is the fraction of oppositely charged ions bound in ion pairs; and K_A° is the standard-state association constant. The activity coefficients of the free cations, y'_+, and anions, y'_-, are defined $(y'_{\pm})^2 = y'_+ y'_-$; κ_D is the Debye parameter; e is the proton charge; ε is the relative permittivity of the solvent; ε_0 is the permittivity of vacuum; T is the Kelvin temperature; and k_B and N_A are the Boltzmann and Avogadro constants, respectively. The lcCM model counts two oppositely charged ions as an ion pair if their mutual distance, r, is within the limits $a \leq r \leq R$. Expressions for the coefficients S, E, J_1, and J_2 of eq 2 are given by Barthel et al.[22,23] The limiting slope, S, and the parameter E are fully defined by the known data[23,24] for the density, d_s, viscosity, η, and relative permittivity, ε, of the pure solvents (Table 1). The coefficients J_1 and J_2 are functions of the distance parameter, R, representing the distance up to which oppositely charged ions can approach as freely moving particles in the solution. With eq 4 it is assumed that the potential of mean force between cations and anions can be split into a Coulomb contribution and non-Coulombic interactions, $W_{\pm}^*$, of maximum range R.

For associated electrolytes, as in the present case, data analysis is carried out by a nonlinear least-squares fit with coefficients S, E, and J_1 of eq 2 preset to their calculated values and with Λ^{∞}, K_A°, and J_2 as the adjustable parameters.[22,23] The lower limit, a, of the association integral is the distance of closest approach (contact distance) of cation and anion, $a = a_+ + a_-$, calculated from the ionic radii of the anions, $a_- = 0.232$ nm for BF_4^-,[22] 0.181 nm for Cl^-,[22] and from the value of $a_+ = 0.133$ nm for $[bmim]^+$, which assumes that the anion is located above the imidazolium ring of the cation.[26] From extended investigations on electrolyte solutions in different solvents, it was found[22] that the upper limit of association is given by an expression of the type $R = a + n \cdot s$, where s is the length of an orientated solvent molecule and n is an integer number. Values of $s = (0.47$ and $0.64)$ nm for MeOH and DMSO, respectively, were taken from the literature.[23,24] Assuming the possible existence of contact (CIP) and solvent-shared (SSIP) ion pairs in the solution, $n = 1$ was used throughout in the data analysis.

Results and Discussion

Figure 1 compares the experimental Λ values for [bmim][Cl] solutions in methanol with the results of the lcCM calculations, eqs 2 to 4, for all investigated temperatures. Figure 2 shows a similar comparison for all solutions at 298.15 K. The derived molar conductivities at infinite dilution, Λ^{∞}, together with the corresponding standard-state association constants, K_A°, and the radius, $R(J_2)$, calculated from the last term of eq 2, are summarized in Table 4. The value for $R(J_2)$ can be used as a compatibility control of the fit as it should be similar to the input radius, $R = a + s$, chosen for the calculation of J_1 and $y_{\pm}$.[22] Obviously, R and $R(J_2)$ agree well for the [bmim][BF4] solutions in both solvents, whereas this is not the case for [bmim][Cl]. This may suggest that Cl^-, probably due to its smaller size, can approach the cation closer than the sum of the ion radii. At 273.15 K, the evaluation of $R(J_2)$ was not possible since a negative value was obtained for J_2 with the three-parameter fit.

As can be seen from Table 4, the K_A° values for [bmim][Cl] in methanol and DMSO are rather similar and indicate moderate association. There are no data in the literature on the association of related compounds in DMSO and methanol, but similar values

Table 2. Molar Conductivities, Λ, as a Function of IL Molality, *m*, and Density Gradients, *b*, for Solutions of [bmim][Cl] and [bmim][BF$_4$] in MeOH

	T/K								
	273.15	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15
$10^3 \cdot m$	$\Lambda/\mathrm{S \cdot cm^2 \cdot mol^{-1}}$								
	[bmim][BF$_4$], $b/\mathrm{kg^2 \cdot dm^{-3} \cdot mol^{-1}} = 0.0735$								
1.05038	79.728	85.775	92.115	98.674	105.443	112.441	119.665	127.070	134.618
1.42860	78.597	84.551	90.807	97.259	103.923	110.791	117.895	125.185	132.615
1.96017	77.171	83.092	89.225	95.544	102.073	108.813	115.772	122.921	130.210
2.53671	75.651	81.680	87.705	93.917	100.333	106.953	113.784	120.799	127.957
3.18639	74.345	80.068	85.977	92.077	98.372	104.860	111.550	118.426	125.431
3.96735	72.935	78.558	84.375	90.370	96.552	102.929	109.500	116.245	123.123
4.85896	71.498	77.031	82.734	88.633	94.702	100.970	107.425	114.043	120.790
5.84102	70.087	75.519	81.135	86.923	92.893	99.051	105.386	111.884	118.514
	[bmim][Cl], $b/\mathrm{kg^2 \cdot dm^{-3} \cdot mol^{-1}} = 0.0527$								
0.21706	73.393	79.262	85.336	91.641	98.195	105.039	112.158	119.554	127.274
0.44777	72.782	78.342	84.382	90.616	97.114	103.863	110.902	118.256	125.880
0.70917	71.799	77.563	83.560	89.780	96.220	102.917	109.877	117.084	124.513
1.00642	70.861	76.578	82.474	88.580	94.915	101.496	108.331	115.437	122.757
1.30533	70.238	75.829	81.655	87.677	93.939	100.424	107.176	114.180	121.390
1.66986	69.550	75.087	80.837	86.781	92.964	99.376	106.027	112.917	120.017
2.16050	68.767	74.242	79.912	85.775	91.860	98.178	104.727	111.520	118.515
2.70660	68.140	73.481	79.077	84.860	90.881	97.109	103.574	110.267	117.153
3.33304	67.423	72.725	78.251	83.961	89.891	96.027	102.412	109.007	115.810
4.01962	66.807	72.036	77.501	83.144	89.008	95.056	101.388	107.961	114.654

Table 3. Molar Conductivities, Λ, as a Function of IL Molality, *m*, and Density Gradients, *b*, for Solutions of [bmim][Cl] and [bmim][BF$_4$] in DMSO

	T/K					
	293.15	298.15	303.15	308.15	313.15	318.15
$10^3 \cdot m$	$\Lambda/\mathrm{S \cdot cm^2 \cdot mol^{-1}}$					
	[bmim][BF$_4$], $b/\mathrm{kg^2 \cdot dm^{-3} \cdot mol^{-1}} = 0.0259$					
0.59708	36.272	40.134	44.107	48.196	52.392	56.710
0.98170	35.999	39.794	43.725	47.783	51.927	56.206
1.31746	35.787	39.554	43.460	47.484	51.609	55.847
1.77251	35.525	39.264	43.139	47.129	51.222	55.438
2.40734	35.220	38.932	42.759	46.717	50.772	54.948
3.19485	34.899	38.573	42.379	46.301	50.318	54.460
4.07642	34.599	38.232	41.995	45.879	49.863	53.964
5.02788	34.309	37.913	41.650	45.490	49.439	53.503
6.09927	34.012	37.588	41.286	45.104	49.016	53.043
	[bmim][Cl], $b/\mathrm{kg^2 \cdot dm^{-3} \cdot mol^{-1}} = 0.0080$					
0.14598	34.012	37.784	41.710	45.748	49.923	54.246
0.36112	33.668	37.410	41.279	45.277	49.403	53.679
0.58071	33.354	37.040	40.878	44.849	48.931	53.164
0.85356	33.054	36.710	40.516	44.454	48.504	52.689
1.12879	32.776	36.432	40.206	44.116	48.138	52.303
1.47486	32.530	36.131	39.870	43.752	47.741	51.869
1.88094	32.237	35.828	39.534	43.382	47.337	51.432
2.30760	31.990	35.530	39.213	43.029	46.958	51.006
2.76938	31.699	35.251	38.905	42.689	46.588	50.620
3.33992	31.448	34.928	38.544	42.298	46.168	50.166

were also found for the association constant of ammonium chloride in both solvents at 298 K with $K_\mathrm{A}^\circ = 23.16\ \mathrm{dm^3 \cdot mol^{-1}}$ in DMSO[24] and $K_\mathrm{A}^\circ = 21.12\ \mathrm{dm^3 \cdot mol^{-1}}$ in methanol.[23] On the other hand, [bmim][BF$_4$] is significantly more associated in methanol than in DMSO, similar to tetrabutylammonium tetrabutylborate (Bu$_4$NBBu$_4$), showing $K_\mathrm{A}^\circ = 1.27\ \mathrm{dm^3 \cdot mol^{-1}}$ in DMSO[24] and $K_\mathrm{A}^\circ = 42.11\ \mathrm{dm^3 \cdot mol^{-1}}$ in methanol[23] at 298 K. Obviously, the structure and size of the ions have an important influence on the ion-pairing process.

Interestingly, in methanol K_A° is larger for the tetrafluorborate than for the chloride, whereas in DMSO the chloride is more associated. This suggests that BF$_4^-$ is better solvated by DMSO than Cl$^-$, probably due to its larger polarizability, whereas methanol−BF$_4^-$ interactions, in contrast to the methanol−Cl$^-$ hydrogen bonds,[28] are too weak to compete with the hydrogen bonds between the methanol molecules. A comparison can be made with observed association properties of tetrabutylammonium chloride (Bu$_4$NCl) and tetrabutylammonium tetraphenylborate (Bu$_4$NBPh$_4$) in methanol. Values of $K_\mathrm{A}^\circ = 26.0\ \mathrm{dm^3 \cdot mol^{-1}}$ for Bu$_4$NCl and $69.9\ \mathrm{dm^3 \cdot mol^{-1}}$ for Bu$_4$BPh$_4$ in MeOH at 298 K[23] confirm the previous statement about the

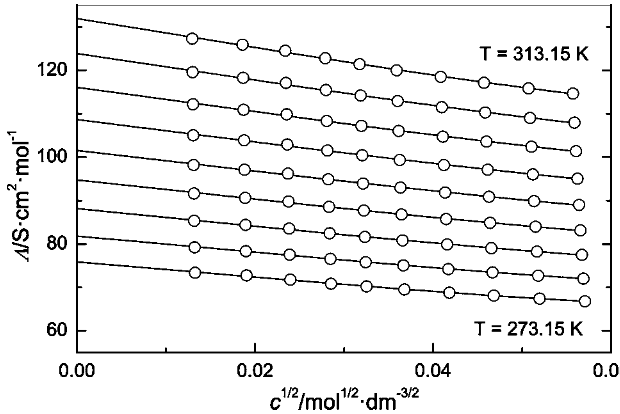

Figure 1. Molar conductivities, Λ (○), of [bmim][Cl] solutions in MeOH from $T = (273.15\ \text{to}\ 313.15)$ K in steps of 5 K and in the concentration range $0.0005 < c/\mathrm{dm^3 \cdot mol^{-1}} < 0.005$. Lines show the results of the lcCM calculations.

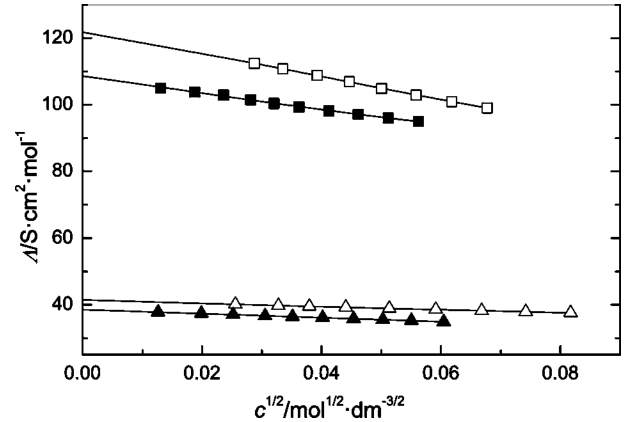

Figure 2. Molar conductivities, Λ, of □, [bmim][BF$_4$] and ■, [bmim][Cl] in MeOH and of △, [bmim][BF$_4$] and ▲, [bmim][Cl] in DMSO at 298.15 K. The lines show the results of the lcCM calculations.

Table 4. Limiting Molar Conductivities, Λ^∞, Association Constants, K_A°, and Values for the Parameter $R(J_2)$ for Solutions of [bmim][BF$_4$] and [bmim][Cl] in MeOH and DMSO[a]

T	Λ^∞	K_A°	$R(J_2)$	Λ^∞	K_A°	$R(J_2)$
K	S·cm^2·mol^{-1}	dm^3·mol^{-1}	nm	S·cm^2·mol^{-1}	dm^3·mol^{-1}	nm
			MeOH			
	[bmim][BF$_4$], R/nm = 0.835			[bmim][Cl], R/nm = 0.784		
273.15	86.30	40.4	0.857	75.86	20.4	-
278.15	92.63	34.4	1.03	81.83	17.1	0.236
283.15	99.55	35.0	1.01	88.16	16.3	0.575
288.15	106.74	36.0	0.972	94.71	15.9	0.575
293.15	114.16	36.8	0.946	101.53	15.4	0.654
298.15	121.84	37.7	0.917	108.64	15.5	0.706
303.15	129.80	38.6	0.897	116.07	16.5	0.675
308.15	137.94	39.0	0.892	123.82	17.9	0.617
313.15	146.23	39.3	0.891	131.90	20.2	0.530
			DMSO			
	[bmim][BF$_4$], R/nm = 1.005			[bmim][Cl], R/nm = 0.954		
293.15	37.52	3.6	1.09	34.69	13.5	0.739
298.15	41.51	4.6	1.03	38.53	13.4	0.756
303.15	45.62	5.1	1.01	42.53	14.0	0.671
308.15	49.85	5.3	0.997	46.63	13.4	0.762
313.15	54.19	5.5	0.987	50.88	13.9	0.667
318.15	58.66	5.6	0.983	55.29	14.5	0.549

[a] The assumed upper limit of association, R, is indicated.

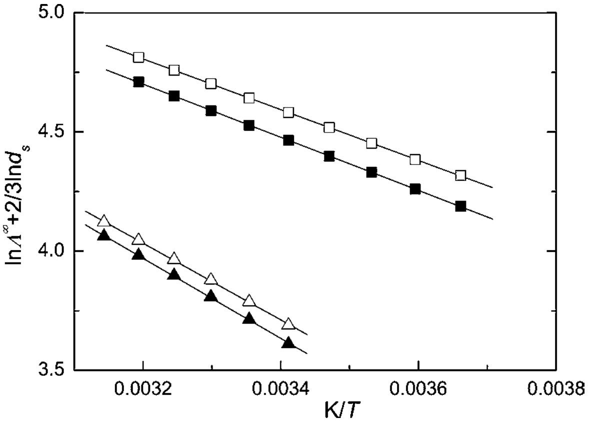

Figure 3. Plot of $\ln \Lambda^\infty + (2/3)\ln d_s$ as a function of $1/T$ for □, [bmim][BF$_4$] and ■, [bmim][Cl] in MeOH and for △, [bmim][BF$_4$] and ▲, [bmim][Cl] in DMSO. The slope yielded the Eyring activation enthalpy of charge transport, $\Delta H^\ddagger$ (Table 5).

Table 5. Eyring Activation Enthalpy, $\Delta H^\ddagger$, of Charge Transport According to Equation 5

	$\Delta H^\ddagger$/kJ·mol^{-1}	
	[bmim][BF$_4$]	[bmim][Cl]
MeOH	8.85 ± 0.02	9.27 ± 0.02
DMSO	13.37 ± 0.15	13.97 ± 0.15

influence of the anion nature on the association in the investigated solvents.

As expected from the viscosities of the pure solvents, the Λ^∞ values of both ILs are much larger for solutions in methanol than in DMSO (Table 4). From the temperature dependence of Λ^∞ the Eyring activation enthalpy of charge transport, $\Delta H^\ddagger$, can be determined[29] via

$$\ln \Lambda^\infty + \frac{2}{3}\ln d_s = -\frac{\Delta H^\ddagger}{RT} + B \tag{5}$$

where B is a constant (Figure 3). The obtained values, compiled in Table 5, suggest that $\Delta H^\ddagger$ mainly depends on the solvent. However, all present values for $\Delta H^\ddagger$ are only slightly larger than the corresponding Eyring activation enthalpies of viscous flow for the pure solvents, (7.776 ± 0.005) kJ·mol^{-1} for methanol and (11.76 ± 0.12) kJ·mol^{-1} for DMSO, calculated from the data of Table 1. This indicates that charge transport in these solutions requires ion desolvation and rearrangement of solvent molecules in the vicinity of the ion to some extent. Apparently, these processes are slightly more expressed with [bmim][Cl] than with [bmim][BF$_4$].

From the limiting molar conductivities, $\Lambda^\infty(T)$, of Table 4 and known limiting ion conductivities, $\lambda^\infty(X^-, T)$, of the anions, $X^- = Cl^-$ and BF_4^-, the limiting ion conductivity, $\lambda^\infty([bmim]^+, T)$, of the [bmim]$^+$ cation can be calculated as

$$\lambda^\infty([bmim]^+, T) = \Lambda^\infty(T) - \lambda^\infty(X^-, T) \tag{6}$$

The obtained data are summarized in Table 6. Unfortunately, for methanol, $\lambda^\infty(Cl^-, T)$ is only available at T = (278, 288, and 298) K,[23] and no published values for $\lambda^\infty(BF_4^-, T)$ seem to exist. For DMSO, only data for 298 K were found in the literature but this time for both anions, Cl$^-$[24] and BF$_4^-$.[25] Thus, a crosscheck of $\lambda^\infty([bmim]^+, T)$ is possible. As can be seen from Table 6, the results obtained via the Cl$^-$ and the BF$_4^-$ routes for the limiting conductivity of the [bmim]$^+$ cation in DMSO agree within 2.5 %, which is rather satisfactory.

On the basis of Walden's rule[22]

$$\lambda_i^\infty(T)\cdot\eta = \frac{Fe|z|}{6\pi a_i^{(\eta)}} \tag{7}$$

the solvent-dependent effective radius, $a^{(\eta)}([bmim]^+)$, of [bmim]$^+$ in methanol and DMSO was calculated from $\lambda^\infty([bmim]^+, T)$ (Table 6) and the solvent viscosities (Table 1). For methanol, the obtained values (Table 6) exhibit a small increase of $a^{(\eta)}([bmim]^+)$ with temperature. At 298.15 K the value for methanol, $a^{(\eta)}([bmim]^+) = 0.268$ nm, is about 4 % smaller than that for DMSO (0.279 nm). In any case, the obtained effective radii for [bmim]$^+$ are smaller than the van der Waals radius of the cation, $r([bmim]^+, vdW) = 0.328$ nm.[30] It should be noted that Walden's rule treats ion migration as the movement of a rigid sphere through a viscous continuum, and also the van der Waals radius was calculated by assuming a spherical shape. Since the shape of [bmim]$^+$ is far from spherical, $a^{(\eta)}([bmim]^+)$ gives only a rough estimation of the real dimension of the cation in the investigated solvents. Nevertheless, the observed discrepancy between van der Waals and effective radii suggests that the

Table 6. Molar Ion Conductivities, λ^∞, Walden Products, $\lambda^\infty\cdot\eta$, and Hydrodynamic Radii, $a^{(\eta)}$, of [bmim]$^+$ in MeOH and DMSO

T	$\lambda^\infty([BF]_4^-)$	$\lambda^\infty([bmim]^+)$	$\lambda^\infty(Cl^-)$	$\lambda^\infty([bmim]^+)$	$\bar{\lambda}^\infty([bmim]^+)$	$10^6\cdot\lambda^\infty([bmim]^+)\cdot\eta$	$a^{(\eta)}([bmim]^+)$
K	S·cm^2·mol^{-1}	S·cm^2·mol^{-1}	S·cm^2·mol^{-1}	S·cm^2·mol^{-1}	S·cm^2·mol^{-1}	S·kg·m·s^{-1}·mol^{-1}	nm
				MeOH			
278.15			39.14[23]	42.69		3.118	0.262
288.15			45.48[23]	49.23		3.088	0.265
298.15			52.39[23]	56.25		3.059	0.268
				DMSO			
298.15	26.62[25]	14.89	24.00[24]	14.53	14.71	2.934	0.279

$[\text{bmim}]^+$ cation does not possess a well-defined solvation shell in methanol or in DMSO.

Conclusion

Molar conductivities, Λ, were determined as a function of temperature for dilute solutions, $m \leq 0.005\ \text{mol}\cdot\text{kg}^{-1}$, of the ionic liquids [bmim][Cl] and $[\text{bmim}][\text{BF}_4]$ in the polar solvents methanol and DMSO. The data were analyzed with Barthel's low-concentration chemical model.[22]

Both ILs show moderate ion association in methanol, with K_A° being significantly larger for the BF_4^- salt. On the other hand, ion association is generally smaller in DMSO with K_A° now being significantly smaller for the tetrafluoroborate than for the chloride. The temperature dependence of K_A° is, at best, small for all systems.

From the derived limiting molar conductivities, $\Lambda^\infty(T)$, the Eyring activation enthalpy of charge transport, $\Delta H^\ddagger$, was determined for all electrolytes. It was found that $\Delta H^\ddagger$ depends on the solvent but varies only weakly with the dissolved IL. However, for all studied systems $\Delta H^\ddagger$ was larger than the corresponding Eyring activation enthalpy of viscous flow for the pure solvent. Where possible, ionic conductivities, $\lambda^\infty([\text{bmim}]^+)$, and effective radii, $a^{(\eta)}([\text{bmim}]^+)$, of the cation were determined. From the results it can be assumed that the solvation of the $[\text{bmim}]^+$ cation in methanol and DMSO is not very pronounced.

Acknowledgment

M. B.-R. and R. B. would like to thank Josef Barthel for his long-term support and encouragement of their research.

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Received for review June 25, 2009. Accepted August 17, 2009. Financial support by the Deutsche Forschungsgemeinschaft in the framework of Priority Program SPP 1191, "Ionic Liquids", and by the Slovenian Research Agency (grant P1-0201), is gratefully acknowledged.

JE900531B