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1-Ethyl-3-methylimidazolium Ethylsulfate in Water, Acetonitrile, and Dichloromethane: Molar Conductivities and Association Constants

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ABSTRACT: Molar conductivities, Λ, of dilute solutions of the ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate in water, acetonitrile (AN), and dichloromethane (DCM) were determined as a function of temperature (AN: $T = (273.15 \text{ to } 313.15)$ K; DCM: $T = (273.15 \text{ to } 308.15)$ K; water: $T = (278.15 \text{ to } 313.15)$ K) in the concentration range $c = (\approx 0.25 \text{ to } \approx 5) \cdot 10^{-3}\ \text{mol} \cdot \text{dm}^{-3}$. The data were analyzed with Barthel's low-concentration chemical (lcCM) model to obtain the limiting molar conductivities, $\Lambda^\infty(T)$, and association constants, $K_A^\circ(T)$, of this electrolyte in the investigated solvents. From $\Lambda^\infty(T)$ the Eyring activation enthalpy of charge transport was determined and found to be slightly larger than the corresponding value for viscous flow of the solvent. Strong ion pairing was found for the electrolyte in DCM ($K_A^\circ \approx 6 \cdot 10^4\ \text{mol}^{-1} \cdot \text{dm}^3$), whereas ion association in AN is rather weak ($K_A^\circ \approx 40\ \text{mol}^{-1} \cdot \text{dm}^3$). From the temperature dependence of $K_A^\circ(T)$ the enthalpy and entropy of the ion-pairing process were calculated, and ion association was found to be entropy-driven for both nonaqueous solvents. In water the salt is fully dissociated.

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, which makes them attractive for many potential applications.[1−4] Arguably, RTILs based on substituted imidazolium cations have been most intensively studied up to now,[5−7] but systematic studies of the transport properties of binary mixtures of RTILs and polar solvents, such as their electrical conductivity, κ, are still scarce and generally focus on aqueous systems and high RTIL concentrations.[8−13] Only recently conductivity studies of RTIL mixtures with aqueous[14] and nonaqueous solvents[15,16] aiming at the investigation of ion association have become available. These studies revealed that the stability of the ion pair depends significantly on the alkyl-chain length of the cation, on the structure of the anion and on the solvent.

One of the most promising RTILs for industrial application is 1-ethyl-3-methylimidazolium ethylsulfate [emim][EtSO$_4$].[17] This compound has an unusually high dielectric constant[18] and a relatively large electrochemical window,[19] is useful as a reaction medium,[20,21] and has applications in separation technology.[22−24] However, despite its potential utility, almost nothing is known about the temperature dependence of transport properties of [emim][EtSO$_4$] solutions. Only recently, the dielectric spectra for neat [emim][EtSO$_4$] and its mixtures with dichloromethane (DCM) have been reported.[25] It appears that [emim][EtSO$_4$] retains its molten-salt-like character up to relatively high dilutions in this solvent. The electrolyte solutions formed at low RTIL concentrations exhibit strong ion association forming contact ion pairs (CIPs). The publication of Hunger et al.[25] also reports conductivity data for [emim][EtSO$_4$]/DCM mixtures, but the concentrations probed there were too large to provide reliable information on the infinite-dilution limit, which is one of the two reference states (in addition to the pure RTIL) in mixture studies.

Accordingly, in this paper we report precise measurements of the molar conductivity, Λ, of dilute solutions of [emim][EtSO$_4$] in the low-permittivity solvent DCM (relative permittivity $\varepsilon = 8.82$ at 298.15 K[26]). These investigations were supplemented by corresponding measurements in the protic solvent water ($\varepsilon = 78.36$ at 298.15 K[27]) and the dipolar aprotic solvent acetonitrile (AN, $\varepsilon = 35.96$ at 298.15 K[28]) to study the influence of solvent permittivity on ion association. Measurements were performed over the temperature range of $T = (273.15 \text{ to } 313.15)$ K. From the experimental data association constants, K_A°, and limiting molar conductivities at infinite dilution, Λ^∞, were determined. From the temperature dependence of K_A° the standard Gibbs energy, ΔG_A°, enthalpy, ΔH_A°, and entropy, ΔS_A°, of the ion-pairing process were estimated.

EXPERIMENTAL SECTION

Materials. The RTIL [emim][EtSO$_4$] (purity > 99 %) was obtained from Iolitec (Denzlingen, Germany) and dried for 7 days at ≈ 313 K with a high-vacuum line ($p < 10^{-3}$ Pa), yielding water mass fractions of $< 20 \cdot 10^{-6}$ with coulometric Karl Fischer titration. No halide impurities were detected by potentiometric titration in aqueous solution against a standard solution of AgNO$_3$. No contaminants were detected with ^{1}H NMR and ^{13}C NMR spectroscopy. The hygroscopic IL was stored and handled in a nitrogen-filled glovebox. N$_2$-protection was also maintained when preparing the mixtures and during all subsequent steps of sample handling, including the measurements.

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Acetonitrile (Merck, Darmstadt, Germany; Reag. Ph Eur. stated purity > 99.9 %, water content < 0.02 %), and DCM (Merck, extra pure Ph Eur. > 99.8 %, water content < 0.01 %) were used as received. The conductivities, κ, of the solvents were in the range of (0.1 (AN) to 10 (DCM))$\cdot 10^{-7}$ S$\cdot$cm^{-1}.

Demineralized water was distilled twice in a quartz bidistillation apparatus (Destamat Bi 18E, Heraeus). The final product with specific conductivity $\kappa < 6\cdot 10^{-7}$ S$\cdot$cm^{-1} was distilled into a flask permitting storage and transfer of water into the measuring cell under an atmosphere of nitrogen.

Stock solutions (Table 1) were prepared by weight on an analytical balance. No buoyancy corrections were applied.

Density Measurements. The densities, d, of the stock solutions (d_1) and the final solutions (d_2) in the conductivity cell (Table 1), were determined by the method of Kratky et al.[29] 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.[30] The precision of the measurements was ± 0.01 kg m^{-3}. Considering the possible sources of error (calibration, measurement, purity of materials), the estimated uncertainty of d is within ± 0.05 kg m^{-3}.

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

$$d = d_s + b\cdot m \tag{1}$$

where d_s is the density of the solvent and m the molality of the IL. The data for d_s and the corresponding relative permittivities, ε, and the viscosities, η, of the pure solvents which are summarized in Table 2 were taken from the literature.[26−28] The density gradients, $b = (d_2 - d_1)/(m_2 - m_1)$, of the studied systems, which are assumed to be independent of temperature, are included in Table 3.

Table 1. Densities of the Final Solutions (m_2) in the Conductivity Cell and of the Stock Solutions (m_1) Used for Sample Preparation at 298.15 K

m	d
mol$\cdot$kg^{-1}	kg$\cdot$dm^{-3}
Water	
(m_2) 0.00508637	0.997281
(m_1) 0.0693387	1.000107
Acetonitrile	
(m_2) 0.00654571	0.777183
(m_1) 0.144490	0.788755
DCM	
(m_2) 0.00393095	1.316389
(m_1) 0.135159	1.316676

Conductivity Measurements. Conductivity measurements were performed with a three-electrode flow cell (cell constant $C = (0.8114 \pm 0.0001)$ cm^{-1} at 298.15 K) connected to a mixing chamber and mounted in a lid for immersion in a temperature bath.[31,32] The cell was calibrated with potassium chloride solutions.[33] 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.[34] This system allows automatic setting of each temperature of the measurement program with a reproducibility better than 0.003 K.

At the beginning of each measurement cycle the cell was filled under nitrogen atmosphere with a known mass of solvent. 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 gas-tight syringe and the temperature program repeated.

The measurement procedure, which included correction for lead resistance and linear extrapolation of the recorded frequency-dependent conductivities, $\kappa'(\nu) = f(1/\nu)$, to $1/\nu = 0$ to eliminate electrode polarization effects, was described in detail elsewhere.[34] 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 Table 3 as a function of IL molality, m. The latter relates to the corresponding (temperature-dependent) molar concentration, c, via $c = md/(1 + M_2m)$ where M_2 is the molar mass of the solute (RTIL). 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, $\Lambda(c)$ (Table 2, Figures 1 and 2), were analyzed in the framework of the low-concentration chemical model (lcCM) of Barthel.[35] This approach uses the set

Table 2. Densities, d_s, Viscosities, η, and Relative Permittivities, ε, of Water, Acetontrile, and Dichloromethane as a Function of Temperature, T

T	d_s	$10^3\cdot\eta$		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	kg$\cdot$dm^{-3}	Pa$\cdot$s	ε
		Water[27]			Acetontrile[28]			DCM[26]	
273.15				0.80357	0.4439	40.11	1.36267	0.527	9.84
278.15	0.99997	1.5192	85.90	0.79825	0.4196	39.24	1.35342	0.505	9.61
283.15	0.99970	1.3069	83.95	0.79289	0.3975	38.39	1.34416	0.482	9.39
288.15	0.99910	1.1382	82.04	0.78751	0.3772	37.56	1.3349	0.460	9.19
293.15	0.99821	1.0020	80.18	0.7821	0.3585	36.76	1.32564	0.437	9.00
298.15	0.99705	0.8903	78.35	0.77667	0.3413	35.96	1.31638	0.415	8.82
303.15	0.99565	0.7975	76.58	0.77121	0.3253	35.19	1.30712	0.392	8.65
308.15	0.99404	0.7195	74.85	0.76572	0.3105	34.43	1.29786	0.370	8.50
313.15	0.99222	0.6530	73.16	0.76020	0.2967	33.69			

Table 3. Molar Conductivities, Λ, of Solutions of [emim][EtSO$_4$] in Water, Acetonitrile, and Dichloromethane as a Function of RTIL Molality, m, and Temperature, T[a]

	T/K								
$10^3\cdot m$	273.15	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15
$\mathrm{mol\cdot kg^{-1}}$	$\Lambda/\mathrm{S\cdot cm^2\cdot mol^{-1}}$								
Water, $b/\mathrm{kg^2\cdot dm^{-3}\cdot mol^{-1}} = 0.0441$									
0.6367		49.598	57.155	65.118	73.408	82.055	90.983	100.223	109.645
1.0704		49.391	56.897	64.802	73.039	81.630	90.523	99.699	109.159
1.5267		49.163	56.636	64.496	72.705	81.250	90.088	99.213	108.592
1.9911		48.923	56.374	64.206	72.366	80.879	89.674	98.751	108.133
2.4800		48.766	56.159	63.952	72.073	80.539	89.300	98.348	107.649
3.1138		48.486	55.846	63.605	71.687	80.112	88.818	97.823	107.101
3.7674		48.261	55.588	63.311	71.350	79.739	88.395	97.357	106.611
4.3845		47.904	55.336	63.021	71.023	79.372	87.992	96.893	106.095
5.0864		47.828	55.088	62.738	70.712	79.028	87.612	96.453	105.620
Acetonitrile, $b/\mathrm{kg^2\cdot dm^{-3}\cdot mol^{-1}} = 0.0838$									
0.37064	128.206	135.596	143.088	150.717	158.431	166.279	174.226	182.260	190.448
0.7493	125.470	132.705	140.036	147.467	154.993	162.623	170.397	178.232	186.217
1.1757	123.127	130.214	137.411	144.716	152.114	159.609	167.223	174.917	182.729
1.6981	120.847	127.824	134.892	142.067	149.339	156.699	164.144	171.711	179.374
2.1851	118.935	125.799	132.760	139.813	146.968	154.200	161.542	168.981	176.505
2.6948	117.153	123.920	130.778	137.731	144.771	151.900	159.129	166.449	173.860
3.2685	115.391	122.064	128.822	135.667	142.611	149.632	156.745	163.960	171.245
3.8823	113.714	120.287	126.953	133.704	140.538	147.453	154.456	161.549	168.731
4.6706	111.700	118.163	124.722	131.360	138.080	144.864	151.768	158.751	165.805
5.3744	110.158	116.547	123.002	129.549	136.176	142.875	149.686	156.555	163.504
5.9869	108.928	115.247	121.647	128.141	134.703	141.338	148.048	154.853	161.731
6.5457	107.909	114.166	120.508	126.928	133.432	140.000	146.655	153.377	160.208
DCM, $b/\mathrm{kg^2\cdot dm^{-3}\cdot mol^{-1}} = 0.0022$									
0.53986	4.064	4.194	4.324	4.454	4.554	4.620	4.710	4.771	
0.8656	3.364	3.471	3.579	3.684	3.768	3.829	3.904	3.958	
1.1521	3.033	3.131	3.228	3.322	3.398	3.455	3.521	3.571	
1.5037	2.764	2.855	2.943	3.028	3.098	3.152	3.212	3.258	
1.8085	2.603	2.689	2.772	2.852	2.918	2.971	3.029	3.073	
2.0991	2.493	2.575	2.653	2.730	2.794	2.845	2.900	2.942	
2.3758	2.409	2.489	2.566	2.640	2.702	2.753	2.806	2.849	
2.7225	2.334	2.412	2.486	2.557	2.618	2.668	2.720	2.762	
3.0735	2.276	2.352	2.425	2.494	2.554	2.604	2.655	2.698	
3.3332	2.240	2.315	2.387	2.455	2.514	2.564	2.615	2.657	
3.6071	2.213	2.288	2.359	2.427	2.488	2.538	2.588	2.630	
3.9309	2.190	2.264	2.334	2.401	2.459	2.510	2.560	2.601	

[a] Density gradients, b, of the solutions are also included.

of equations

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

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

and

$$K_A^{\circ} = 4\pi N_A \int_a^R r^2 \exp\left[\frac{2q}{r} - \frac{W_{\pm}^{*}}{k_B T}\right] \mathrm{d}r \qquad (4)$$

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'_{-}, define $(y'_{\pm})^2 = y'_{+}y'_{-}$; κ_D is the Debye parameter, e the proton charge, ε is the relative permittivity of the solvent, ε_0 is the permittivity of

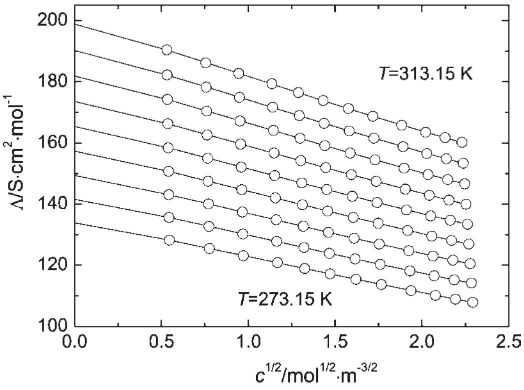

Figure 1. Molar conductivities, Λ; ○, of [emim][EtSO$_4$] solutions in AN from T = (273.15 to 313.15) K in steps of 5 K and in the concentration range 0.25 ≲ c/mol·m^{-3} ≲ 5.5. Lines show the results of the lcCM calculations.

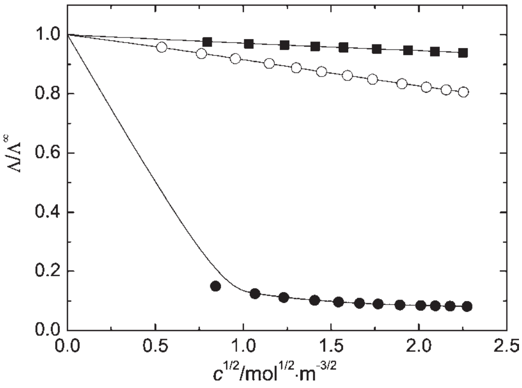

Figure 2. Reduced molar conductivities, Λ/Λ^∞, of [emim][EtSO$_4$] in ■, water; ○, AN and ●, DCM at 298.15 K. The lines show the results of the lcCM calculations.

vacuum, and T is the Kelvin temperature; 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 $a \le r \le R$. Expressions for the coefficients S, E, J_1, and J_2 of eq 2 are given by Barthel et al.[35,36] The limiting slope, S, and the parameter E are fully defined by the known data[36] 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, 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.[35,36] 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 radius of the SO_4^{2-} anion, a_- = 0.258 nm[35], and from the value of a_+ = 0.133 nm for [emim]$^+$, which assumes that the $-SO_4^-$ group of the anion is located above the imidazolium ring of the cation.[37,38] Thus, a is assumed to be the mean distance of closest approach between the centers of charge of the cation and anion. From extended investigations of electrolyte solutions in different solvents it was found[35] 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 an integer number. Values of s = (0.58 and 0.28) nm for AN and water, respectively, were taken from the literature.[27,28] For DCM, the length of the oriented C−Cl bond, $s = l_{C-Cl}$ = 0.177 nm was applied.[39] 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

The obtained molar conductivities were analyzed with the procedure described above. Best values of Λ^∞, K_A°, and J_2 were obtained by minimizing the standard deviation σ_Λ

$$\sigma_\Lambda = \left[\sum_{j=1}^{N_p} (\Lambda_{j,\mathrm{fit}} - \Lambda_j)^2/(N_p - 3)\right]^{1/2} \qquad (5)$$

defined by the differences between experimental, Λ_j, and calculated, $\Lambda_{j,\mathrm{fit}}$, values of N_p data points j. As an example, Figure 1 shows the molar conductivities of the studied [emim][EtSO$_4$] solutions in AN and the resulting fits with the lcCM model, eqs 2 to 4. 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 3. The fit value for $R(J_2)$ can be used as a compatibility control as it should be similar to the input distance parameter, $R = a + s$, chosen for the calculation of J_1 and $y_\pm$.[35]

For the experimental data of molar conductivities for [emim]-[EtSO$_4$] at 313.15 K in water, a three-parameter fit was not successful; therefore, $R(J_2)$ was not fitted. The results obtained by a two-parameter fit (Λ^∞, K_A°) are presented in Table 3 in parentheses and were not applied by further procedures.

Ion Association. For the AN solutions R and $R(J_2)$ agree well, and association constants of $K_A^\circ \approx 40$ dm^3 mol^{-1} were obtained, indicating moderate association of [emim][EtSO$_4$] to ion pairs in this solvent. With increasing temperature, K_A° increases slightly. To our knowledge association constants of other RTILs in this solvent have not yet been determined, but we may compare our data with results obtained for other salts with organic cations. For instance at 298 K K_A° = 76.9 dm^3·mol^{-1} was obtained for tetramethylammonium chloride in AN, and values of (64.3, 38.4, and 27.5) dm^3·mol^{-1} for the corresponding bromide, iodide, and picrate salts. Other electrolytes with organic cations have association constants of similar magnitude in AN.[28] Thus, with regards to ion-pair formation in dilute solutions, the behavior of [emim][EtSO$_4$] in AN is not special.

For water $R(J_2)$ is a factor of ~1.5 larger than R. Such deviations are common for weak ion association, and the obtained association constants summarized in Table 4 are very small indeed. Actually, these values of $K_A^\circ \approx 0.01$ dm^3·mol^{-1} are too small to be regarded as reliable, and we may safely say that at least for c < 0.01 mol·dm^{-3} the RTIL [emim][EtSO$_4$] is completely dissociated in water. This contrasts with many other salts containing organic cations where ion association is generally also weak but not negligible. For instance K_A° values of (2.17, 2.78, and 2.15) dm^3·mol^{-1} were obtained for tetramethylammonium chloride, bromide, and iodide in water at 298 K.[40] This suggests the conclusion that both [emim]$^+$ and [EtSO$_4$]$^-$ ions are well-hydrated.

Table 4. Limiting Molar Conductivities, Λ^∞, Association Constants, K_A°, and Values for the Parameter $R(J_2)$ for Solutions of [emim][EtSO$_4$] in Water, Acetonitrile, and Dichloromethane[a]

T	Λ^∞	K_A°	$R(J_2)$	Λ^∞	K_A°	$R(J_2)$	Λ^∞	K_A°
K	$S\cdot cm^2\cdot mol^{-1}$	$mol^{-1}\cdot dm^3$	nm	$S\cdot cm^2\cdot mol^{-1}$	$mol^{-1}\cdot dm^3$	nm	$S\cdot cm^2\cdot mol^{-1}$	10^4 $mol^{-1}\cdot dm^3$
	Water, R/nm = 0.671			Acetonitrile, R/nm = 0.971			DCM, R/nm = 0.568	
273.15				133.83 ± 0.05	39.6 ± 0.6	0.863	24.2 ± 1.3	4.9 ± 0.7
278.15	50.80 ± 0.13	0.014 ± 3.1	1.171	141.54 ± 0.05	39.8 ± 0.6	0.858	25.9 ± 1.5	5.4 ± 0.8
283.15	58.54 ± 0.08	0.016 ± 1.8	1.086	149.36 ± 0.05	40.0 ± 0.6	0.857	26.8 ± 1.5	5.5 ± 0.8
288.15	66.69 ± 0.03	0.009 ± 0.05	1.068	157.32 ± 0.06	40.4 ± 0.7	0.845	27.3 ± 1.4	5.3 ± 0.7
293.15	75.19 ± 0.03	0.009 ± 0.06	1.056	165.37 ± 0.07	40.7 ± 0.7	0.847	28.3 ± 1.4	5.5 ± 0.7
298.15	84.05 ± 0.03	0.008 ± 0.06	1.037	173.57 ± 0.08	41.2 ± 0.8	0.838	28.3 ± 1.4	6.6 ± 0.7
303.15	93.23 ± 0.11	0.017 ± 1.5	1.035	181.89 ± 0.07	41.7 ± 0.7	0.831	31.4 ± 1.2	6.6 ± 0.6
308.15	102.70 ± 0.10	0.01 ± 1.2	1.031	190.27 ± 0.08	41.9 ± 0.8	0.842	32.8 ± 1.0	7.1 ± 0.6
313.15	(112.48 ± 0.08)	(0.7 ± 0.3)		198.86 ± 0.09	42.7 ± 0.8	0.826		

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

For the DCM solutions it was impossible to evaluate $R(J_2)$ because negative values were obtained for J_2 with the present three-parameter fit. Negative $R(J_2)$ values are typical for systems with very strong ion-pair formation.[27] This pronounced tendency to ion association in DCM is clearly seen in Figure 2, which compares the reduced molar conductivities, Λ/Λ^∞, for [emim][EtSO$_4$] in the investigated solvents at 298.15 K. The relative conductivity of [emim][EtSO$_4$] in DCM is extremely low, indicating that in this solvent the concentration of free ions is much smaller than in water and AN. Accordingly, the listed K_A° values of Table 3 are very large. This observation is in line with literature data for various imidazolium RTILs in DCM varying in the range ($4.0 \lesssim \log K_A^\circ/(dm^3\cdot mol^{-1}) \lesssim 5.6$) at 298.15 K.[15] For the same temperature Hunger et al.[25] determined with dielectric spectroscopy the value of $\log K_A^\circ = (4.8 \pm 0.6)$ $dm^3\cdot mol^{-1}$ for [emim][EtSO$_4$], which is in excellent agreement with the present result, $\log K_A^\circ = (4.82 \pm 0.05)$ $dm^3\cdot mol^{-1}$.

From the temperature dependence of the Gibbs energy of ion pair formation, ΔG_A°, defined as

$$\Delta G_A^\circ(T) = -RT \ln K_A(T) \tag{6}$$

the corresponding entropy, $\Delta S_A^\circ = (\partial \Delta G_A^\circ/\partial T)_p$, and enthalpy, $\Delta H_A^\circ = \Delta G_A^\circ + T\Delta S_A^\circ$, of ion association at atmospheric pressure are available. As commonly found,[35] $\Delta G_A^\circ(T)$ can also for AN and DCM be expressed by the polynomial

$$\Delta G_A^\circ(T) = A_0 + A_1(298.15 - T) + A_2(298.15 - T)^2 \tag{7}$$

where A_0 and A_1 can be identified with the standard-state Gibbs energy, $\Delta G_{A,298}^\circ$, and entropy, $\Delta S_{A,298}^\circ$, of ion association, respectively.

For the AN and DCM systems, where ion association is relevant, Table 5 summarizes the obtained parameters of eq 7, together with the corresponding standard-state enthalpies of ion association, $\Delta H_{A,298}^\circ$ (note that for DCM $A_2 = 0$ within experimental uncertainty). For both solvents $\Delta H_{A,298}^\circ$ is positive, that is, unfavorable to ion association, but this is overcompensated by the large entropy of ion association. Interestingly, both $\Delta S_{A,298}^\circ$ and $\Delta H_{A,298}^\circ$ increase when going from AN to DCM. This suggests that [emim][EtSO$_4$] is more strongly solvated by DCM, a view also supported by the Walden products (see below). Unfortunately, it is currently not possible to decide whether this is due to the cation or the anion.

Table 5. Coefficients, $A_0 = \Delta G_{A,298}^\circ$, $A_1 = \Delta S_{A,298}^\circ$, and A_2, of eq 7 and Standard-State Enthalpy of Ion Association, $\Delta H_{A,298}^\circ$, for [emim][EtSO$_4$] in AN and DCM

	A_0	A_1	A_2	$\Delta H_{A,298}^\circ$
	$kJ\cdot mol^{-1}$	$J\cdot K^{-1}\cdot mol^{-1}$	$J\cdot mol^{-1}\cdot K^{-2}$	$kJ\cdot mol^{-1}$
AN	−9.214 ± 0.003	36.1 ± 0.2	−0.06 ± 0.01	1.55 ± 0.06
DCM	−27.39 ± 0.06	115 ± 4		6.9 ± 1.2

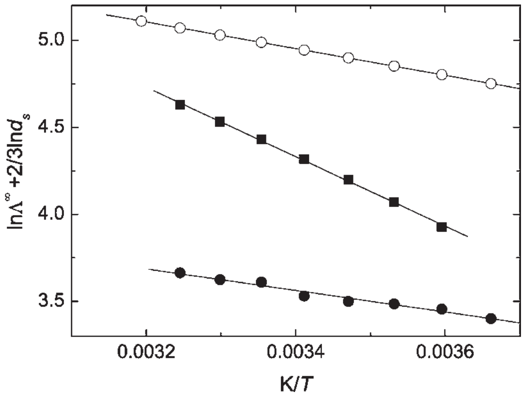

Figure 3. Plot of $\ln \Lambda^\infty + 2/3 \ln d_s$ as a function of $1/T$ for [emim][EtSO$_4$] in ■, water; ○, AN; and ■, DCM. The slope yielded the Eyring activation enthalpy of charge transport, $\Delta H_\Lambda^\ddagger$ (Table 5).

Ion Transport. Because of the large association constants in DCM, Λ drops rapidly already at very low RTIL concentrations (Figure 2). As a consequence, the uncertainties in Λ^∞ are significantly larger for this solvent than for water and AN (Table 4). Nevertheless, also for DCM a smooth increase of Λ^∞ with temperature was observed. From these data the Eyring activation enthalpy of charge transport, $\Delta H_\Lambda^\ddagger$, was determined[41] via

$$\ln \Lambda^\infty + \frac{2}{3} \ln d_s = -\frac{\Delta H_\Lambda^\ddagger}{RT} + B \tag{8}$$

where B is a constant (Figure 3). The obtained values for $\Delta H_\Lambda^\ddagger$ are compiled in Table 6 together with the corresponding Eyring

Table 6. Eyring Activation Enthalpy, $\Delta H^{\ddagger}_{\Lambda}$, of Charge Transport for [emim][EtSO$_4$] According to Equation 5[a]

	$\Delta H^{\ddagger}_{\Lambda}$	$\Delta H^{\ddagger}_{\eta}$
	kJ·mol^{-1}	kJ·mol^{-1}
water	16.6 ± 0.3	15.0 ± 0.3
AN	6.38 ± 0.02	4.73 ± 0.06
DCM	5.2 ± 0.3	4.6 ± 0.2

[a] The corresponding Eyring activation enthalpies of viscous flow, $\Delta H^{\ddagger}_{\eta}$, are given for comparison.

activation enthalpies of viscous flow for the pure solvents, $\Delta H^{\ddagger}_{\eta}$, calculated from the data of Table 1.

Obviously, $\Delta H^{\ddagger}_{\Lambda}$ depends mainly on the solvent, but $\Delta H^{\ddagger}_{\Lambda} > \Delta H^{\ddagger}_{\eta}$ for all solvents. This suggests that to some extent charge transport in these solutions requires ion desolvation and rearrangement of solvent molecules in the vicinity of the ions. Apparently, this effect is slightly more pronounced in AN than in water and DCM. Differences in ion solvation are also reflected by the largely differing Walden products, $\Lambda^{\infty}\eta$, for the three solvents. At 298.15 K the values of Walden products are (74.82, 59.24, and 11.74)·10^{-3} Pa·s·S·cm^2·mol^{-1} in water, AN, and DCM, respectively, suggesting that ion solvation is getting stronger when going from water to AN to DCM. This is in line with the inference from $\Delta H^{\circ}_{\text{A}}$ and $\Delta S^{\circ}_{\text{A}}$ (Table 5). However, without ionic conductivities for [emim]$^+$ and [EtSO4]$^-$, which would permit calculation of their hydrodynamic radii, further evaluation is not possible.

CONCLUSION

Molar conductivities, Λ, were determined as a function of temperature for dilute solutions, $m \leq 0.006$ mol·kg^{-1}, of the ionic liquid [emim][EtSO$_4$] in typical examples of three solvent classes: the protic high-permittivity solvent water, the dipolar aprotic solvent AN, and the low-polarity solvent DCM. The data were analyzed with Barthel's lcCM.[35] As expected, the obtained K°_{A} values show that the association of [emim][EtSO$_4$] increases significantly when the static permittivity of the solvent is decreased. While ion pairing is negligible in water, association is entropy-driven in AN and DCM. The values of $\Delta S^{\circ}_{\text{A},298}$ and $\Delta H^{\circ}_{\text{A},298}$ for AN and DCM, as well as the Walden products of all three solvents, suggest that ion solvation is strongest in DCM.

From the derived limiting molar conductivities, $\Lambda^{\infty}(T)$, the Eyring activation enthalpy of charge transport, $\Delta H^{\ddagger}_{\Lambda}$, was determined. It was found that this quantity depends on the solvent and is somewhat larger than the corresponding Eyring activation enthalpy of viscous flow for the pure solvents.

Overall, in the dilute solutions studied, the ionic liquid [emim][EtSO$_4$] behaves like a conventional electrolyte with an organic cation.

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