Apparent Molar Volumes and Electrical Conductance of Ionic Liquids [C$_n$mim]Br (n = 8, 10, 12) in Ethylene Glycol, *N*,*N*-Dimethylformamide, and Dimethylsulfoxide at 298.15 K

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Solution densities and conductivities for solutions of [C$_n$mim]Br (n = 8, 10, 12) ionic liquids (ILs) in ethylene glycol, *N*,*N*-dimethylformamide, and dimethylsulfoxide have been determined at 298.15 K as a function of ionic liquid concentration. The apparent molar volumes, standard partial molar volumes, molar conductivities, and the limiting molar conductivities of the ILs have been derived from the experimental data. On the basis of the values of the standard partial molar volume and the limiting molar conductivity of the Br$^-$ anion available in the literature, the standard partial molar volumes and the limiting molar conductivities for the cations have also been reported in the three organic solvents. These data help to examine the effect of alkyl chain length of the cations and properties of the solvents. It was shown that the standard partial molar volumes of the ILs and their cations increased, but the limiting molar conductivities decreased linearly with the increase of the alkyl chain length. The fluidity of the solvents played an important role in the conductivity properties.

Introduction

In recent years, ionic liquids (ILs) have attracted increasing attention in scientific research by virtue of their possible applications in new environmentally friendly industrial processes.[1−6] ILs are a new class of substances that remain in the liquid state in a wide range of temperatures. The most interesting properties of these compounds are that they possess negligible vapor pressure, good thermal and chemical stability under ordinary conditions, and excellent solubility for organic and inorganic compounds.[7−10] To apply ILs in different processes and reactions, it is necessary to know their fundamental physical and chemical properties. A number of investigations have been reported for the physico-chemical properties of ILs and their mixtures with molecular solvents such as densities, viscosities, conductivities, enthalpy, or heat capacity.[11−23] However, only a few studies have been made on dilute solutions of ionic liquids, from which the limiting molar quantities could be obtained. Actually, these limiting molar quantities are very important for the study of the interactions between ion and solvents and for the possible prediction of ILs in specific applications such as IL-based chemical reactions.

In the present work, densities and conductivities for solutions of 1-alkyl-3-methylimidazolium bromine [C$_n$mim]Br (n = 8, 10, 12) in ethylene glycol (EG), *N*,*N*-dimethylformamide (DMF), and dimethylsulfoxide (DMSO) have been measured at 298.15 K as a function of ionic liquid concentrations at atmospheric pressure. From these data, apparent molar volumes, standard partial molar volumes, and the limiting molar conductivity have been calculated. These results were used to understand the effects of both alkyl chain length of the cations and properties of the solvents on the standard partial molar volumes and the limiting molar conductivity of the ILs.

Experimental Section

Chemicals. 1-Methylimidazole (99 %) was purchased from Shanghai Chem. Co. All 1-bromoalkanes (99 %) were from Acros Organic, which were distilled before use. [C$_n$mim]Br (n = 8, 10, 12) were synthesized and purified following the procedures reported in the literature.[24,25] These ILs were dried under vacuum at 343 K for 2 to 3 days in the presence of P_2O_5. The mass fraction of water in the ionic liquids was less than 0.02 %, as analyzed by Karl Fischer titration.

N,*N*-Dimethylformamide and dimethylsulfoxide (Tianjin Kermel Chem. Co., 99.5 %) were dried over 0.4 nm molecular sieves (Fluka) and then distilled before use. Ethylene glycol (Tianjin Hengxing Chem. Co., 99.5 %) was dried under sodium hydroxide and then distilled. After that, the solvent was dried by 0.4 nm molecular sieves (Fluka) and then distilled again. The middle fraction was collected for use. The water contents of all the solvents are less than 100 ppm.

Apparatus and Procedure. The stock solutions (around 0.05 $\text{mol}\cdot\text{kg}^{-1}$) were prepared by mass and then were successively diluted to obtain the test samples. Concentrations of the dilute solutions ranged from (0.003 to 0.04) $\text{mol}\cdot\text{kg}^{-1}$. Solution densities were determined by an Anton Paar DMA 60/602 vibrating-tube digital densimeter with a resolution of $1\cdot10^{-6}$ $\text{g}\cdot\text{cm}^{-3}$. The temperature around the density meter cell was controlled by circulating water from a constant-temperature bath (Schott, German). The CT-1450 temperature controller and CK-100 ultracryostat were employed to maintain the bath temperature at (298.15 ± 0.01) K. The densimeter was calibrated with known densities of pure water and dry air everyday. The uncertainty in density was estimated to be $\pm\ 3\cdot10^{-6}$ $\text{g}\cdot\text{cm}^{-3}$.

Solution conductivities were determined at 298.15 K by a Wayne-Kerr 6430B Auto Balance Bridge with a resolution of $1\cdot10^{-5}$ $\mu\text{S}\cdot\text{cm}^{-1}$. A Shanghai DJS-1 electrode was used. The conductance cell was equipped with a water circulating jacket,

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Table 1. Experimental Densities and Apparent Molar Volumes of [C$_n$mim]Br (n = 8, 10, 12) in DMSO, DMF, and EG at 298.15 K

[C$_8$mim]Br			[C$_{10}$mim]Br			[C$_{12}$mim]Br		
$10^3 \cdot m_1$ $\text{mol}\cdot\text{g}^{-1}$	ρ $\text{g}\cdot\text{cm}^3$	$V_{\Phi,1}$ $\text{cm}^3\cdot\text{mol}^{-1}$	$10^3 \cdot m_1$ $\text{mol}\cdot\text{g}^{-1}$	ρ $\text{g}\cdot\text{cm}^3$	$V_{\Phi,1}$ $\text{cm}^3\cdot\text{mol}^{-1}$	$10^3 \cdot m_1$ $\text{mol}\cdot\text{g}^{-1}$	ρ $\text{g}\cdot\text{cm}^3$	$V_{\Phi,1}$ $\text{cm}^3\cdot\text{mol}^{-1}$
				dimethylsulfoxide				
0	1.095332	--	0	1.095332	--	0	1.095347	--
0.003697	1.095431	228.84	0.005147	1.095402	265.55	0.002680	1.095355	299.97
0.007705	1.095536	229.07	0.008680	1.095455	265.06	0.004967	1.095363	299.77
0.01147	1.095634	229.17	0.01336	1.095529	264.57	0.007868	1.095374	299.59
0.01568	1.095742	229.31	0.01682	1.095585	264.31	0.01038	1.095384	299.48
0.01953	1.095840	229.39	0.02087	1.095652	264.05	0.01304	1.095395	299.38
0.02373	1.095946	229.49	0.02779	1.095770	263.66	0.01600	1.095407	299.32
0.02785	1.096051	229.52	0.03347	1.095870	263.38	0.01873	1.095419	299.24
0.03185	1.096150	229.61	0.04096	1.096000	263.15	0.02082	1.095428	299.20
0.03581	1.096248	229.67	0.04462	1.096070	262.94	0.02457	1.095445	299.11
0.03956	1.096340	229.73	0.05299	1.096220	262.72	0.02736	1.095458	299.05
				ethylene glycol				
0	1.109957	--	0	1.109977	--	0	1.109947	--
0.006765	1.110043	237.54	0.002798	1.109988	270.06	0.003873	1.109909	306.46
0.01325	1.110124	237.60	0.005415	1.109996	270.40	0.007663	1.109872	306.50
0.02074	1.110217	237.64	0.008253	1.110003	270.69	0.01013	1.109847	306.52
0.02364	1.110252	237.68	0.01114	1.110009	270.91	0.01330	1.109815	306.57
0.03075	1.110338	237.73	0.01398	1.110014	271.09	0.01680	1.109780	306.58
0.03492	1.110387	237.79	0.01720	1.110019	271.26	0.02023	1.109746	306.60
0.03798	1.110425	237.77	0.01950	1.110022	271.36	0.03123	1.109635	306.68
0.04271	1.110480	237.82	0.02259	1.110024	271.55	0.03429	1.109604	306.70
			0.02552	1.110026	271.68			
				N,*N*-dimethylformamide				
0	0.944305	--	0	0.944305	--	0	0.944305	--
0.003600	0.944562	210.99	0.004548	0.944601	248.02	0.003861	0.944545	280.91
0.007420	0.944824	212.80	0.009331	0.944904	248.99	0.008055	0.944798	282.03
0.01114	0.945075	213.68	0.01416	0.945206	249.58	0.01230	0.945047	282.90
0.01485	0.945316	214.71	0.01889	0.945493	250.33	0.01627	0.945277	283.49
0.01862	0.945557	215.65	0.02351	0.945774	250.70	0.02032	0.945508	284.07
0.02243	0.945792	216.65	0.02843	0.946065	251.30	0.02446	0.945745	284.37
0.02634	0.946030	217.50	0.03329	0.946353	251.63	0.02703	0.945890	284.59
0.03009	0.946260	218.03	0.03813	0.946640	251.87	0.03337	0.946237	285.31
0.03685	0.946653	219.36	0.04346	0.946942	252.43	0.03725	0.946450	285.62
0.04079	0.946877	220.04	0.04852	0.947237	252.63	0.04099	0.946651	285.94

Table 2. Fitting Parameters and Standard Deviations (SD) of Equation 2 for [C$_n$mim]Br (n = 8, 10, 12) in DMSO, EG, and DMF at 298.15 K

	[C$_8$mim]Br			[C$_{10}$mim]Br			[C$_{12}$mim]Br		
	$V^0_{\Phi,1}$ $\text{cm}^3\cdot\text{mol}^{-1}$	S_v $\text{cm}^3\cdot\text{kg}^{1/2}\cdot\text{mol}^{-3/2}$	SD	$V^0_{\Phi,1}$ $\text{cm}^3\cdot\text{mol}^{-1}$	S_v $\text{cm}^3\cdot\text{kg}^{1/2}\cdot\text{mol}^{-3/2}$	SD	$V^0_{\Phi,1}$ $\text{cm}^3\cdot\text{mol}^{-1}$	S_v $\text{cm}^3\cdot\text{kg}^{1/2}\cdot\text{mol}^{-3/2}$	SD
EG	237.34 ± 0.02	2.30 ± 0.11	0.02	269.31 ± 0.03	14.82 ± 0.24	0.03	306.33 ± 0.01	1.96 ± 0.06	0.02
DMSO	228.50 ± 0.03	6.23 ± 0.18	0.03	266.68 ± 0.09	−17.70 ± 0.55	0.09	300.32 ± 0.04	−7.87 ± 0.30	0.03
DMF	207.12 ± 0.14	63.46 ± 0.95	0.13	246.03 ± 0.10	30.45 ± 0.61	0.09	278.89 ± 0.12	35.13 ± 0.79	0.11

and the temperature was controlled within ± 0.01 K with a HAAKE V26 thermostat (Thermo Electron, Germany). The cell was calibrated with aqueous KCl solutions at different concentrations, and a cell constant of 0.996 cm^{-1} was determined. The uncertainty in conductance measurements is about ± 0.02 %.

Results and Discussion

Apparent Molar Volumes and Standard Partial Molar Volumes of the ILs. The experimental densities for solutions of the studied ILs at 298.15 K and atmospheric pressure are reported in Table 1. The results were used to calculate the apparent molar volumes using the equation

$$V_\Phi = \frac{M}{\rho} - \frac{(\rho - \rho_0)}{m_1 \rho_0 \rho} \tag{1}$$

where ρ and ρ_0 are densities (g·cm^{-3}) of the solutions and pure solvent, respectively. M is the molar mass (g·mol^{-1}), and m_1 is the molality (mol·g^{-1}) of the IL (1) in IL (1) + solvent (2). The values of apparent molar volumes calculated with eq 1 are also listed in Table 1.

The standard partial molar volume of ILs, $V^0_{\Phi,1}$, is the limiting value of their partial (or apparent) molar volume as their concentration approaches zero. At this limit, ions are surrounded only by the solvent, with other ions being an infinite distance. Therefore, the standard partial molar volume is a measure only for the interactions between the ions and the solvent. The standard partial molar volumes of the ILs have been derived from the empirical linear equation[26]

$$V_{\Phi,1} = V^0{}_{\Phi,1} + S_\text{v} m_1^{1/2} \tag{2}$$

where the slope, S_v, indicates the ion−ion interactions. In the concentration range studied, S_v is generally positive but may be negative for some electrolytes, particularly for tetraalkylammonium salts.[27−29] Values of $V^0_{\Phi,1}$ and S_v were obtained by a least-squares analysis (Figure 1) and included in Table 2 along with the standard deviations (SD) of fit. It can be seen that the standard partial molar volumes for the ILs increased with increasing alkyl chain length of the cations in a given solvent, and they decreased in the order EG > DMSO > DMF for a given ionic liquid. $E_\text{T}(30)$ is one of the solvatochromic

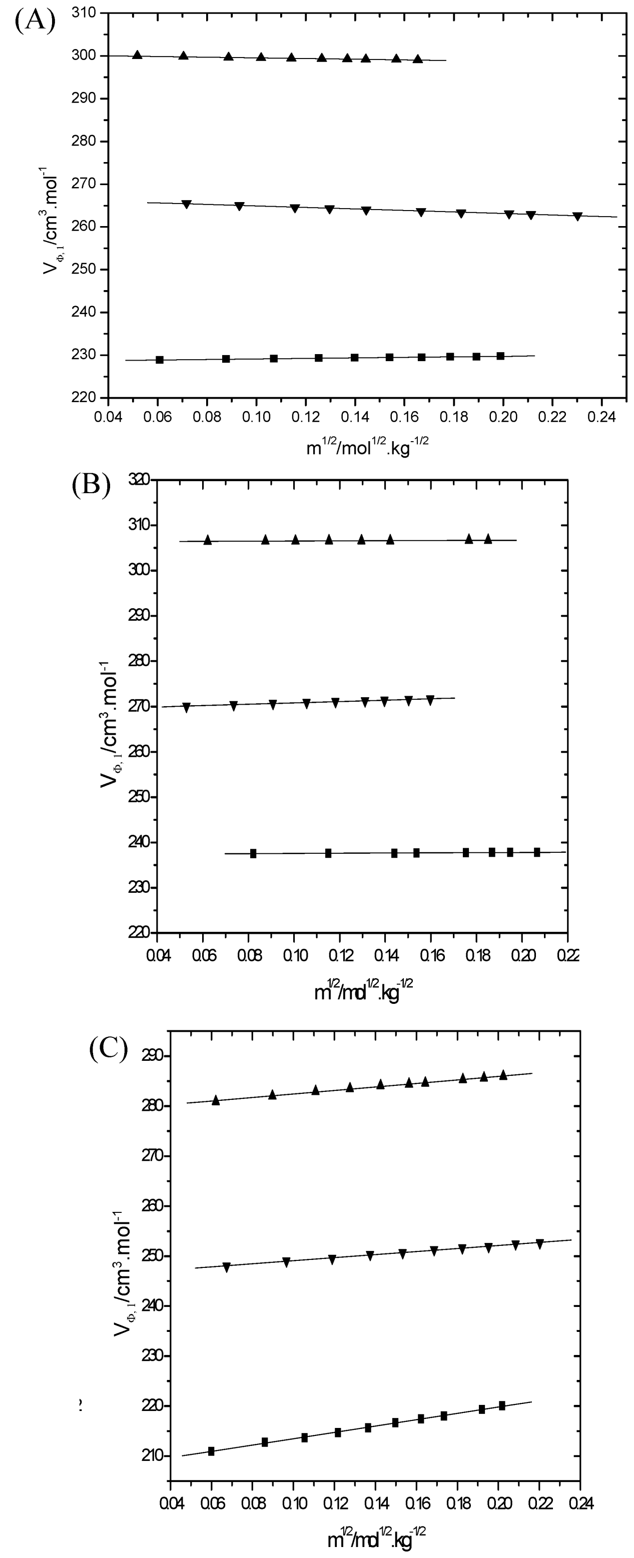

Figure 1. Plots of the apparent molar volume ($V_{\Phi,1}$) of the ILs versus the square root of the IL concentration ($m^{1/2}$) in different solvents at 298.15 K: (A) DMSO; (B) EG; (C) DMF; ■, [C$_8$mim]Br; ▼, [C$_{10}$mim]Br; ▲, [C$_{12}$mim]Br.

parameters of solvent, which reflects the solvent polarity. It is known that the $E_T(30)$ values of the solvents decrease in the order: EG (56.3) > DMSO (45.1) > DMF (43.8).[30] Therefore, the values of $V^0_{\Phi,1}$ increase with increasing polarity of the solvents due to the stronger solvation of the ILs by the higher polarity of solvent.

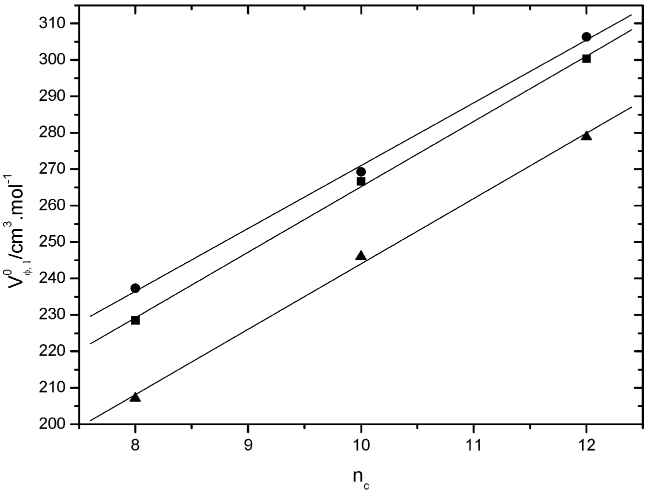

Figure 2. Linear plots of the standard molar partial volumes for [C$_n$mim]Br (n = 8, 10, 12) vs the number of carbon atoms (n_c) in the alkyl chain of the ILs: ■, DMSO; ●, EG; ▲, DMF.

Table 3. Fitting Parameters of Equation 3

	DMSO	EG	DMF
a/cm$^3\cdot$mol^{-1}	85.6 ± 6.6	98.5 ± 7.4	64.6 ± 8.9
$V^0_\Phi(CH_2)$/cm$^3\cdot$mol^{-1}	17.8 ± 0.7	17.3 ± 0.7	17.9 ± 0.9

Table 4. Standard Partial Molar Volumes for the Cations [C$_n$mim]$^+$ (n = 8, 10, 12) and the Anion Br$^-$ at 298.15 K in Different Solvents and the Fitting Parameters of Equation 4

	DMSO	EG	DMF
V^0_{Φ,Br^-}/cm$^3\cdot$mol^{-1}	17[a]	31[a]	9[a]
$V^0_{\Phi,[C_8mim]^+}$/cm$^3\cdot$mol^{-1}	211.5	206.3	198.1
$V^0_{\Phi,[C_{10}mim]^+}$/cm$^3\cdot$mol^{-1}	249.7	238.3	237.0
$V^0_{\Phi,[C_{12}mim]^+}$/cm$^3\cdot$mol^{-1}	283.3	275.3	269.9
α/cm$^3\cdot$mol^{-1}	68.6 ± 6.6	67.5 ± 7.4	55.6 ± 8.9
V^0_Φ/cm$^3\cdot$mol^{-1}	18.0 ± 0.7	17.3 ± 0.7	17.9 ± 0.9

[a] Ref 26.

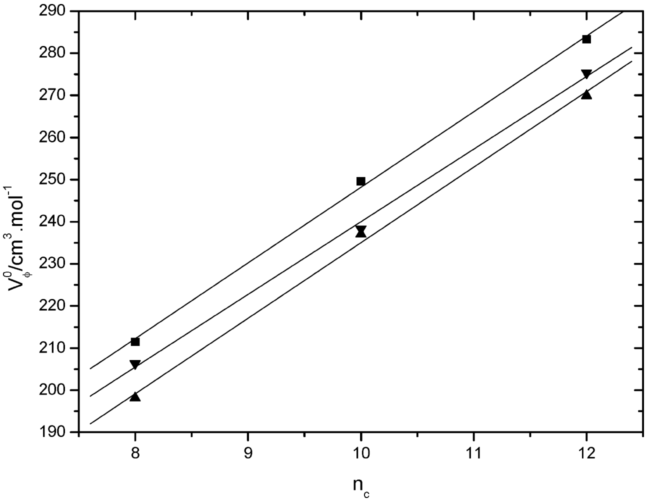

Figure 3. Linear plots of the standard molar partial volumes for the cations [C$_n$mim]$^+$ (n = 8, 10, 12) vs the number of carbon atoms (n_c) in the alkyl chain of the ILs: ■, DMSO; ▼, EG; ▲, DMF.

A linear relationship between the standard partial molar volumes and the number of carbon atoms (n_c) in the alkyl chain of the ILs is shown in Figure 2. This can be represented by the equation[31]

$$V^0_{\Phi,1} = a + bn_c \tag{3}$$

where a stands for the sum of the standard partial molar volumes of the 3-methylimidazolium cation and the anion Br$^-$, and the

Table 5. Solution Conductivities (κ) and the Molar Conductivities (Λ_m) of [$C_n$mim]Br (n = 8, 10, 12) at 298.15 K in DMSO, DMF, and EG as a Function of Concentrations of the ILs

[C_8mim]Br			[C_{10}mim]Br			[C_{12}mim]Br		
10^4c / $mol \cdot L^{-1}$	κ / $\mu S \cdot cm^{-1}$	Λ_m / $S \cdot cm^2 \cdot mol^{-1}$	10^4c / $mol \cdot L^{-1}$	κ / $\mu S \cdot cm^{-1}$	Λ_m / $S \cdot cm^2 \cdot mol^{-1}$	10^4c / $mol \cdot L^{-1}$	κ / $\mu S \cdot cm^{-1}$	Λ_m / $S \cdot cm^2 \cdot mol^{-1}$
			Dimethylsulfoxide					
3.084	10.999	35.66	2.071	7.2672	35.08	3.026	10.415	34.42
3.997	14.193	35.51	3.447	12.013	34.85	3.758	12.885	34.29
4.924	17.433	35.40	4.551	15.802	34.72	4.555	15.563	34.16
5.853	20.652	35.29	5.770	19.959	34.59	5.343	18.199	34.06
6.583	23.178	35.21	6.934	23.891	34.46	6.078	20.646	33.97
7.657	26.873	35.10	8.066	27.695	34.33	6.771	22.943	33.89
8.527	29.848	35.01	8.974	30.743	34.26	7.464	25.234	33.81
9.411	32.876	34.93	10.43	35.611	34.13	8.059	27.189	33.74
10.33	35.981	34.85	12.34	41.931	33.97	9.021	30.353	33.65
			Ethylene glycol					
3.384	2.2948	6.78	3.546	2.3639	6.67	3.480	2.2762	6.54
4.129	2.7954	6.77	4.359	2.9024	6.66	4.233	2.7632	6.53
4.841	3.2701	6.75	5.147	3.4170	6.64	4.995	3.2552	6.52
5.608	3.7807	6.74	5.865	3.8881	6.63	5.785	3.7608	6.50
6.367	4.2872	6.73	6.739	4.4585	6.61	6.521	4.2308	6.49
7.095	4.7682	6.72	7.633	5.0409	6.60	7.213	4.6736	6.48
7.842	5.2632	6.71	8.415	5.5471	6.59	8.076	5.2208	6.46
8.592	5.7569	6.70	9.056	5.9611	6.58	8.687	5.6080	6.45
9.615	6.4291	6.69	9.847	6.4719	6.57	9.337	6.0180	6.44
10.54	7.0333	6.68	10.65	6.9876	6.56	10.12	6.5106	6.43
			N,*N*-Dimethylformamide					
2.813	22.058	78.41	1.732	13.502	77.94	1.357	10.437	76.91
3.412	26.643	78.08	2.484	19.233	77.42	1.826	13.983	76.56
3.997	31.079	77.75	3.119	24.037	77.08	2.263	17.270	76.31
4.885	37.776	77.32	3.859	29.603	76.72	2.718	20.667	76.05
5.571	42.898	77.00	4.585	35.017	76.36	3.169	24.024	75.81
6.412	49.137	76.63	5.275	40.130	76.07	3.578	27.066	75.64
7.099	54.221	76.38	5.939	44.991	75.75	4.043	30.484	75.41
7.743	58.939	76.12	6.636	50.097	75.49	4.399	33.111	75.27
8.340	63.303	75.90	7.275	54.729	75.23	4.725	35.485	75.10
8.925	67.545	75.68	7.761	58.221	75.02	5.219	39.114	74.94

slope, b, denotes the contribution per CH_2 group, $V^0_\Phi(CH_2)$, in the alkyl chain of the imidazolium cations to the standard partial molar volumes of the ILs in a given solvent. These values are represented in Table 3. It can be seen that within experimental errors, the values of $V^0_\Phi(CH_2)$ are almost constant, (17.7 ± 0.5) $cm^3 \cdot mol^{-1}$, in different solvents. It is interesting to note that the $V^0_\Phi(CH_2)$ value derived in this study was close to (17.30 ± 0.09) $cm^3 \cdot mol^{-1}$ derived from tetraalkylammonium bromide in different solvents.[30] This suggests that the contribution per CH_2 group to the standard partial molar volumes of the cations is independent of the solvents. The interactions between the alkyl chain and the solvents are very weak, and the alkyl chain remains in the unsolvated state. However, it was observed that the values of $V^0_{\Phi,1}$ are different in different solvents, which is due to the difference in the interactions of Br^- and 3-methylimidazolium cations with different solvents. The different a values confirmed this conclusion. By using the linear relationships shown in eq 3, the standard partial molar volumes of homologous 1-alkyl-3-methylimidazolium bromide can be predicted in the given solvent.

Standard Partial Molar Volumes for Cations of the ILs. On the basis of the values of standard partial molar volumes of Br^- in different solvents reported in the literature,[26] the standard partial molar volumes for cations of [$C_n$mim]Br (n = 8, 10, 12) were obtained and reported in Table 4. It is interesting to note that there are close relationships between the standard partial molar volumes of $[C_n\text{mim}]^+$ and the number of carbon atoms in the alkyl chain of the imidazolium ring. As shown in Figure 3, the standard partial molar volumes of $[C_n\text{mim}]^+$ increase linearly with increasing alkyl chain length of the cations in all the investigated solvents. This linear relationship can be represented by[31]

$$V^0_{\Phi,[C_n\text{mim}]} = \alpha + \beta n_c \tag{4}$$

where α stands for the standard partial molar volume of 3-methylimidazolium cation and β denotes the contribution per CH_2 group in the alkyl chains, $V^0_\Phi(CH_2)$, to the standard partial molar volume of the cations in different solvents. These values are also represented in Table 4. As can be expected, within experimental errors, β values are also almost constant [(17.7 ± 0.5) $cm^3 \cdot mol^{-1}$] in different solvents. However, the values of $V^0_{\Phi,[C_n\text{mim}]}{}^+$ are different from solvent to solvent, which results from the difference in the interactions between the 3-methylimidazolium cation and the solvents.

Limiting Molar Conductivities of the ILs and Their Cations. Conductometry provides us with information on the ionic association and the relative solvating ability of solvents for the ions. The molar conductivities of ILs in solutions have been calculated by

$$\Lambda_m = 10^3\kappa/c \tag{5}$$

where κ is the conductivity of the IL solutions after subtracting conductivity of the solvents and c is concentration of the ILs in solutions. The results of molar conductivities were listed in Table 5. According to Kohlrausch's law, molar conductivity for 1:1 electrolytes in a dilute solution is often related to its concentration by[32]

$$\Lambda_m = \Lambda_m{}^0 - Sc^{1/2} \tag{6}$$

where $\Lambda_m{}^0$ is the limiting molar conductivity of the ILs and S is a parameter reflecting the association interactions between

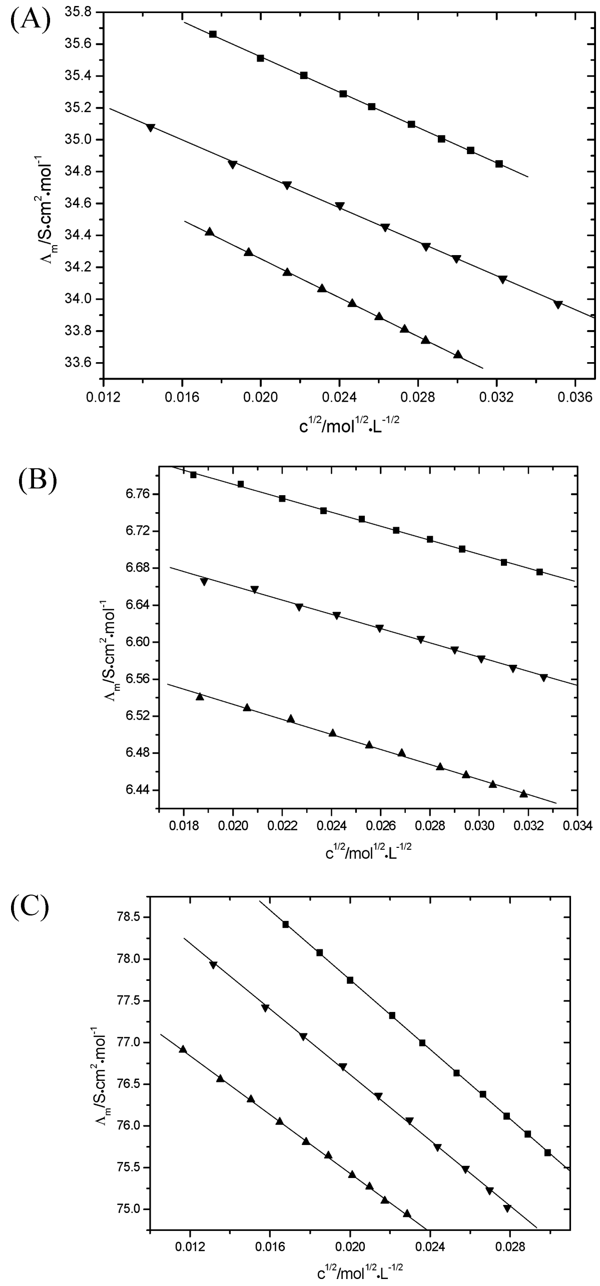

Figure 4. Plots of the molar conductivities (Λ_m) of the ILs vs the square root of the IL concentration ($c^{1/2}$) in different solvents at 298.15 K: (A) DMSO; (B) EG; (C) DMF; ■, [C$_8$mim]Br; ▼, [C$_{10}$mim]Br; ▲, [C$_{12}$mim]Br.

cations and anions. The values of $\Lambda_m{}^0$ and S were obtained by a least-squares linear regression procedure (as shown in Figure 4), and the results were given in Table 6. It is known that the Debye−Hückel−Onsager limiting equation has the same form as eq 6. Therefore, it is interesting to test if the limiting slopes of the straight lines in Figure 4 can be predicted by the Debye−Hückel−Onsager limiting law. Theoretically, the slope (S^{DH}) of the Debye−Hückel−Onsager limiting law for a 1:1 strong electrolyte can be calculated by the equation[33]

$$S^{DH} = A_1\Lambda_m{}^0 + B \tag{7}$$

where A_1 (mol$^{-1/2}\cdot$L$^{-1/2}$) = $82.04\cdot10^4/(\varepsilon T)^{3/2}$; B/(S$\cdot$cm$^2\cdot$mol$^{-3/2}\cdot$L$^{-1/2}$) = $82.49/\{\eta(\varepsilon T)^{1/2}\}$; and ε and η are the dielectric constant and the viscosity (P) of the solvent. The results calculated are also listed in Table 6. It can be seen that the S^{DH} values are in agreement with experimental ones within experimental error. This confirms that the S values can be predicted by the Debye−Hückel−Onsager limiting law.

It can be seen that the values of $\Lambda_m{}^0$ for [C$_n$mim]Br (n = 8, 10, 12) decrease with increasing alkyl chain length of the ILs in a given organic solvent. This is attributed to the increase of their intrinsic volumes with the alkyl chain length and also depends on the hydrophobic character of the methylene group −CH$_2$−. A similar phenomenon was observed for tetraalkylammonium bromide in organic solvents.[34] The limiting molar conductivity of the Br$^-$ anion is found to be (53.4, 23.76, and 5.21) S$\cdot$cm$^2\cdot$mol^{-1}, respectively, in DMF, DMSO, and EG at 298.15 K.[33] From these values, data of the limiting molar conductivities for the cations, $\Lambda_m{}^{0+}$, can be obtained. Then, the transport number for cations of the ILs in infinite dilution solutions has been calculated from $t^+ = \Lambda_m{}^{0+}/\Lambda^0{}_m$, and the results were also represented in Table 6. As can be expected, the cation transference number of [C$_n$mim]Br (n = 8, 10, 12) is less than 0.5, indicating that the cations can diffuse much slower than the anion because of their bulky size. For each of the ILs and their cations, the trend in the limiting molar conductivity in different organic solvents is in the order: DMF > DMSO > EG. This order is contrary to the solvent polarity order. Therefore, the limiting molar conductivities of a given IL in different organic solvents decrease with increasing polarity of the solvents, which is attributed to the increased interaction between the ILs and the higher polarity of solvent. This conclusion is in line with that obtained from the volume properties.

It is known that the viscosities of solvent investigated were (0.796, 1.948, and 19.90) mPa$\cdot$s for DMF, DMSO, and EG, respectively.[33] It is interesting to note that a good linear relationship exists between the limiting molar conductivities for each of the ILs or their cations and the reverse of the viscosity ($1/\eta$) for the solvents, as shown in Figure 5. This suggests that the fluidity of the solvents played an important role in the limiting molar conductivities of the ILs. The much lower values of the limiting molar conductivities of the ILs in EG can be ascribed to the much higher viscosity of this solvent.

According to the Walden law, if the Walden product is constant in different solvents, the solutes are not solvated; on the contrary, the solutes will be solvated by the solvents. It can be seen that the observed Walden product is not constant, indicating that the ionic liquids were solvated to different extents by the studied solvents.

Analysis of the data in Table 6 reveals another linear relation between the limiting molar conductivities of [C$_n$mim]$^+$ (n = 8, 10, 12) and the number of carbon atoms in the alkyl chain of cations. The slope of the linear plots shown in Figure 6 presents the contribution of per CH$_2$ group, $\Lambda^0{}_{CH2}$, to the limiting molar conductivity of the cations. By using a linear least-squares analysis, values of $\Lambda^0{}_{CH2}$ were found to be [(−0.29 ± 0.06), (−0.74 ± 0.03), and (−0.06 ± 0.0)] S$\cdot$cm$^{-2}\cdot$mol^{-1} in DMSO, DMF, and EG, respectively. This information may be useful for the molecular design of ILs.

Conclusion

In the present work, data on the densities, conductivities, apparent molar volumes, molar conductivities, standard partial molar volumes, and the limiting molar conductivities have been reported at 298.15 K, for the first time, for [C$_n$mim]Br (n = 8, 10, 12) in ethylene glycol, *N*,*N*-dimethylformamide, and dimethylsulfoxide. On the basis of the literature values of the Br$^-$ anion, the standard partial molar volumes and the limiting molar

Table 6. Limiting Molar Conductivities for the ILs (Λ^0_m) and the Cations (Λ^{0+}_m), the Cationic Transport Number (t^+) at 298.15 K, the Slope (S) and Standard Deviations (SD) of Equation 6, and the Slope (S^{DH}) of the Debye−Hückel−Onsager Limiting Law

		Λ^0_m				Λ^{0+}_m	
ILs	solvent	$S\cdot cm^2\cdot mol^{-1}$	S	S^{DH}	SD	$S\cdot cm^2\cdot mol^{-1}$	t^+
[C$_8$mim]Br	EG	6.92 ± 0.01	7.6 ± 0.1	8.7	0.01	1.7	0.25
	DMSO	36.63 ± 0.01	55.4 ± 0.4	53.5	0.01	12.9	0.35
	DMF	81.92 ± 0.02	208.6 ± 0.7	157.8	0.01	28.5	0.35
[C$_{10}$mim]Br	EG	6.81 ± 0.01	7.7 ± 0.2	8.6	0.01	1.6	0.23
	DMSO	35.85 ± 0.01	53.3 ± 0.5	53.1	0.01	12.1	0.34
	DMF	80.55 ± 0.04	196.9 ± 2.0	156.8	0.03	27.2	0.34
[C$_{12}$mim]Br	EG	6.70 ± 0.01	8.1 ± 0.2	8.5	0.01	1.5	0.22
	DMSO	35.47 ± 0.01	60.9 ± 0.4	53.0	0.01	11.7	0.33
	DMF	78.96 ± 0.03	176.3 ± 1.4	155.7	0.02	25.6	0.32

conductivities of the cations have also been reported in the three organic solvents. It was found that the standard partial molar volumes of the ILs and their cations increased linearly with increasing alkyl chain length in all the solvents investigated. The contribution of the alkyl chain to the standard partial molar volumes of the ILs and their cations depends only on the alkyl chain length and is independent of the solvents. The limiting molar conductivities of the ILs and their cations decrease linearly with the increase of the alkyl chain length. This attributes to the increase of their intrinsic volumes with the alkyl chain length. The limiting molar conductivities of the ILs and their cations in different organic solvents decreased in the order: DMF > DMSO > EG. A linear relationship was also found between the limiting molar conductivities of ILs or their cations and the fluidity of the solvents, suggesting the important role played by the viscosity of the solvents in the conductivity properties.

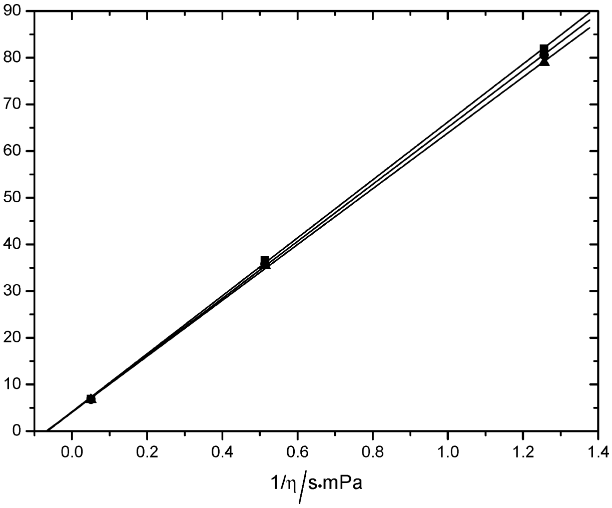

Figure 5. Linear plots of the limiting molar conductivities for the ILs versus the reverse of the viscosity of the solvents: ■, [C$_8$mim]Br; ●, [C$_{10}$mim]Br; ▲, [C$_{12}$mim]Br.

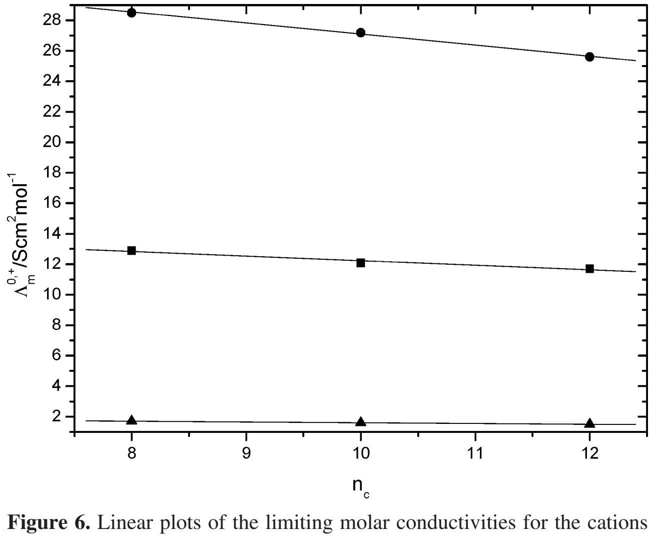

Figure 6. Linear plots of the limiting molar conductivities for the cations versus the number of carbon atoms (n_c) in the alkyl chain of the ILs: ■, DMSO; ●, DMF; ▲, EG.

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