

Ionic Association and Solvation of the Ionic Liquid 1-Hexyl-3-methylimidazolium Chloride in Molecular Solvents Revealed by Vapor Pressure Osmometry, Conductometry, Volumetry, and Acoustic Measurements

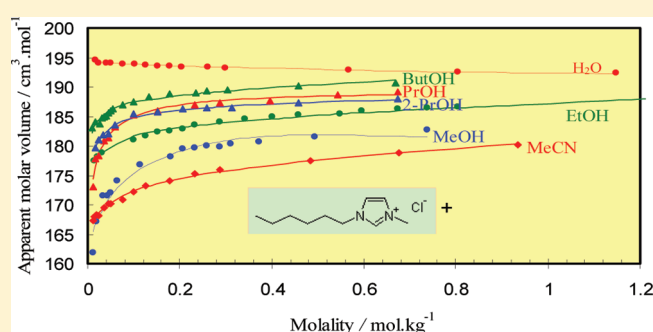
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Supporting Information

ABSTRACT: A systematic study of osmotic coefficient, conductivity, volumetric and acoustic properties of solutions of ionic liquid 1-hexyl-3-methylimidazolium chloride ($[\text{C}_6\text{mim}][\text{Cl}]$) in various molecular solvents has been made at different temperatures in order to study of ionic association and solvation behavior of $[\text{C}_6\text{mim}][\text{Cl}]$ in different solutions. Precise measurements on electrical conductances of solutions of $[\text{C}_6\text{mim}][\text{Cl}]$ in water, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and acetonitrile at 293.15, 298.15, and 303.15 K are reported and analyzed with Barthel's low-concentration chemical model (lcCM) to obtain the limiting molar conductivities and association constants of this ionic liquid in the investigated solvents.

Strong ion pairing was found for the ionic liquid in 2-propanol, 1-butanol, and 1-propanol, whereas ion association in acetonitrile, methanol and ethanol is rather weak and in water the ionic liquid is fully dissociated. In the second part of this work, the apparent molar volumes and isentropic compressibilities of $[\text{C}_6\text{mim}][\text{Cl}]$ in water, methanol, ethanol, acetonitrile, 1-propanol, 2-propanol, and 1-butanol are obtained at the 288.15–313.15 K temperature range at 5 K intervals at atmospheric pressure from the precise measurements of density and sound velocity. The infinite dilution apparent molar volume and isentropic compressibility values of the free ions and ion pairs of $[\text{C}_6\text{mim}][\text{Cl}]$ in the investigated solvents as well as the excess molar volume of the investigated solutions are determined and their variations with temperature and type of solvents are also studied. Finally, the experimental measurements of osmotic coefficient at 318.15 K for binary solutions of $[\text{C}_6\text{mim}][\text{Cl}]$ in water, methanol, ethanol, 2-propanol, and acetonitrile are taken using the vapor pressure osmometry (VPO) method and from which the values of the solvent activity, vapor pressure, activity coefficients, and Gibbs free energies are calculated. The results are interpreted in terms of ion association, ion-dipole interactions, and structural factors of the ionic liquid and investigated organic solvents. The ionic liquid is solvated to a different extent by the molecular solvents, and ionic association is affected significantly by ionic solvation.



INTRODUCTION

Ionic liquids (ILs) are organic salts that are liquids at temperatures below 373.15 K. They have received considerable attention as alternatives to the traditional organic solvents. Due to the phenomenal growth of publications dealing with their interesting physical and chemical properties^{1,2} and possible applications,³ they have been attracting intense interest in the scientific literature. In solution, the solvation and ionic association of ILs determine the unique properties of these systems and also most of the applications of ILs are closely related to these phenomena occurred in the IL solutions. In addition, a fundamental issue in the design of novel ionic liquids is the understanding of the nature/strength of cation–anion interactions and intermolecular forces in the bulk ionic fluid due to their intrinsic relation with most of their physicochemical properties, such as melting temperature, density, viscosity, surface tension, and vapor pressure.⁴

Although ILs because of their ionic nature form strong ion pairs in both the liquid state^{4–12} and the gas phase,^{13,14} systematic quantitative studies on the ionic association in IL solutions from the different thermodynamic properties are still scarce. Qualitative studies of ionic association behavior for some ILs in water and in organic solvents have been studied by NMR,^{15–17} infrared,^{16,17} electrospray ionization mass spectroscopy,^{4,18,19} and conductivity^{5,6,15,20,21} measurements. Only recently conductivity studies of IL mixtures aiming at the quantitative investigation of ion association have become available.^{22–30}

The ILs based on 1-alkyl-3-methylimidazolium cation ($[\text{C}_n\text{mim}]^+$) are one of the most important and promising class of ILs since they can be used for synthesis of IL with different anions

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including organic ones.^{3,31–35} That is why $[\text{C}_n\text{mim}]\text{Br}$ together with $[\text{C}_n\text{mim}]\text{Cl}$ represent a potential source of numerous ILs, and the study of their thermodynamic properties is of great importance. Among all the imidazolium based ILs, 1-alkyl-3-methylimidazolium bromide ionic liquids are the most studied ILs and despite the potential utility of $[\text{C}_n\text{mim}]\text{Cl}$, few of its physical properties have been reported. Considering the fact that the acoustic, volumetric, osmotic and conductometric behavior of IL-containing systems are of great relevance in assessing solvation and ion association of IL and also for the development of thermodynamic models specific to IL-containing systems, herein a systematic study of osmotic coefficient, conductivity, volumetric and acoustic properties of solutions of ionic liquid 1-hexyl-3-methylimidazolium chloride ($[\text{C}_6\text{mim}][\text{Cl}]$) in various molecular solvents has been made at different temperature in order to study of ionic association and solvation behavior of $[\text{C}_6\text{mim}][\text{Cl}]$ as well as their variation with the physicochemical properties of the molecular solvents. For these purposes, in the present work, the experimental measurements of osmotic coefficient at 318.15 K for binary solutions of $[\text{C}_6\text{mim}][\text{Cl}]$ in water, methanol, ethanol, 2-propanol, and acetonitrile, the electrical conductivities for binary solutions of $[\text{C}_6\text{mim}][\text{Cl}]$ in water, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and acetonitrile at 293.15, 298.15, and 303.15 K and density and sound velocity for solutions of $[\text{C}_6\text{mim}][\text{Cl}]$ in water, methanol, ethanol, acetonitrile, 1-propanol, 2-propanol, and 1-butanol at 288.15, 293.15, 298.15, 303.15, 308.15, and 313.15 K are taken.

EXPERIMENTAL SECTION

Materials. $[\text{C}_6\text{mim}][\text{Cl}]$ (>99.0% w/w), methanol (>0.999% w/w), ethanol (>0.999% w/w), acetonitrile (>0.999% w/w), 1-propanol (>0.998% w/w), 2-propanol (>0.995% w/w), 1-butanol (>0.990% w/w), NaCl (>99.5% w/w), and LiBr (>0.990% w/w) were obtained from Merck and were used without further purification. NaCl and LiBr were dried in an electrical oven at about 110 °C for 24 h prior to use. $[\text{C}_6\text{mim}][\text{Cl}]$ was dried in high vacuum at 333.15 K using a rotary evaporator for at least 4 h in 0.7 kPa. The moisture of $[\text{C}_6\text{mim}][\text{Cl}]$ was controlled by Karl Fischer method during the experimental method. Double distilled and deionized water was used.

Experimental Procedures. All of the solutions were prepared by mass on a Sartorius CP124S balance precise to within $\pm 1 \times 10^{-7}$ kg. Conductometric measurements were taken in a digital conductivity meter (Metrohm model 712) with a sensitivity of 0.1% and a dipping-type conductivity cell with platinized electrodes at a frequency of 1 MHz. The cell was calibrated with 0.01 mol dm⁻³ aqueous KCl solutions, and a cell constant of (0.855 ± 0.002) cm⁻¹ was determined. All measurements were performed in a double-walled glass container at a certain temperature maintained by a Julabo circulating thermostat with a precision of 0.02 K. The measurements of conductivities of the IL solutions were carried out by continuous addition of a concentrated IL solution into a known quantity of solvent taken in the container. The total uncertainty for this property at dilute molalities was estimated to be about 0.1%.

The density and sound velocity of the mixtures were measured at different temperatures with a digital vibrating-tube analyzer (Anton Paar DSA 5000, Austria) with proportional temperature control that kept the samples at working temperature within $\pm 10^{-3}$ K. The apparatus was calibrated with double distilled deionized, and degassed water, and dry air at atmospheric pressure according to the instrument catalog. Densities and ultrasonic velocities can be measured to $\pm 10^{-3}$ kg m⁻³ and $\pm 10^{-2}$ m s⁻¹,

Table 1. Relative Permittivities, ϵ , Viscosities, η , and Length of Orientated Solvent Molecules, s , of the Investigated Solvents at 293.15, 298.15, and 303.15 K

solvent	s/nm	$T = 293.15 \text{ K}$		$T = 298.15 \text{ K}$		$T = 303.15 \text{ K}$	
		ϵ	$10^3 \eta/\text{Pa s}$	ϵ	$10^3 \eta/\text{Pa s}$	ϵ	$10^3 \eta/\text{Pa s}$
water	0.28	80.18	1.0020	78.35	0.8903	76.58	0.7975
methanol	0.47	33.61	0.5834	32.63	0.5438	31.69	0.5080
ethanol	0.57	25.30	1.2047	24.356	1.0931	23.599	0.9939
1-propanol	0.69	20.80	2.1971	20.46	1.9471	19.78	1.7261
2-propanol	0.63	20.18	2.4043	19.387	2.0718	18.585	1.7772
1-butanol	0.75	17.84	2.9374	17.33	2.5695	16.69	2.2597
acetonitrile	0.58	36.76	0.3585	35.96	0.3413	35.19	0.3253

respectively, under the most favorable conditions. The experimental uncertainty of density and ultrasonic velocity measurements was $\pm 3 \times 10^{-3}$ kg m⁻³ and $\pm 10^{-1}$ m s⁻¹, respectively.

In this study, the VPO method was used to obtain the solvent activities of the investigated IL solutions. The vapor pressure osmometry was performed with the help of an Osmomat K-7000 (Knauer Inc.). The measuring chamber of osmometer contains a reservoir of solvent, paper wicks to provide a saturated solvent atmosphere, and two thermistors that are placed in an airtight cell which measure resistance changes caused by changes in temperature. First, a droplet of pure solvent is attached to each thermistor with the help of a microsyringe, and after 5 min of equilibration, the reading is adjusted to zero. Then the pure solvent on one thermistor is replaced by the IL solution and condensation of solvent from the vapor phase into the IL solution at the thermistor takes place. Due to the heat of condensation, the thermistor containing IL solution will be warmed and vapor pressure rises. These processes continue until the vapor pressure of the IL solution equals the vapor pressure of the pure solvent. The change in temperature changes the resistance of the thermistors. A bridge circuit measures the resistance difference of both thermistors. As long as changes in temperature are small, the resistance is proportional to ΔT . Generally, a time of 4–8 min suffices to reach this steady state. First, the instrument was calibrated using aqueous NaCl or non-aqueous LiBr solutions as reference with known osmotic coefficients in the proper concentration range, yielding a function that correlates the panel readings to the corresponding concentrations of the reference solutions and therefore their osmotic coefficients. Then in the same conditions, the panel readings were measured for the studied IL solutions. For each solution, at least five determinations (zero point adjustment and new solution) were performed and the mean value is reported. Generally, the deviations from the mean value were less than 1%. The cell temperature, which is electronically controlled, has a standard uncertainty of $\pm 1.10^{-3}$ K. For a certain IL solution with molality m which has a same instrument reading as a reference solution with molality m_{ref} and osmotic coefficient ϕ_{ref} the osmotic coefficient ϕ was obtained according to

$$\phi = (\nu_{\text{ref}} m_{\text{ref}} \phi_{\text{ref}}) / (\nu m) \quad (1)$$

where ν_{ref} and ν respectively are the stoichiometric number of reference electrolyte and IL. Osmotic coefficient for the reference NaCl + water,³⁶ LiBr + methanol,³⁷ ethanol,³⁸ acetonitrile,³⁹ and 2-propanol⁴⁰ solutions at different concentrations have been calculated from the correlation given in the corresponding literature.

RESULTS AND DISCUSSION

Conductance Properties. Conductometry is an electrochemical technique, which provides us valuable information on ion–ion and ion–solvent interactions in solution. The measured molar conductances (Λ) of the binary $[C_6mim][Cl]$ + water, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and acetonitrile systems as a function of molar concentration (c) at 293.15, 298.15, and 303.15 K are given in Table 1 of the Supporting Information. Figure 1 shows the concentration dependence of the molar conductivity for the investigated systems at 298.15 K. By increasing the IL concentration, the cation–anion interaction increases and the negative initial slope of Λ against IL concentration is attributed to these interactions. In the case of aqueous solution because of the smaller

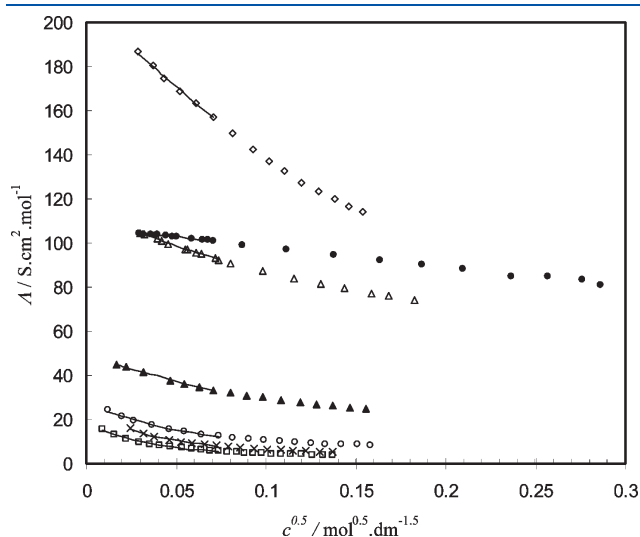


Figure 1. Variation of molar conductivities, Λ , with the square root of molarity, $c^{0.5}$, at 298.15 K for the solutions of $[C_6mim][Cl]$ in: ●, water; △, methanol; ▲, ethanol; ○, 1-propanol; ×, 2-propanol; □, 1-butanol; and ◇, acetonitrile; —, calculated by the lcCM.

cation–anion interaction, the concentration dependence of Λ is much less negative than those in organic solutions. Furthermore as can be seen from Figure 1, among all investigated systems only molar conductivity of the $[C_6mim][Cl]$ + water system depends linearly on $c^{0.5}$. This is because $[C_6mim][Cl]$ is fully dissociated in water, and there are no significant interactions between the ions.

The experimental conductance data at low concentration ($c < 0.006 \text{ mol.dm}^{-3}$) have been analyzed in the framework of the low-concentration chemical model (lcCM) of Barthel⁴¹ by means of the following set of equations:

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

$$K_A = \frac{1 - \alpha}{\alpha^2 c y_{\pm}^{\prime 2}}; \quad y_{\pm}^{\prime} = \exp\left(-\frac{\kappa q}{1 + \kappa R}\right); \quad c^\circ = 1 \text{ mol dm}^{-3} \quad (3)$$

$$\kappa^2 = 16\pi N_A q \alpha c; \quad q = \frac{e^2}{8\pi \epsilon_0 \epsilon k_B T} \quad (4)$$

$$K_A = 4\pi N_A \int_a^R r^2 \exp\left[\frac{2q}{r} - \frac{W^*(r)}{k_B T}\right] dr \quad (5)$$

where Λ^∞ is the molar conductivity at infinite dilution, $(1 - \alpha)$ is the fraction of oppositely charged ions acting as ion pairs, K_A is the standard-state association constant, y_{\pm}^{\prime} is the mean activity coefficient for the dissociated part of the electrolyte (the so-called free ions), κ is the Debye parameter, R distance parameter, e is the proton charge, ϵ is the relative permittivity of the solvent, ϵ_0 is the permittivity of the vacuum, T is the Kelvin temperature, and k_B and N_A are the Boltzman 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 $a \leq r \leq R$. $W^*(r)$ is the mean force potential of the non-electrostatic forces in the region $a \leq r \leq R$, which commonly is

Table 2. Limiting Molar Conductivities, Λ^∞ , Association Constants, K_A , Values for the Parameter $R(J_2)$, and Standard Deviation, σ_Λ , for Solutions of $[C_6mim][Cl]$ in the Investigated Solvents at 293.15, 298.15, and 303.15 K

solvent	T = 293.15 K			T = 298.15 K			T = 303.15 K		
	$\Lambda^\infty /$ S cm ² mol ^{−1}	$K_A /$ dm ³ mol ^{−1}	$R(J_2) /$ nm	$\Lambda^\infty /$ S cm ² mol ^{−1}	$K_A /$ dm ³ mol ^{−1}	$R(J_2) /$ nm	$\Lambda^\infty /$ S cm ² mol ^{−1}	$K_A /$ dm ³ mol ^{−1}	$R(J_2) /$ nm
water	96.34	4.6	0.377	106.95	2.4	0.736	123.10	7.8	0.245
		$\sigma_\Lambda = 0.062$			$\sigma_\Lambda = 0.104$			$\sigma_\Lambda = 0.776$	
methanol	110.21	45.0	0.019	113.15	28.6	0.019	121.24	33.4	0.031
		$\sigma_\Lambda = 0.527$			$\sigma_\Lambda = 0.208$			$\sigma_\Lambda = 0.601$	
ethanol	43.76	102	0.358	48.38	90	0.692	54.00	97	0.642
		$\sigma_\Lambda = 0.187$			$\sigma_\Lambda = 0.103$			$\sigma_\Lambda = 0.226$	
1-propanol	21.61	295.4	0.028	25.74	352.6	0.001	29.34	361.4	0.013
		$\sigma_\Lambda = 0.120$			$\sigma_\Lambda = 0.474$			$\sigma_\Lambda = 0.296$	
2-propanol	18.29	650	0.0002	22.71	790	0.0001	27.18	972	0.133
		$\sigma_\Lambda = 0.206$			$\sigma_\Lambda = 0.178$			$\sigma_\Lambda = 0.322$	
1-butanol	13.382	615	0.0002	16.77	920	0.006	18.02	800	0.001
		$\sigma_\Lambda = 0.027$			$\sigma_\Lambda = 0.213$			$\sigma_\Lambda = 0.061$	
acetonitrile	181.59	54.7	0.026	202.58	53.5	0.156	213.12	13	1.699
		$\sigma_\Lambda = 0.855$			$\sigma_\Lambda = 1.006$			$\sigma_\Lambda = 0.220$	

Table 3. Limiting Molar Conductivities, Λ^∞ , and Association Constants, K_A , of some ILs in Different Solvents at 298.15 K Taken from Literature

$\Lambda^\infty /$ S cm ² mol ⁻¹	$K_A /$ dm ³ mol ⁻¹	$\Lambda^\infty /$ S cm ² mol ⁻¹	$K_A /$ dm ³ mol ⁻¹	$\Lambda^\infty /$ S cm ² mol ⁻¹	$K_A /$ dm ³ mol ⁻¹	$\Lambda^\infty /$ S cm ² mol ⁻¹	$K_A /$ dm ³ mol ⁻¹	$\Lambda^\infty /$ S cm ² mol ⁻¹	$K_A /$ dm ³ mol ⁻¹
[C ₄ mim][Cl] + water ²⁹		[C ₅ mim][Cl] + water ³⁰		[C ₄ mim][Cl] + methanol ²⁵		[C ₆ mim][Br] + water ²⁶		[C ₆ mim][Br] + water ²⁹	
109.47	7.92	89.31	4.9	108.64	15.5	108.36	4.90	103.74	5.41
[C ₆ mim][Br] + methanol ²⁷		[C ₆ mim][Br] + 1-propanol ²⁷		[C ₆ mim][Br] + acetonitrile ²⁷		[C ₆ mim][BF ₄] + water ²²		[C ₆ mim][PF ₆] + water ²²	
130.9	147	27.2	724	178.1	130		6.0		7.4

introduced as a temperature-dependent step potential

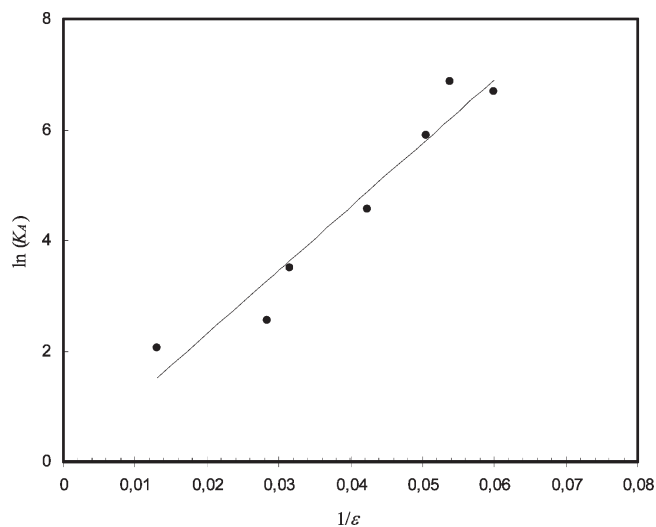
$$W^*(r) = \text{const for } a \leq r \leq R$$

$$W^*(r) = 0 \text{ for } R \leq r \leq \infty \quad (6)$$

The coefficients of eq 2 are given in the literature.⁴¹ The limiting slope S and the parameter E are completely calculable when the solvent data are available (see Table 1). The coefficients J_1 and J_2 are functions of the distance parameter R , representing the distance to which oppositely charged ions can approach as freely moving particles in the solution.

For associated electrolytes, as in the present case, data analysis is carried out by a nonlinear least-squares iterations with coefficients S , E , and J_1 of eq 2 preset to their theoretical values and with Λ^∞ , K_A , and J_2 as the adjustable parameters.⁴¹ The lower limit, a , of the association integral is the distance of closest approach of cation and anion, $a = a_+ + a_-$, calculated from the ionic radii of cation, $a_+ = 0.353$ nm for [C₆mim]⁺,⁵ and anion, $a_- = 0.181$ nm for Cl⁻.⁴¹ The upper limit of ion association, R , appeared in the relations for J_1 and y_{\pm} is given by an expression of the type⁴¹ $R = a + s$, where s is the length of orientated solvent molecules in the ion pair which is independent of temperature. The obtained values of Λ^∞ , K_A and $R(J_2)$ for all the investigated systems are summarized in Table 2. A direct comparison of our Λ^∞ and K_A values with literature ones is not possible for the IL studied in this work, because as far as we know those are not available in the literature. However, in order to check the quality of the obtained data, the obtained Λ^∞ and K_A values in this work have been compared with the values reported in the literature for some similar ILs (see Table 3).

As can be seen, other ILs have association constants of similar magnitude in the investigated solvents. The data in Tables 2 and 3 show that the anion species dependence of the association constants of the [C₆mim][X] in water follows the order [PF₆]⁻ > [BF₄]⁻ > Br⁻ > Cl⁻. Considering the trend [PF₆]⁻ < [BF₄]⁻ < Br⁻ < Cl⁻ for the electrostatic interaction with the [C₆mim]⁺, it would be expected that at the same condition, the association constant of these ILs should be observed in the sequence [PF₆]⁻ < [BF₄]⁻ < Br⁻ < Cl⁻ which is opposite with those observed experimentally. In fact the anions with higher surface charge hydrate more water molecules than the anions with lower surface charge and in the case of anions with higher surface charge, this solvation reduces their associations with the cation, which shapes the order observed experimentally. In fact the formation of ion pairs is strongly influenced by the ionic solvation and the relative strength of ionic association of the IL is controlled by the net result of competition between the intrinsic interactions of cations with anions and the ionic solvation. The similar behavior was obtained by Wang et al.²⁷

**Figure 2.** Plot of the logarithm of the association constant, $\ln(K_A)$, for [C₆mim][Cl] versus the reciprocal of dielectric constant, $1/\epsilon$, of the solvents at 303.15 K.

The data given in Tables 1 and 2 show that the ionic association constants of [C₆mim]Cl increase as the relative permittivities of the solvents decrease. It was found that a linear relationship exists between the logarithm of K_A of the IL and the reciprocal of the dielectric constants of the solvents as manifested in Figure 2. This is qualitatively consistent with the classical ionic association theory of electrolytes⁴² and electrostatic interaction between the cation and anion is mainly responsible for their association.

From the values of the limiting molar conductivities of the chloride anion reported to be 98.83,⁴³ 52.29,⁴³ 76.4,⁴³ 21.89,⁴³ 10.45,⁴⁴ 10.55,⁴⁵ and 7.76⁴⁶ S cm² mol⁻¹ respectively in acetonitrile, methanol, water, ethanol, 1-propanol, 2-propanol, and 1-butanol at 298.15 K, the corresponding data of the limiting molar conductivities for [C₆mim]⁺ were obtained as 103.75, 60.86, 30.55, 26.49, 15.29, 12.16, and 9.01 S cm² mol⁻¹ respectively. By applying the values of limiting molar conductivities of Br⁻ in different solvents (100.09 S cm² mol⁻¹ in acetonitrile⁴⁷ and 56.55 S cm² mol⁻¹ in methanol⁴⁸), the limiting molar conductivities obtained by Wang et al.²⁷ for [C₆mim]⁺ are 78.01 and 74.35 S cm² mol⁻¹ in acetonitrile and methanol, respectively, which differ significantly from the values obtained in this work. Wang et al. in the two separate works also reported very different values 35.4²⁷ and 69.1⁴⁹ S cm² mol⁻¹ for the limiting molar conductivities of [C₆mim]⁺ in water. That is to say the published data on ionic liquids in the literature are only rarely

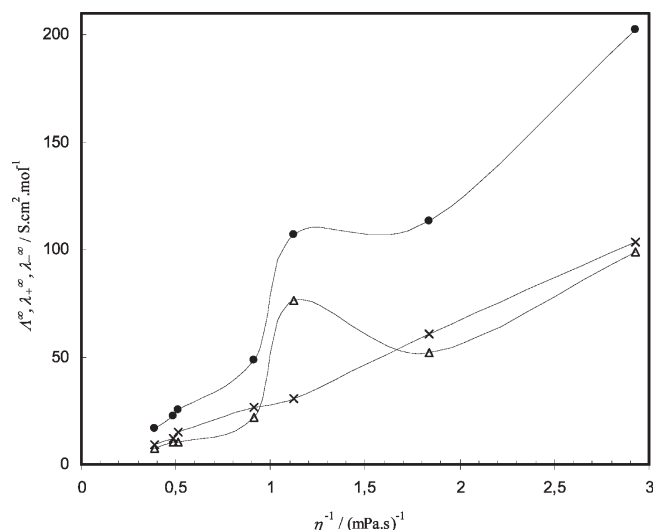


Figure 3. Variation of the limiting molar conductivity with the reciprocal of the viscosity of the solvents at 298.15 K: ●, [C₆mim][Cl]; Δ, Cl[−]; ×, [C₆mim]⁺.

consistent. In fact ILs (especially imidazolium based ILs) are very hygroscopic and in many cases the used ILs are synthesized (such as refs 27 and 49). Therefore the values of obtained data can be depended on the method of preparation and purification, the cleanness of applied substance and moisture of ILs as well as the concentration range of the ILs solutions used for the correlation of experimental data.

In fact except for Cl[−] (and therefore for [C₆mim]Cl too) in the aqueous solution a linear relationship exists between the values of the limiting molar conductivity and the reciprocal of the viscosities of the solvents as manifested in Figure 3, and therefore, we can say that the fluidity of the solvents played a predominant role in the limiting molar conductivities. The results show that, despite a significant difference in the size of Cl[−] and [C₆mim]⁺, the ionic transport numbers of [C₆mim]⁺ in the investigated nonaqueous solvents are higher than 0.5. This implies that although the cationic radius is much larger than that of the anion however in nonaqueous solutions the cation [C₆mim]⁺ can move faster than Cl[−]. Ionic mobility in a known solution is strongly influenced by the ionic radius as well as the ionic solvation. Therefore, we can conclude that Cl[−] anion was highly solvated in the investigated nonaqueous solvents as compared with the [C₆mim]⁺. However the ionic transport number of [C₆mim]⁺ in water is 0.29, which suggests that solvation of the Cl[−] anion in water is relatively weaker than that in the investigated nonaqueous solvents. The standard partial molar volumes of Cl[−] in water, methanol, ethanol and acetonitrile are 17.83,⁵⁰ 15,⁵¹ 12,⁵¹ and 3⁵¹ cm³ mol^{−1}, respectively, which supports the above explanation. In fact the small volume is attributed to the strong attractive interactions due to the solvation of ions and the large solvation shell around the ions causes their low mobility. Differences in ion solvation can also be reflected by the differing Walden product, λ[∞]η, for the investigated solvents. At each temperature the value of λ[∞]η for Cl[−] in water is larger than those in the investigated nonaqueous solvents which also indicates that solvation of the Cl[−] anion in water is weaker than that in the investigated nonaqueous solvents. Furthermore, in water additional strong hydrophobic interactions are present that affect more than the ion size and viscosity parameters.⁵²

Temperature dependence of Λ[∞] can be expressed by the following equation:⁵³

$$\ln \Lambda^{\infty} + \frac{2}{3} \ln d_s = -\frac{\Delta H^*}{RT} + B \quad (7)$$

where d_s is density of solvent, ΔH^* is Eyring activation enthalpy of charge transfer and B is a constant. Values $\Delta H^* = (6.438, 11.166, 14.990, 17.967, 21.580, 22.114, \text{ and } 28.746) \text{ kJ} \cdot \text{mol}^{-1}$ for methanol, acetonitrile, ethanol, water, 1-butanol, 1-propanol, and 2-propanol, respectively. These values are larger than the corresponding Eyring activation enthalpies of viscous flow for the pure 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.^{25,28}

Volumetric and Acoustic Properties. The experimental density (d) and speed of sound (u) data for the binary [C₆mim]-[Cl] + water, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and acetonitrile systems as a function of IL molality (m) at 288.15, 293.15, 298.15, 303.15, 308.15, and 313.15 K are given in Table 2 of the Supporting Information. The apparent molar volume, ϕ_V , and apparent molar isentropic compressibility, ϕ_K , of [C₆mim][Cl] in the investigated solutions were determined from the experimental density and sound velocity data using the following equations:

$$\phi_V = \frac{1000}{m d d_s} (d_s - d) + \frac{M}{d} \quad (8)$$

$$\phi_K = -\left(\frac{\partial \phi_V}{\partial P}\right)_s = \frac{1000(\kappa_s d_s - \kappa_{ss} d)}{m d d_s} + \frac{M \kappa_s}{d} \quad (9)$$

where κ_{ss} and κ_s are isentropic compressibilities of solvent and solution, respectively. The isentropic compressibility is defined as

$$\kappa_s = \frac{1}{d u^2} \quad (10)$$

In the above equations, M is the molecular mass of the IL, m is its molality, d_s and d are the densities of the solvent and the solution, respectively, and u_s and u are the sound velocities of the solvent and the solution, respectively. The variation of ϕ_V , ϕ_K , κ_s , and excess molar volume (V^E) as a function of the molality of [C₆mim][Cl] at 298.15 K are shown in Figure 4. The values of ϕ_V for [C₆mim][Cl] in water decreased along with an increase in the IL molality, however that in the other investigated nonaqueous solvents initially increase sharply with IL molality as a result of the ion–ion interactions and at high concentration the values of ϕ_V vary very slightly with IL molality until a constant value is reached. The volume of an ion pair, which forms in nonaqueous solvents whose dielectric constants are lower than that of water, is larger than the sum of the volume of the free ions due to the greater electrostrictive effect of the ions on the solvent molecules. The volume change occurring on ion pairing in nonaqueous solvents, $\Delta_{IP} V^\circ$, is the difference between the sum of the standard partial molar volumes of the ions, V° (IL), and the standard molar volume of the ion pair, V_{IP}° , (hypothetical, since at infinite dilution complete dissociation takes place) which can be calculated from the following relation:⁵⁴

$$\phi_V = \alpha(V^\circ(\text{IL}) + S_V c^{0.5}) + (1 - \alpha)V_{IP}^\circ + b_V c \quad (11)$$

where the fraction dissociated, α , is obtained independently from eqs 3 and 4, S_V is the theoretical (Debye–Hückel) limiting slope and b_V is an empirical constant. For each system, the values of α and

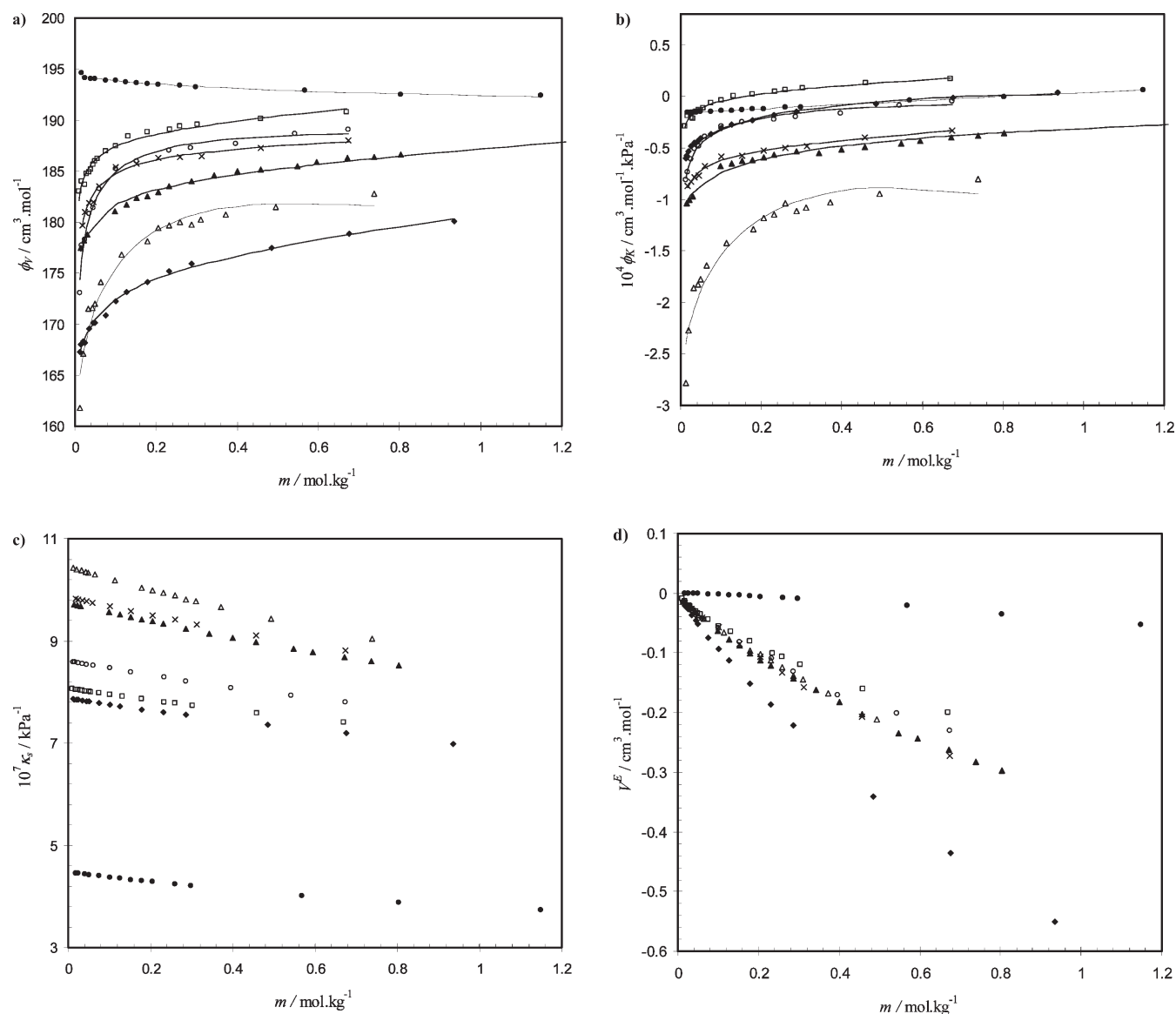


Figure 4. (a) Plot of apparent molar volume of $[C_6mim][Cl]$, ϕ_v , in different solutions against molality of the ionic liquid, m , at 298.15 K. (b) Plot of apparent molar isentropic compressibility of $[C_6mim][Cl]$, ϕ_κ , in different solutions against molality of the ionic liquid, m , at 298.15 K. (c) Plot of isentropic compressibility of different solutions of $[C_6mim][Cl]$, κ_s , against molality of the ionic liquid, m , at 298.15 K. (d) Plot of excess molar volumes, V^E , of different solutions of $[C_6mim][Cl]$ against molality of the ionic liquid, m , at 298.15 K: ●, water; Δ, methanol; ▲, ethanol; ○, 1-propanol; ×, 2-propanol; □, 1-butanol; and ◆, acetonitrile; —, eqs 11 (ϕ_v) and 18 (ϕ_κ).

S_V at 298.15 K were used for all the investigated temperatures. S_V is the Debye–Hückel slope for the apparent molar volume and for 1:1 electrolytes can be calculated from the following equation:⁵⁵

$$S_V = \frac{6RTA_\phi}{d_s^{0.5}} \left\{ \left(\frac{\partial \ln \varepsilon}{\partial P} \right)_T - \frac{\kappa_T}{3} \right\} \quad (12)$$

where A_ϕ , ε , κ_T , P , and d_s are Debye–Hückel constant for osmotic coefficient on the molal base, the dielectric constant, the isothermal compressibility, pressure and density of solvent, respectively. The A_ϕ values for different solvents can be obtained from the following equation:

$$A_\phi = \frac{1}{3} (2\pi N_A d_s)^{0.5} (e^2 / 4\pi \varepsilon_0 \varepsilon k_B T)^{1.5} \quad (13)$$

It was shown that, the values for $(\partial \ln \varepsilon / \partial P)_T$ could be estimated from the following relation:⁵⁶

$$\left(\frac{\partial \ln \varepsilon}{\partial P} \right)_T = 1.039 \kappa_T - 0.920 \frac{\kappa_T}{\varepsilon} \quad (14)$$

The required $\kappa_T = (\partial \ln d / \partial P)_T$ values were calculated from the pressure dependence of density values in the form of the Tait equation which are available for different solvents with respect to pressure.^{57–59} The calculated κ_T , $(\partial \ln \varepsilon / \partial P)_T$ and S_V values together with the values for some other physical properties for the investigated solvents are given in Table 4. The obtained values of $V^\circ(\text{IL})$ and V_{IP}° are given in Table 5.

As can be seen from Table 5, the values of $V^\circ(\text{IL})$ of $[C_6mim][Cl]$ in nonaqueous solvents decrease by increasing temperature; however, the values of $V^\circ(\text{IL})$ in water increase as

Table 4. Physical Properties for Different Solvents at 298.15 K

component	$d/\text{g cm}^{-3}$	$u/\text{m s}^{-1}$	$10^6 \kappa_T/\text{kPa}^{-1}$	$10^{12}(\partial\kappa_T/\partial P)_T/\text{kPa}^{-2}$	$10^6(\partial \ln \varepsilon/\partial P)_T/\text{kPa}^{-1}$	$10^{12}(\partial^2 \ln \varepsilon/\partial P^2)_T/\text{kPa}^{-2}$	$A_\phi/\text{kg}^{0.5} \text{mol}^{-0.5}$	$S_V/\text{cm}^3 \text{dm}^{1.5} \text{mol}^{-1.5}$	$10^5 S_K/\text{cm}^3 \text{dm}^{1.5} \text{kPa}^{-1} \text{mol}^{-1.5}$
water	0.997047	1496.73	0.4523 ^a	−0.1152 ^a	0.4757 ^a	−0.7935 ^a	0.39165	1.8956	−0.5329
methanol	0.786531	1102.16	1.2285	−13.6770	1.2417	−13.7818	1.29429	18.0654	−22.2750
ethanol	0.785164	1143.03	1.1198	−11.9411	1.1211	−11.9083	2.00526	25.1737	−29.5094
1-propanol	0.799544	1205.03	0.9765	−9.4049	0.9707	−9.3062	2.62823	28.2064	−29.7093
2-propanol	0.781038	1139.17	1.1227	−12.9027	1.1133	−12.7343	2.81624	35.0270	−43.8549
1-butanol	0.805879	1239.85	0.9135	−8.2564	0.9007	−8.0965	3.38415	33.4271	−32.9554
acetonitrile	0.776582	1278.49	1.117	−10.225	1.132	−10.3298	1.11164	14.253	−14.6106

^a Reference 60.Table 5. Sum of the Standard Partial Molar Volumes of the Free Ions, $V^\circ(\text{IL})/(\text{cm}^3 \text{mol}^{-1})$, the Standard Molar Volume of the Ion Pair, $V_{\text{IP}}^\circ/(\text{cm}^3 \text{mol}^{-1})$, the Standard Partial Molar Expansibilities of Free Ions, $E^\circ(\text{IL})/\text{cm}^3 \text{mol}^{-1} \text{K}^{-1}$, and Ion Pair, $E_{\text{IP}}^\circ/\text{cm}^3 \text{mol}^{-1} \text{K}^{-1}$, for $[\text{C}_6\text{mim}][\text{Cl}]$ in the Investigated Solvents in this Work at Different Temperatures, T

$T = 288.15 \text{ K}$		$T = 293.15 \text{ K}$		$T = 298.15 \text{ K}$		$T = 303.15 \text{ K}$		$T = 308.15 \text{ K}$		$T = 313.15 \text{ K}$	
$V^\circ(\text{IL})$	V_{IP}°	$V^\circ(\text{IL})$	V_{IP}°	$V^\circ(\text{IL})$	V_{IP}°	$V^\circ(\text{IL})$	V_{IP}°	$V^\circ(\text{IL})$	V_{IP}°	$V^\circ(\text{IL})$	V_{IP}°
$[\text{C}_6\text{mim}][\text{Cl}] + \text{water}; E^\circ(\text{IL}) = 0.1798 \text{ cm}^3 \text{mol}^{-1} \text{K}^{-1}$											
192.699		193.622		194.611		195.471		196.377		197.166	
$[\text{C}_6\text{mim}][\text{Cl}] + \text{methanol}; E^\circ(\text{IL}) = -0.1965 \text{ cm}^3 \text{mol}^{-1} \text{K}^{-1}; E_{\text{IP}}^\circ = 0.0561 \text{ cm}^3 \text{mol}^{-1} \text{K}^{-1}$											
158.011	190.629	157.394	190.703	156.279	191.273	155.415	191.448	154.303	191.705	153.160	191.958
$[\text{C}_6\text{mim}][\text{Cl}] + \text{ethanol}; E^\circ(\text{IL}) = -0.2096 \text{ cm}^3 \text{mol}^{-1} \text{K}^{-1}; E_{\text{IP}}^\circ = 0.0234 \text{ cm}^3 \text{mol}^{-1} \text{K}^{-1}$											
173.121	182.666	171.795	182.976	170.365	183.259	169.736	183.247	168.692	183.319	167.733	183.282
$[\text{C}_6\text{mim}][\text{Cl}] + 1\text{-propanol}; E^\circ(\text{IL}) = -0.1541 \text{ cm}^3 \text{mol}^{-1} \text{K}^{-1}; E_{\text{IP}}^\circ = 0.0207 \text{ cm}^3 \text{mol}^{-1} \text{K}^{-1}$											
150.189	190.762	149.421	190.965	148.050	191.223	147.673	191.256	146.475	191.399	146.638	191.22
$[\text{C}_6\text{mim}][\text{Cl}] + 2\text{-propanol}; E^\circ(\text{IL}) = -0.2547 \text{ cm}^3 \text{mol}^{-1} \text{K}^{-1}; E_{\text{IP}}^\circ = -0.0352 \text{ cm}^3 \text{mol}^{-1} \text{K}^{-1}$											
154.269	188.065	153.670	187.918	152.244	187.859	150.559	187.767	149.388	187.478	148.262	187.115
$[\text{C}_6\text{mim}][\text{Cl}] + 1\text{-butanol}; E^\circ(\text{IL}) = -0.1385 \text{ cm}^3 \text{mol}^{-1} \text{K}^{-1}; E_{\text{IP}}^\circ = 0.0364 \text{ cm}^3 \text{mol}^{-1} \text{K}^{-1}$											
166.582	188.131	165.256	188.384	164.225	188.674	165.134	188.681	162.877	189.051	162.981	189.005
$[\text{C}_6\text{mim}][\text{Cl}] + \text{acetonitrile}; E^\circ(\text{IL}) = -0.2110 \text{ cm}^3 \text{mol}^{-1} \text{K}^{-1}; E_{\text{IP}}^\circ = -0.0285 \text{ cm}^3 \text{mol}^{-1} \text{K}^{-1}$											
164.265	175.614	163.39	175.512	162.131	175.582	161.434	175.216	160.255	175.101	158.902	174.937

temperature increases. In the most cases, the values of V_{IP}° increase very slightly by increasing temperature. The standard partial molar expansibilities of free ions, $E^\circ(\text{IL}) = (\partial V^\circ(\text{IL})/\partial T)$, and ion pair, $E_{\text{IP}}^\circ = (\partial V_{\text{IP}}^\circ/\partial T)_P$, for different solutions of the studied ionic liquid were determined and have also been given in Table 5. Furthermore, the volume change occurring on ion pairing, $\Delta_{\text{IP}}V^\circ$, increases by increasing the temperature and whose values for the investigated solvents decrease in the order 1-propanol > 2-propanol > methanol > 1-butanol > acetonitrile > ethanol. At infinite dilution, each ion is surrounded only by the solvent molecules and therefore the infinite dilution molar volume is unaffected by ion + ion interaction and it is a measure only of the ion + solvent interaction. The infinite dilution apparent molar volume of a solute can be expressed as the sum of two contributions:

$$V^\circ(\text{IL}) = V_{\text{int}}^\circ + V_{\text{elec}}^\circ \quad (15)$$

where V_{int}° is the intrinsic volume of the solute molecule which is inaccessible to solvent and V_{elec}° is the difference between volume of the solvation shell of a solute and volume of the bulk solvent (electrostriction). It is evident that V_{int}° is independent of temperature and certain properties of solvent. However V_{elec}° which is negative depends on the charge and size of the ion, temperature and on certain properties of the solvent. At least two opposite

phenomena have influence on the changes of the infinite dilution apparent molar volumes of the ions with temperature. First of them consists in fact that the structure of the solvent is weakened by the elevation of temperature and consequently the electrostriction operates much more effectively and then the values of V_{elec}° become more negative. In the case of solvents whose compressibilities increase by increasing temperature (such as nonaqueous solvents, see Figure 5) this effect seems to predominate. Second, one can expect that increase in the temperature will cause increase of the volume of disordered region of the solvation sphere.⁶¹ At a given temperature, the obtained values of $V^\circ(\text{IL})$ for $[\text{C}_6\text{mim}][\text{Cl}]$ in the investigated solvents decrease in the order water > ethanol > 1-butanol > acetonitrile > methanol > 2-propanol > 1-propanol. However, the obtained values of V_{IP}° decrease in the order methanol \approx 1-propanol > 1-butanol > 2-propanol > ethanol > acetonitrile. The infinite dilution solvation numbers of $[\text{C}_6\text{mim}][\text{Cl}]$ in the investigated solvents, n° , can be calculated from⁶⁰

$$n^\circ = \frac{V^\circ(\text{IL}) - V_{\text{int}}^\circ}{\Delta V_{\text{el}}} \quad (16)$$

where ΔV_{el} is the mean molar electrostriction volume of solvents which has the values of −2.91, −5.99, −14.41, −26.67, and −4.93 $\text{cm}^3 \text{mol}^{-1}$ respectively for water, methanol, 1-propanol,

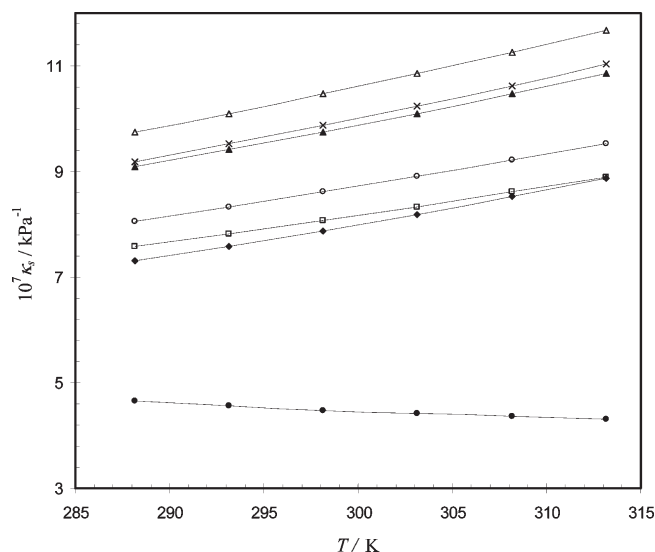


Figure 5. Variation of the isentropic compressibility of pure solvents, κ_s , with temperature, T : ●, water; Δ, methanol; ▲, ethanol; ○, 1-propanol; ×, 2-propanol; □, 1-butanol; and ◆, acetonitrile.

2-propanol, and acetonitrile at 298.15 K.⁶⁰ From the intrinsic volumes of $[\text{C}_6\text{mim}]^+$ and Cl^- , which are 145.74⁶² and 25.5⁶³ $\text{cm}^3 \text{mol}^{-1}$, respectively, the intrinsic volume of the IL was obtained as 171.24 $\text{cm}^3 \text{mol}^{-1}$. The corresponding n° values of $[\text{C}_6\text{mim}][\text{Cl}]$ at 298.15 K in those solvents for which ΔV_{el} are available were obtained as 2.5, 1.6, 0.7, and 1.8 respectively for methanol, 1-propanol, 2-propanol, and acetonitrile. The volume in water can not be analyzed in these terms, since in this case $V^\circ(\text{IL}) > V^\circ_{\text{int}}$, leading to negative n° value (negatively hydrated structure breaking ion⁶⁰). This is because the solvation of the Cl^- anion in water is very weaker than that in the investigated nonaqueous solvents as discussed above. The number of solvent molecules released on ion pairing, Δn_{IP} , can be calculated from the⁶⁰

$$\Delta n_{\text{IP}} = \frac{\Delta_{\text{IP}} V^\circ}{\Delta V_{\text{el}}} \quad (17)$$

The corresponding Δn_{IP} values of $[\text{C}_6\text{mim}][\text{Cl}]$ at 298.15 K were obtained as 5.8, 3.0, 1.3, and 2.7 respectively in methanol, 1-propanol, 2-propanol, and acetonitrile.

In Figure 6 the temperature and concentration dependence of ϕ_V are given for $[\text{C}_6\text{mim}][\text{Cl}]$ in ethanol for which the data in the high concentration range have been determined. The similar behavior can be expected for the other nonaqueous solvents. The values of ϕ_V for the low ($m < 0.63 \text{ mol kg}^{-1}$) and high ($m > 0.63 \text{ mol kg}^{-1}$) IL molality respectively decrease and increase by increasing temperature. Therefore we can conclude that in nonaqueous solvents although the sum of molar volume of ions C_6mim^+ and Cl^- decrease by increasing temperature however the molar volume of the ion pair $\text{C}_6\text{mim}^+\text{Cl}^-$ increases with temperature. The values of excess molar volume (V^E) for the all nonaqueous systems are negative and become more negative with increasing temperature in the whole concentration range. However the values of V^E for aqueous solutions of $[\text{C}_6\text{mim}][\text{Cl}]$, which are much less negative than those for nonaqueous solutions, become less negative with increasing temperature. At each temperature, the values of V^E decrease in the order water (molar volume of pure water = 18.07 $\text{cm}^3 \text{mol}^{-1}$) > 1-butanol

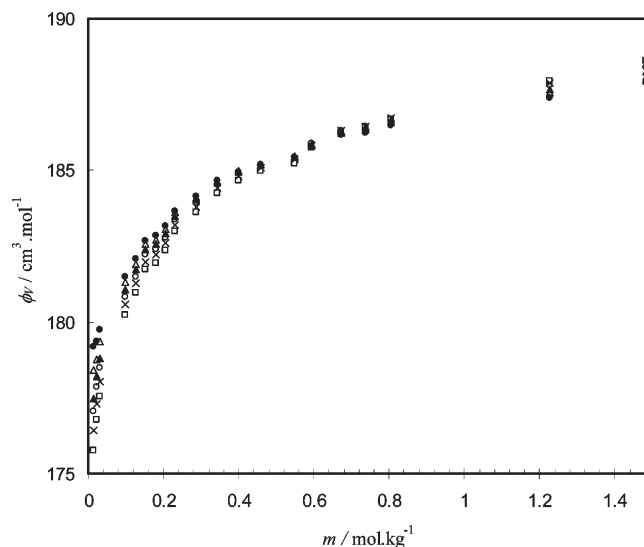


Figure 6. Variation of the apparent molar volume of $[\text{C}_6\text{mim}][\text{Cl}]$, ϕ_V , in ethanol against molality of the ionic liquid, m , at: ●, 288.15 K; Δ, 293.15 K; ▲, 298.15 K; ○, 303.15 K; ×, 308.15 K; □, 313.15 K.

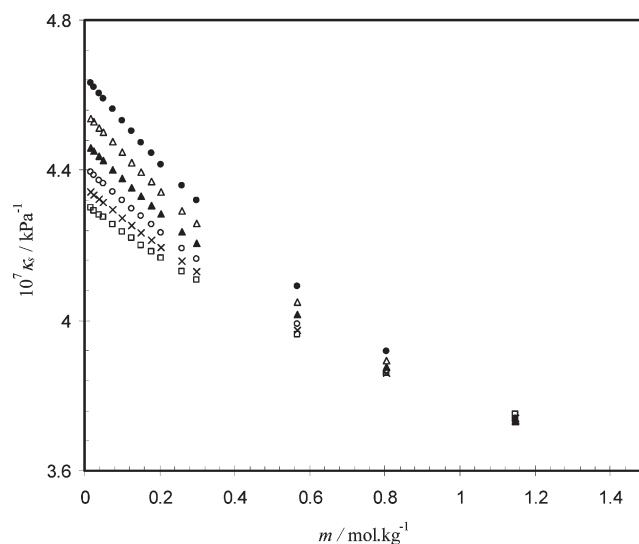


Figure 7. Variation of the isentropic compressibility of aqueous solutions of $[\text{C}_6\text{mim}][\text{Cl}]$, κ_s , against molality of the ionic liquid, m , at: ●, 288.15 K; Δ, 293.15 K; ▲, 298.15 K; ○, 303.15 K; ×, 308.15 K; and □, 313.15 K.

(91.98 $\text{cm}^3 \text{mol}^{-1}$) > 1-propanol (75.17 $\text{cm}^3 \text{mol}^{-1}$) \approx methanol (40.74 $\text{cm}^3 \text{mol}^{-1}$) \approx 2-propanol (76.95 $\text{cm}^3 \text{mol}^{-1}$) \approx ethanol (58.68 $\text{cm}^3 \text{mol}^{-1}$) > acetonitrile (52.86 $\text{cm}^3 \text{mol}^{-1}$).

The isentropic compressibility, κ_s , of all the solutions decreases with increasing concentration of IL. Although, the values of κ_s for pure nonaqueous solvents and for nonaqueous IL solutions increase with increasing temperature in the whole IL concentration range, however, for pure water and aqueous solutions with low concentration of IL, the values of κ_s decrease with increasing temperature. Furthermore, for both pure solvents and (IL + solvent) solutions with a known IL concentration, the values of κ_s follow the order water < acetonitrile < 1-butanol < 1-propanol < ethanol < 2-propanol < methanol. The isentropic

Table 6. Sum of the Standard Partial Molar Isentropic Compressibility of the Ions, $K^\circ(\text{IL})/(\text{cm}^3 \text{mol}^{-1} \text{kPa}^{-1})$, and the Standard Molar Isentropic Compressibility of the Ion Pair, $K_{\text{IP}}/(\text{cm}^3 \text{mol}^{-1} \text{kPa}^{-1})$, for $[\text{C}_6\text{mim}][\text{Cl}]$ in the Investigated Solvents in this Work at Different Temperatures, T

$T = 288.15 \text{ K}$		$T = 293.15 \text{ K}$		$T = 298.15 \text{ K}$		$T = 303.15 \text{ K}$		$T = 308.15 \text{ K}$		$T = 313.15 \text{ K}$	
$10^4 K^\circ(\text{IL})$	$10^4 K_{\text{IP}}^\circ$	$10^4 K^\circ(\text{IL})$	$10^4 K_{\text{IP}}^\circ$	$10^4 K^\circ(\text{IL})$	$10^4 K_{\text{IP}}^\circ$	$10^4 K^\circ(\text{IL})$	$10^4 K_{\text{IP}}^\circ$	$10^4 K^\circ(\text{IL})$	$10^4 K_{\text{IP}}^\circ$	$10^4 K^\circ(\text{IL})$	$10^4 K_{\text{IP}}^\circ$
$[\text{C}_6\text{mim}][\text{Cl}] + \text{water}$											
−0.3965		−0.2683		−0.1586		−0.0688		0.0144		0.0856	
$[\text{C}_6\text{mim}][\text{Cl}] + \text{methanol}$											
−2.5454	0.7728	−2.7805	0.7406	−3.0249	0.7184	−3.3031	0.6605	−3.6799	0.6870	−3.9522	0.5922
$[\text{C}_6\text{mim}][\text{Cl}] + \text{ethanol}$											
−0.9499	0.0444	−1.1390	−0.0052	−1.3622	−0.0593	−1.5973	−0.1208	−1.8143	−0.1989	−2.0785	−0.2846
$[\text{C}_6\text{mim}][\text{Cl}] + 1\text{-propanol}$											
−1.5662	0.2496	−1.8249	0.2366	−1.8778	0.1766	−2.2667	0.1765	−2.4179	0.1100	−2.7341	0.0814
$[\text{C}_6\text{mim}][\text{Cl}] + 2\text{-propanol}$											
−1.5744	−0.1445	−1.9210	−0.1959	−2.0561	−0.2867	−2.3378	−0.3811	−2.6459	−0.4827	−2.7898	−0.6200
$[\text{C}_6\text{mim}][\text{Cl}] + 1\text{-butanol}$											
−0.7493	0.2222	−1.0258	0.2081	−1.1030	0.1728	−1.2186	0.1320	−1.3754	0.0876	−1.4988	0.0435
$[\text{C}_6\text{mim}][\text{Cl}] + \text{acetonitrile}$											
−0.5465	0.2909	−0.6033	0.2291	−0.7548	0.2118	−0.8837	0.1514	−1.0195	0.0989	−1.2098	0.0574

compressibility of a solution can be taken as the sum of two contributions, κ_s (solvent intrinsic) and κ_s (solute intrinsic). For the concentration range investigated in this study (low concentrations) the κ_s (solvent intrinsic) is the dominant contribution to the total value of κ_s and therefore the effect of temperature and type of solvent on the isentropic compressibility of the investigated IL solutions is similar to those of pure solvents. It was found that⁶⁴ at each temperature the isentropic compressibility of pure IL is smaller than that of water (and therefore all other investigated solvents) and similar to the organic solvents increases by increasing temperature. By increasing the IL concentration, the contribution of κ_s (solvent intrinsic) decreases and therefore the values of κ_s for the solution also decrease. In the case of IL + water system, for the temperature range investigated in this work, $d\kappa_s(\text{solute intrinsic})/dT > 0$ and $d\kappa_s(\text{solvent intrinsic})/dT < 0$. The results show that the value of $\partial\kappa_s/\partial T$ is much less negative in dilute aqueous IL solution than in pure water, and as the concentration of IL increases, $\partial\kappa_s/\partial T$ becomes less negative. As can be seen from Figure 7, at a specific IL concentration (about 1.15 mol kg^{-1}) in which the $\kappa_s(\text{water intrinsic})$ and $\kappa_s(\text{solute intrinsic})$ have the same contributions, the isentropic compressibility isotherms of aqueous solution of IL intersect. Therefore, one can assume that the isentropic compressibilities for the corresponding concentration are independent of temperature and at this concentration $d\kappa_s(\text{solute intrinsic})/dT + d\kappa_s(\text{solvent intrinsic})/dT = 0$. In fact, the $\kappa_s(\text{solvent intrinsic})$ is the dominant contribution to the total value of κ_s from pure water up to the converging concentration, and beyond that $\kappa_s(\text{solute intrinsic})$ is the substantial contribution.

As can be seen from Figure 4b, similar to the apparent molar volume, at low concentrations the values of ϕ_K for $[\text{C}_6\text{mim}][\text{Cl}]$ in nonaqueous solvents increase sharply with IL molality as a result of the ion–ion interactions. However at high concentration the values of ϕ_K vary very slightly with IL molality until a constant value is reached. The values of ϕ_K for the nonaqueous systems are negative in most cases and become more negative with increasing temperature in the whole concentration range.

However the values of ϕ_K of $[\text{C}_6\text{mim}][\text{Cl}]$ in water increase with increasing temperature. The negative values of ϕ_K (loss of compressibility of the medium) indicate that the solvent molecules surrounding the $[\text{C}_6\text{mim}][\text{Cl}]$ would present greater resistance to compression than the bulk. On the other hand, the positive values of ϕ_K indicate that the solvent molecules around the $[\text{C}_6\text{mim}][\text{Cl}]$ are more compressible than the solvent molecules in the bulk solution. By increasing the IL concentration, because of the increasing the ion–ion interactions, the ion–water interaction decreases and therefore the solvent molecules around the $[\text{C}_6\text{mim}][\text{Cl}]$ become more compressible. If we assume that α be independent of pressure, by differentiating eq 11 with respect to pressure, we obtain the following equation for the apparent molar isentropic compressibility:

$$\phi_K = \alpha(K^\circ(\text{IL}) + S_K c^{0.5}) + (1 - \alpha)K_{\text{IP}}^\circ + b_K c \quad (18)$$

where $K^\circ(\text{IL})$ is the sum of the standard partial molar isentropic compressibility of the free ions and K_{IP}° (hypothetical, since at infinite dilution complete dissociation takes place) is the standard molar isentropic compressibility of the ion pair, which have been given in Table 6. For each system, the values of α and S_K at 298.15 K were used for all the investigated temperatures. S_K is the Debye–Hückel slope for the apparent molar compressibility and for 1:1 electrolytes can be calculated from the following equation:⁵⁵

$$S_K = \frac{6RTA_\phi}{d_s^{0.5}} \left[\left(\frac{\partial^2 \ln \epsilon}{\partial P^2} \right)_T - \frac{1}{3} \left(\frac{\partial \kappa_T}{\partial P} \right)_T - \frac{3}{2} \left\{ \left(\frac{\partial \ln \epsilon}{\partial P} \right)_T - \frac{\kappa_T}{3} \right\}^2 \right] \quad (19)$$

From eq 14 we have

$$\left(\frac{\partial^2 \ln \epsilon}{\partial P^2} \right)_T = 1.039 \left(\frac{\partial \kappa_T}{\partial P} \right)_T - \frac{0.920}{\epsilon} \left(\left(\frac{\partial \kappa_T}{\partial P} \right)_T - \kappa_T \left(\frac{\partial \ln \epsilon}{\partial P} \right)_T \right) \quad (20)$$

The calculated S_K values at 298.15 K are also given in Table 4. Both of $K^\circ(\text{IL})$ and K_{IP}° in nonaqueous solvents decrease with increasing temperature. However the values of $K^\circ(\text{IL})$ in

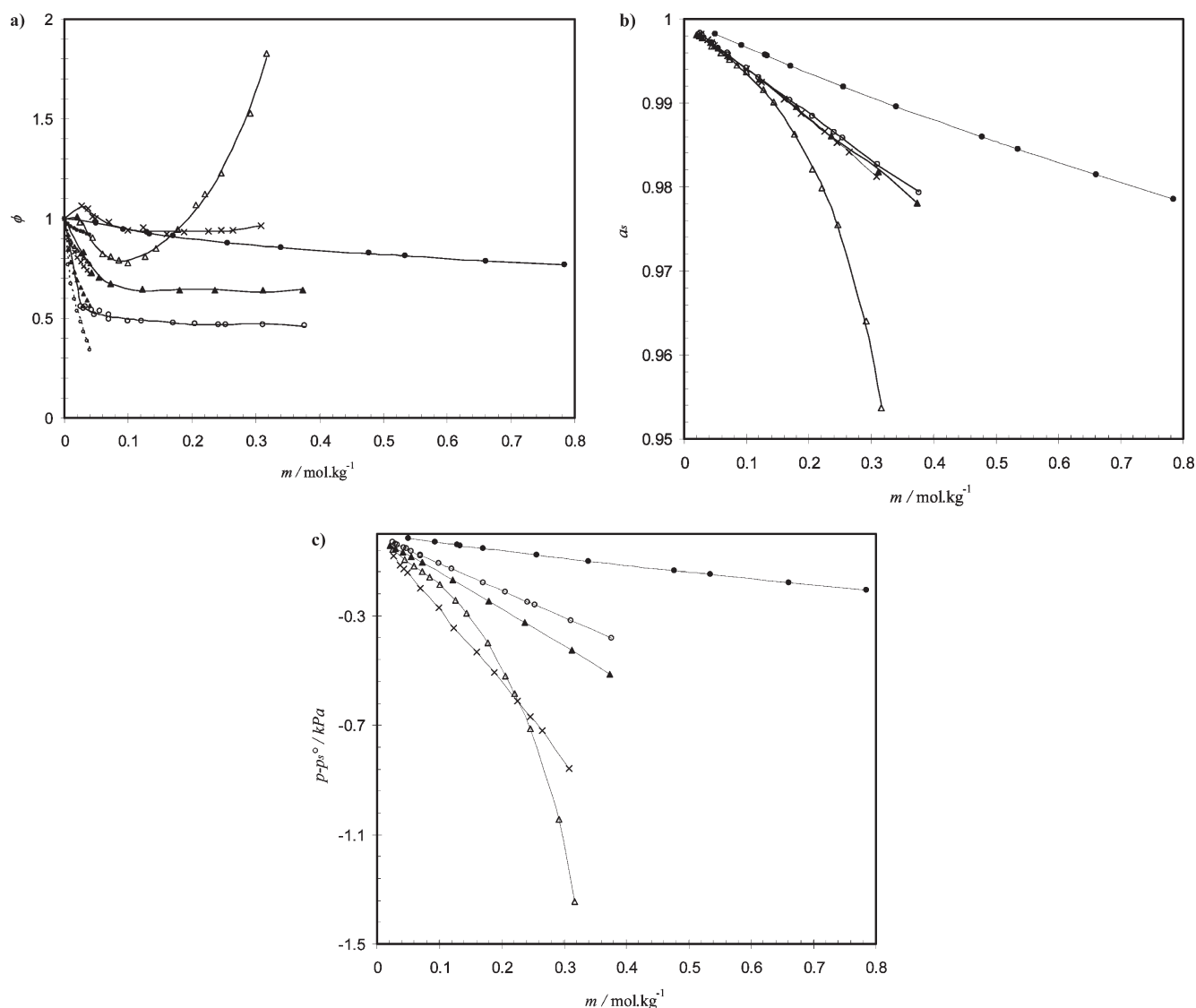


Figure 8. (a) Plot of osmotic coefficient of different solutions of $[C_6mim][Cl]$, ϕ , against molality of the ionic liquid, m , at 318.15 K. (b) Plot of solvent activity of different solutions of $[C_6mim][Cl]$, a_s , against molality of the ionic liquid, m , at 318.15 K. (c) Plot of vapor pressure depression of different solutions of $[C_6mim][Cl]$, $p - p_s^0$, against molality of the ionic liquid, m , at 318.15 K: \times , methanol; Δ , acetonitrile; \blacktriangle , ethanol; \circ , 2-propanol; \bullet , water; —, Pitzer equation; and \cdots , Debye–Hückel limiting law.

aqueous solutions increase with increasing temperature. The values of $K^\circ(\text{IL})$ are more negative than those of K_{IP}° , which indicate that the solvent molecules around the ion pair are more compressible than those around the free ions. Furthermore, the isentropic compressibility changes occurring on ion pairing, $\Delta_{\text{IP}}K^\circ = K_{\text{IP}}^\circ - K^\circ(\text{IL})$, which are positive, increase by increasing the temperature and whose values for the investigated solvents decrease in the order methanol > 1-propanol > 2-propanol > ethanol > 1-butanol > acetonitrile. By increasing the temperatures, the relative permittivities of the solvents decrease and the ion pair formation increases and therefore the large values of $\Delta_{\text{IP}}K^\circ$ or $\Delta_{\text{IP}}V^\circ$ can be expected. At a given temperature, the obtained values of $K^\circ(\text{IL})$ for $[C_6mim][Cl]$ in the investigated solvents decrease in the order water > acetonitrile > 1-butanol > ethanol > 1-propanol > 2-propanol > methanol. However, the obtained values of K_{IP}° decrease in the order methanol > acetonitrile \approx 1-propanol \approx 1-butanol > ethanol > 2-propanol. From Figure 4, panels a and b, we can say that the values of

$\phi_V (= \alpha\phi_{V_i} + (1 - \alpha)\phi_{V_{\text{IP}}})$ and $\phi_K (= \alpha\phi_{K_i} + (1 - \alpha)\phi_{K_{\text{IP}}})$ at finite concentration (both of free ions and ion pairs exist) respectively follow the orders acetonitrile < methanol < ethanol < 2-propanol \approx 1-propanol < 1-butanol < water and methanol < ethanol < 2-propanol < 1-propanol \approx acetonitrile \approx water < 1-butanol.

Osmotic Properties. For the understanding of interactions in liquids, the activity or osmotic coefficients of different components are of great interest. They are the most relevant thermodynamic reference data, and they are often the starting point of any modeling. The experimental osmotic coefficients, ϕ , of the binary $[C_6mim][Cl]$ + water, methanol, ethanol, 2-propanol, and acetonitrile systems measured at 318.15 K are given in Table 3 of the Supporting Information and are shown in Figure 8a. That is to say the osmotic coefficient data reported in Table 3 were determined on the basis of full dissociation of both ionic liquid and reference electrolyte. In other words, both of ν_{ref} and ν in eq 1 were set to 2. In the same solute molality, the magnitudes of

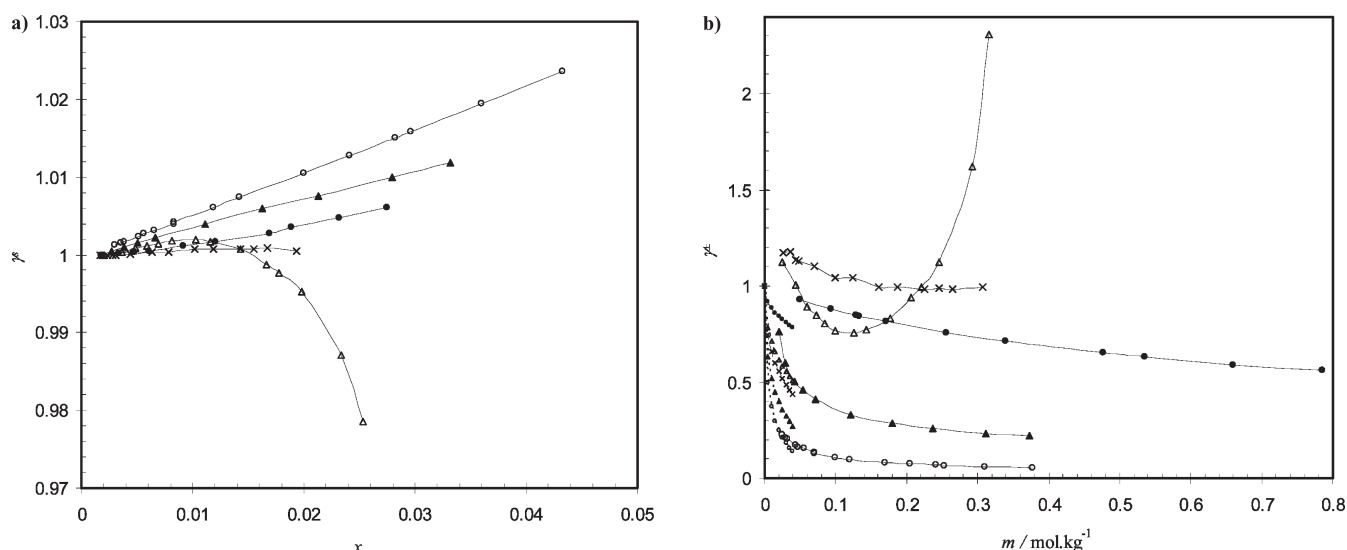


Figure 9. (a) Plot of solvent activity coefficients of different solutions of $[\text{C}_6\text{mim}][\text{Cl}]$, γ_s , against mole fraction of the ionic liquid, x , at 318.15 K. (b) Plot of mean molal activity coefficients of different solutions of $[\text{C}_6\text{mim}][\text{Cl}]$, γ_{\pm} , against molality of the ionic liquid, m , at 318.15 K: \times , methanol; Δ , acetonitrile; \blacktriangle , ethanol; \circ , 2-propanol; \bullet , water; and \cdots , Debye–Hückel limiting law.

the osmotic coefficient of the investigated solutions have the order of 2-propanol < ethanol < acetonitrile ($m < 0.17 \text{ mol kg}^{-1}$) < water < methanol < acetonitrile ($m > 0.17 \text{ mol kg}^{-1}$). From these results and the values of the standard-state association constant given in Table 2 we can say that the higher the ion association, the smaller are the values of the osmotic coefficients. However the osmotic coefficients of methanol solutions because of the stronger ion solvation are larger than those of aqueous solutions. In Figure 8a the results of the Debye–Hückel limiting law (DHLL), $\phi^{\text{DHLL}} = 1 - A_{\phi}|z_+ z_-|I^{0.5}$, have also been given. All of the investigated systems show the positive deviations from DHLL. Several factors account for deviations from DHLL; these include ion association (has a negative contribution to the deviations from DHLL) and strong and specific ion–solvent solvation forces that invalidate the assumption that the solvent is a dielectric medium (has a positive contribution to the deviations from DHLL)³⁹ and overall deviation from DHLL is controlled by the net result of competition between the intrinsic interactions of cations with anions and the ionic solvation.

From the experimental osmotic coefficients, it is possible to calculate the solvent activities and vapor pressures of the investigated solutions using the following relations:

$$\ln(a_s) = -M_s \nu m \phi \quad (21)$$

$$\ln a_s = \ln\left(\frac{p}{p_s^\circ}\right) + \frac{(B_s^\circ - V_s^\circ)(p - p_s^\circ)}{RT} \quad (22)$$

where M_s is the molar mass of the solvent, B_s° is the second virial coefficient of solvent vapor, V_s° is the molar volume of liquid solvent, and p_s° is the vapor pressure of pure solvent. Data of solvent activity and vapor pressures of the investigated solutions are also given in Table 3 of the Supporting Information. In Figure 8, panels b and c, respectively, comparison of the solvent activity and vapor pressure depression data for the studied systems has been made. In the same solute molality, the magnitudes of the solvent activity of the investigated solutions have the order of acetonitrile \ll methanol < ethanol < 2-propanol \ll water and also

the magnitudes of vapor pressure depression data decrease in the order acetonitrile ($m > 0.23 \text{ mol kg}^{-1}$) > methanol > acetonitrile ($m < 0.23 \text{ mol kg}^{-1}$) > ethanol > 2-propanol > water.

The solvent activity was used to obtain the solvent activity coefficient, $\gamma_s = a_s/x_s$. Calculated solvent activity coefficients, γ_s , of the investigated solutions are also given in Table 3 of the Supporting Information and are shown in Figure 9a. Except for acetonitrile solutions, the calculated solvent activity coefficients are very slightly larger than unity (positive deviations from ideal solution behavior) and increase as the solute concentration increases. The calculated values of γ_s of the investigated solutions have the order acetonitrile ($x > 0.014$) < methanol < water < acetonitrile ($x < 0.014$) < ethanol < 2-propanol.

The experimental osmotic coefficients are related to the mean molal activity coefficients, γ_{\pm} , at molality m' by the relation

$$\ln \gamma_{\pm} = \Phi' - 1 + \int_0^{m'} \frac{\Phi - 1}{m} dm \quad (23)$$

The osmotic coefficients were correlated by the extended Pitzer ion-interaction model of Archer^{65,66} which has the following form for 1:1 electrolytes:

$$\begin{aligned} \phi - 1 = & \frac{-A_{\phi}\sqrt{I}}{1 + b\sqrt{I}} + m(\beta^{(0)} + \beta^{(1)}\exp[-\alpha_1\sqrt{I}]) \\ & + \beta^{(2)}\exp[-\alpha_2\sqrt{I}] + m^2(C^{(0)} + C^{(1)}\exp[-\alpha_3\sqrt{I}]) \end{aligned} \quad (24)$$

where $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, $C^{(0)}$, and $C^{(1)}$ are ion interaction parameter of Archer extension of Pitzer model that are dependent on temperature and pressure and are given in Table 7. A_{ϕ} values at 318.15 K for water, methanol, ethanol, 2-propanol, and acetonitrile are 0.4062, 1.38074, 2.17545, 3.2862, and 1.13319 $\text{kg}^{0.5} \text{ mol}^{-0.5}$, respectively. I is the ionic strength in molality. The other constants were $b = 3.2$ (nonaqueous solvents) and 1.2 (water) $\text{kg}^{0.5} \text{ mol}^{-0.5}$, $\alpha_1 = 2 \text{ kg}^{0.5} \text{ mol}^{-0.5}$, $\alpha_2 = 7 \text{ kg}^{0.5} \text{ mol}^{-0.5}$, and $\alpha_3 = 1 \text{ kg}^{0.5} \text{ mol}^{-0.5}$. The calculated values of γ_{\pm} (obtained from eq 23 by using the Pitzer's model, eq 24, for ϕ) are also given in Table 3 of Supporting Information and are shown in

Table 7. Parameters of the Extended Archer Extension of Pitzer Model for Solutions of $[\text{C}_6\text{mim}][\text{Cl}]$ in the Investigated Solvents at 318.15 K

system	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^{(0)}$	$C^{(1)}$
$[\text{C}_6\text{mim}][\text{Cl}] + \text{water}$	4.70626	−8.99018	11.90355	1.65191	−14.12115
$[\text{C}_6\text{mim}][\text{Cl}] + \text{methanol}$	179.00725	−295.15672	171.45546	166.36943	−767.53495
$[\text{C}_6\text{mim}][\text{Cl}] + \text{ethanol}$	170.61578	−283.55654	152.20740	139.91831	−696.61513
$[\text{C}_6\text{mim}][\text{Cl}] + 2\text{-propanol}$	−67.96898	116.11078	−74.0456	−53.87992	272.79214
$[\text{C}_6\text{mim}][\text{Cl}] + \text{acetonitrile}$	386.21546	−629.24662	315.25286	428.75047	−1777.57

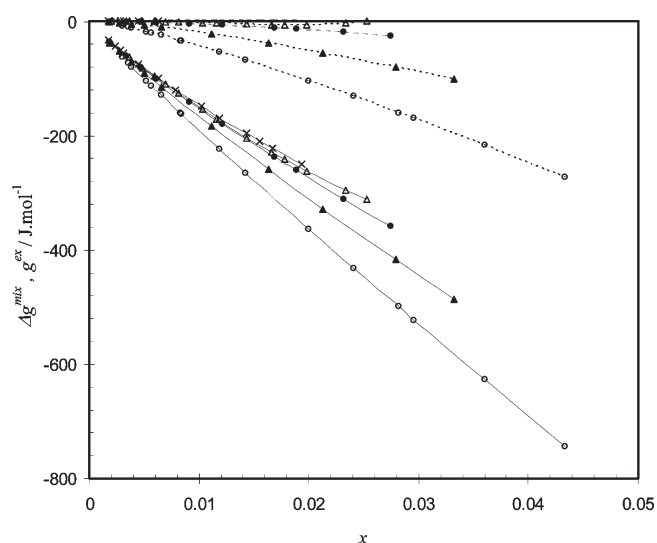
**Figure 10.** Molar excess Gibbs energy, g^{ex} (dotted lines), and molar Gibbs energy change due to mixing, Δg^{mix} (solid lines), of investigated solutions against mole fraction of the ionic liquid, x , at 318.15 K: \times , methanol; Δ , acetonitrile; \blacktriangle , ethanol; \circ , 2-propanol; and \bullet , water.

Figure 9b. For 2-propanol, ethanol, and aqueous solutions, $\gamma_{\pm} < 1$ (negative deviations from ideal-solution behavior) and decreased along with an increase in the solute concentration. Furthermore the observed trend for the calculated γ_{\pm} of investigated solutions is similar to those obtained for ϕ . In Figure 9b the results of the Debye–Hückel limiting law (DHLL), $\gamma_{\pm}^{\text{DHLL}} = \exp(-3A_{\phi} |z_+ z_-| I^{0.5})$, have also been given. All of the investigated systems show the positive deviations from DHLL.

The following relation was used to obtain the mole fraction mean ionic activity coefficient, $\gamma_{\pm}^{(x)}$ from the molal mean ionic activity coefficient γ_{\pm} :

$$\ln \gamma_{\pm}^{(x)} = \ln \gamma_{\pm} + \ln \left(1 + \frac{M_s v m}{1000} \right) \quad (25)$$

The activity coefficient data, which had been converted to mole fraction scale, were used to calculate the molar excess Gibbs free energy (g^{ex}) and the molar Gibbs free energy change due to mixing (Δg^{mix}) of solutions, and the values are shown in Figure 10. The molar excess Gibbs free energy and the molar Gibbs free energy change due to mixing are negative and decrease with increase in concentration of the solutes. As expected, the excess free energies for the solutions are less negative than Δg^{mix} , indicating the importance of enthalpy and entropy effects in these solutions. Furthermore the values for both of g^{ex} and

Δg^{mix} follow the order 2-propanol < ethanol < water < acetonitrile < methanol.

CONCLUSION

Ionic association and solvation behavior of ionic liquid $[\text{C}_6\text{mim}][\text{Cl}]$ have been studied by a systematic measurements of osmotic coefficient, conductivity, volumetric and acoustic properties of its solutions in various molecular solvents at different temperature. From the obtained K_A values, it was found that strong ionic association occurs for the ionic liquid in 2-propanol, 1-butanol, and 1-propanol, whereas ion association in acetonitrile, methanol and ethanol is rather weak and in water the ionic liquid is fully dissociated. In fact similar to the simple electrolytes, a linear relationship exists between the $\ln K_A$ values of the IL and the reciprocal of the dielectric constants of the solvents, which indicates that the electrostatic interaction between the cation and anion is mainly responsible for their association. The limiting molar conductivities of $[\text{C}_6\text{mim}]\text{Cl}$ and $[\text{C}_6\text{mim}]^+$ in the investigated solvents increase linearly (except that of $[\text{C}_6\text{mim}]\text{Cl}$ in water) with the reverse of the viscosity of the solvents, which indicates that the fluidity of the solvents played a predominant role in the limiting molar conductivities. The limiting molar conductivities are also influenced by the ionic solvation. From the ionic transport numbers and the Walden product, it was suggested that Cl^- anion was highly solvated in the investigated nonaqueous solvents as compared with the $[\text{C}_6\text{mim}]^+$ and also the solvation of the Cl^- anion in water is weaker than that in the investigated nonaqueous solvents.

The standard partial molar volume and isentropic compressibilities of the free ions $[\text{C}_6\text{mim}]^+$ and Cl^- and the ion pair $[\text{C}_6\text{mim}]^+\text{Cl}^-$ in the all investigated solvents were obtained at different temperature. The trend of all of the investigated volumetric and acoustic properties of $[\text{C}_6\text{mim}][\text{Cl}]$ in water with temperature is completely opposite to that for nonaqueous solvents. In nonaqueous solvents the sum of the molar volume of ions C_6mim^+ and Cl^- , $V^\circ(\text{IL})$, decrease by increasing temperature but the molar volume of the ion pair $\text{C}_6\text{mim}^+\text{Cl}^-$, V_{IP}° , increases with temperature. However, both of $K^\circ(\text{IL})$ and K_{IP}° in nonaqueous solvents decrease with increasing temperature. Furthermore, the volume and isentropic compressibility changes occurring on ion pairing in nonaqueous solvents, $\Delta_{\text{IP}}V^\circ$ and $\Delta_{\text{IP}}K^\circ$, which are positive, increase by increasing the temperature. The obtained infinite dilution properties Λ^∞ , $V^\circ(\text{IL})$, K_{IP}° , and n° which are a measure of the ion + solvent interaction, indicate that although the solvation of free ions C_6mim^+ and Cl^- in water is weaker than that in the investigated nonaqueous solvents, however, these infinite dilution properties do not show a similar trends for different nonaqueous solvents. At finite concentrations in which the properties of solutions are

controlled by the net result of competition between the intrinsic interactions of cations with anions and the ionic solvation, the values of ϕ_v , ϕ_K , and $p - p_s^\circ$ decrease in the order water > 1-butanol > propanol > ethanol > acetonitrile > methanol, which except for water is the same trend for K_A . From these results we can conclude that either the ion solvation decrease in the order methanol > acetonitrile > ethanol > propanol > 1-butanol > water or the ionic association has a predominant contribution and is mainly responsible for their properties. The positive deviations from DHLL of osmotic coefficient support the former assumption.

■ ASSOCIATED CONTENT

S Supporting Information. Additional tables of data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ REFERENCES

- Weingaertner, H. *Angew. Chem., Int. Ed.* **2008**, 47, 654.
- Parvulescu, V. I.; Hardacre, C. *Chem. Rev.* **2007**, 107, 2615.
- Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH: Weinheim, Germany, 2003.
- Fernandes, A. M.; Rocha, M. A. A.; Freire, M. G.; Marrucho, I. M.; Coutinho, J. A. P.; Santos, L. M. N. B. F. *J. Phys. Chem. B* **2011**, 115, 4033.
- Tokuda, H.; Hayamizu, K.; Ishii, K.; Abu Bin Hasan Susan, M.; Watanabe, M. *J. Phys. Chem. B* **2004**, 108, 16593.
- Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. *J. Phys. Chem. B* **2005**, 109, 6103.
- Tokuda, H.; Ishii, K.; Susan, M. A. B. H.; Tsuzuki, S.; Hayamizu, K.; Watanabe, M. *J. Phys. Chem. B* **2006**, 110, 2833.
- Yokozeki, A.; Kasprzak, D. J.; Shiflett, M. B. *Phys. Chem. Chem. Phys.* **2007**, 9, 5018.
- Fraser, K. J.; Izgorodina, E. I.; Forsyth, M.; Scott, J. L.; MacFarlane, D. R. *Chem. Commun.* **2007**, 3817.
- Paul, A.; Mandal, P. K.; Samanta, A. *J. Phys. Chem. B* **2005**, 109, 9148.
- Wang, Y. T.; Voth, G. A. *J. Am. Chem. Soc.* **2005**, 127, 12192.
- Lopes, J. N. A. C.; Padua, A. A. H. *J. Phys. Chem. B* **2006**, 110, 3330.
- Armstrong, J. P.; Hurst, C.; Jones, R. G.; Licence, P.; Lovelock, K. R. J.; Satterley, C. J.; Villar-Garcia, I. J. *Phys. Chem. Phys.* **2007**, 9, 982.
- Leal, J. P.; Esperanca, J. M. S. S.; da Piedade, M. E. M.; Lopes, J. N. C.; Rebelo, L. P. N.; Seddon, K. R. *J. Phys. Chem. A* **2007**, 111, 6176.
- Avent, A. G.; Chaloner, P. A.; Day, M. P.; Seddon, K. R.; Welton, T. *J. Chem. Soc. Dalton Trans.* **1994**, 3405.
- Tubbs, J. D.; Hoffmann, M. M. *J. Solution Chem.* **2004**, 33, 379.
- Koddermann, T.; Wertz, C.; Heintz, A.; Ludwig, R. *Chem-PhysChem* **2006**, 7, 1944.
- Dorbritz, S.; Ruth, W.; Kragl, U. *Adv. Synth. Catal.* **2005**, 347, 1273.
- Ku, B. K.; de la Mora, J. F. *J. Phys. Chem. B* **2004**, 108, 14915.
- Tokuda, H.; Baek, S. J.; Watanabe, M. *Electrochemistry* **2005**, 73, 620.
- Li, W. J.; Zhang, Z. F.; Han, B. X.; Hu, S. Q.; Xie, Y.; Yang, G. Y. *J. Phys. Chem. B* **2007**, 111, 6452.
- Katsuta, S.; Ogawa, R.; Yamaguchi, N.; Ishitani, T.; Takeda, Y. *J. Chem. Eng. Data* **2007**, 52, 248.
- Katsuta, S.; Imai, K.; Kudo, Y.; Takeda, Y.; Seki, H.; Nakakoshi, M. *J. Chem. Eng. Data* **2008**, 53, 1528.
- Katsuta, S.; Shiozawa, Y.; Imai, K.; Kudo, Y.; Takeda, Y. *J. Chem. Eng. Data* **2010**, 55, 1588.
- Bester-Rogac, M.; Hunger, J.; Stoppa, A.; Buchner, R. *J. Chem. Eng. Data* **2010**, 55, 1799.
- Shekaari, H.; Mansoori, Y.; Sadeghi, R. *J. Chem. Thermodyn.* **2008**, 40, 852.
- Wang, H. Y.; Wang, J. J.; Zhang, S. L.; Pei, Y. C.; Zhuo, K. L. *ChemPhysChem* **2009**, 10, 2516.
- Bester-Rogac, M.; Hunger, J.; Stoppa, A.; Buchner, R. *J. Chem. Eng. Data* **2011**, 56, 1261.
- Shekaari, H.; Mousavi, S. S. *Fluid Phase Equilib.* **2009**, 286, 120.
- Shekaari, H.; Mousavi, S. S.; Mansoori, Y. *Int. J. Thermophys.* **2009**, 30, 499.
- Welton, T. *Chem. Rev.* **1999**, 99, 2071.
- Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, 39, 3772.
- Rogers, R. D.; Seddon, K. R. *Ionic liquids. Industrial applications to green chemistry*; American Chemical Society: Washington, DC, 2002.
- Bonhote, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Gratzel, M. *Inorg. Chem.* **1996**, 35, 1168.
- Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. *Green Chem.* **2001**, 3, 156.
- Clarke, E. C. W.; Glew, D. N. *J. Phys. Chem. Ref. Data* **1985**, 14, 489.
- Nasirzadeh, K.; Papaiconomou, N.; Neueder, R.; Kunz, W. *J. Solution Chem.* **2004**, 33, 227.
- Nasirzadeh, K.; Neueder, R.; Kunz, W. *J. Solution Chem.* **2004**, 33, 1429.
- Nasirzadeh, K.; Neueder, R.; Kunz, W. *J. Chem. Thermodyn.* **2004**, 36, 511.
- Nasirzadeh, K.; Neueder, R.; Kunz, W. *J. Solution Chem.* **2005**, 34, 9.
- Barthel, J. M. G.; Krienke, H.; Kunz, W. *Physical Chemistry of Electrolyte Solutions-Modern Aspects*; Springer: New York, 1998.
- Marcus, Y.; Hefter, G. *Chem. Rev.* **2006**, 106, 4585.
- Izutsu, K. *Electrochemistry in Nonaqueous Solutions*; WILEY-VCH Verlag GmbH: Weinheim, Germany, 2002.
- Evans, D. F.; Gardam, P. J. *Phys. Chem.* **1968**, 72, 3281.
- Matesich, M. A.; Nadas, J. A.; Evans, D. F. *J. Phys. Chem.* **1970**, 74, 4568.
- Evans, D. F.; Gardam, P. J. *Phys. Chem.* **1969**, 73, 158.
- Barthel, J.; Neueder, R. *Electrolyte Data Collection, Part 1c, Nitriles. In DECHEMA Chemistry Data Series*; Eckermann, R.; Kreysa, G., Ed.; DECHEMA: Frankfurt, 1996; Vol. XII.
- Jervis, R. E.; Muir, D. R.; Butler, J. P.; Gordon, J. D. *J. Am. Chem. Soc.* **1953**, 75, 2855.
- Wang, J.; Wang, H.; Zhang, S.; Zhang, H.; Zhao, Y. *J. Phys. Chem. B* **2007**, 111, 6181.
- Millero, F. J. *Chem. Rev.* **1971**, 71, 147.
- Marcus, Y.; Hefter, G. *Chem. Rev.* **2004**, 104, 3405.
- Rudan-Tasic, D.; Zupce, T.; Klotfutar, C.; Bester-Rogac, M. *J. Solution Chem.* **2005**, 34, 631.
- Brummer, S. B.; Hills, G. J. *Trans. Faraday Soc.* **1961**, 57, 1816.
- Marcus, Y.; Ben-Zvi, N.; Shiloh, I. *J. Solution Chem.* **1976**, 5, 87.
- Ananthaswamy, J.; Atkinson, G. *J. Chem. Eng. Data* **1984**, 29, 81.
- Marcus, Y. *J. Mol. Liq.* **2005**, 118, 3.
- Cibulka, I.; Zikova, M. *J. Chem. Eng. Data* **1994**, 39, 876.
- Cibulka, I.; Takagi, T. *J. Chem. Eng. Data* **2002**, 47, 1037.
- Cibulka, I.; Hnedkovsky, L.; Takagi, T. *J. Chem. Eng. Data* **1997**, 42, 415.
- Marcus, Y. *J. Phys. Chem. B* **2005**, 109, 18541.
- Wawer, J.; Krakowiak, J.; Grzybkowski, W. *J. Chem. Thermodyn.* **2008**, 40, 1193.

- (62) Preiss, U. P. R. M.; Slattery, J. M.; Krossing, I. J. *Chem. Eng. Data* **2009**, *48*, 2290.
- (63) Marcus, Y.; Hefter, G. *Chem. Rev.* **2004**, *104*, 3405.
- (64) Sadeghi, R.; Shekaari, H.; Hosseini, R. *J. Chem. Thermodyn.* **2009**, *41*, 273.
- (65) Archer, D. G. *J. Phys. Chem. Ref. Data* **1991**, *20*, 509.
- (66) Archer, D. G. *J. Phys. Chem. Ref. Data* **1992**, *21*, 793.