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Ionic association and conductance of [emim][BF_4] and [bmim][BF_4] in 1-butanol in a wide range of temperature

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ABSTRACT

The electrical conductances of dilute solutions of the ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate [emim][BF_4] and 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4] in 1-butanol have been measured in the temperature range from T/K = (283.15 to 318.15) at 5 K intervals. The ionic association constants, K_A, the limiting molar conductances, Λ_o, and distance parameters, R, were obtained using the low concentration Chemical Model (lcCM). The examined ionic liquids are strongly associated in 1-butanol over the whole temperature range. From the temperature dependence of the limiting molar conductivities the Eyring's activation enthalpy of charge transport was determined. The thermodynamic functions such as Gibbs energy, ΔG^o_A, entropy, ΔS^o_A, and enthalpy of the process of ion pair formation, ΔH^o_A, were calculated from the temperature dependence of the association constants. Negative values of ΔG^o_A indicate that the formation of ion pairs is a spontaneous process. The increase of temperature leads to more negative ΔG^o_A values, which means shifting the equilibrium toward the formation of ion pairs. The entropy values of association are positive, which means that as a result of association, the arrangement of the system decreases in comparison with the arrangement associated with the solvation of free ions.

1. Introduction

Ionic liquids (ILs) possess the outstanding physico-chemical properties, for example low melting temperature, high conductivity, very low vapor pressure at room temperature, selective solubility of water and organics, stable liquid range of over 300 K. Therefore, they can replace many volatile organic solvents in chemical processes. The transport properties of ionic liquids mixtures (conductance, viscosity, and transference numbers) are important because the values provide useful and sensitive information about (ion + solvent) interaction, ionic association, and solvent structure. A survey of literature indicates that most studies report only the specific conductivity data for pure ionic liquids [1–3] or binary and ternary mixtures of ILs with various solvents [1,4–15]. The conductance studies of dilute solutions of ionic liquids in a wide temperature range allow to determine the values of association constants and thermodynamic functions of association. It is well-known the alkyl chain length of the ionic liquid cation, type of anion, temperature and physical properties of the molecular solvents affect the ionic association constants [16–25]. The ionic liquids are solvated to a different extent by the solvents, and the ionic association depends significantly on the ion solvation [16,25]. The results of conductometric studies of imidazolium-based ionic liquids solutions [emim][BF_4] and [bmim][BF_4] in water [26], 1-propanol [27], N,N-dimethylformamide [28] were published by us recently. Similar studies were also carried out by other authors in acetonitrile [29,30], dimethylsulfoxide [23], and methanol [23,31]. Moderate ionic association of ILs occurs in N,N-dimethylformamide, acetonitrile, and methanol, slight in dimethylsulfoxide, whereas it becomes significant in 1-propanol. Water promotes strongly dissociation of the ionic liquids. Studies carried out by us in the low-permittivity solvent dichloromethane show a very strong association of the above mentioned ionic liquids (data prepared for publication).

According to our knowledge, conductometric data for solutions of [emim][BF_4] and [bmim][BF_4] in 1-butanol (BuOH) at various temperatures, have not yet been reported. Therefore, the present work deals with the precise conductivity measurements, which have been carried out in the concentration range $c \approx (0.03 \text{ to } 2) \cdot 10^{-3}$ mol · dm^{-3} of [emim][BF_4] and [bmim][BF_4] in 1-butanol at temperatures range T/K = (from 283.15 to 318.15) at atmospheric pressure. Imidazolium-based ionic liquids were chosen because of their thermal and chemical stability and the insignificant degree of susceptibility to air and moisture. The obtained data were used to calculate the values of the limiting molar conductances, Λ_o, and the association constants, K_A on the

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basis of lcCM model. The Eyring activation enthalpy of charge transport, $\Delta H^{\ddagger}_{\lambda}$, as well as the Gibbs energy, ΔG^{o}_{A}, enthalpy, ΔH^{o}_{A}, and entropy, ΔS^{o}_{A}, of ion pair formation, for the electrolytes have been evaluated.

2. Experimental

2.1. Materials

The specifications of used chemicals are summarized in table 1.

1-Butanol was stored in dark bottles over molecular sieves (Sigma, 0.3 nm) to reduce water content. Before use, it was double distilled and degassed in an ultrasound bath.

2.2. Methods and procedure

All the solutions were prepared by mass using an analytical balance (Sartorius RC 210D) with a precision of $\pm 1 \cdot 10^{-5}$ g.

The measurement procedure was based on the method described by Bešter-Rogač *et al.* [24,32] and used by us in our previous works [26–28,33,34]. Conductivity measurements were performed with a three-electrode cell with the use of a Precision Component Analyzer 6430B (Wayne-Kerr, UK) under argon atmosphere and at the different frequencies, ν, (0.2, 0.5, 1, 1.5, 2, 3, 5, 10, 20) kHz. The temperature was kept constant within 0.003 K (Calibration Thermostat UB 20F with through-flow cooler DLK 25, Lauda, Germany). The cell constant, K, with units cm^{-1}, was determined by measuring the resistance of a cell filled with KCl solution of known specific conductance [35]. The cell constants are equal (1.0264, 1.0277, 1.0295, 1.0311, 1.0331, 1.0351, 1.0370 and 1.03895) in T/K = (283.15, 288.15, 293.15, 298.15, 303.15, 308.15, 313.15 and 318.15), respectively. All measured conductance values, $\lambda = 1/R_{\infty}$, were the results of an extrapolation of the cell resistance, $R(\nu)$, to infinite frequency, $R_{\infty} = \lim_{\nu \to \infty} R(\nu)$ using the empirical function $R(\nu) = R_{\infty} + A/\nu$, where parameter A is specific to the cell. In supporting information (table S1 and figure S1) we present the dependence of $R(\nu)$ versus $1/\nu$ for one selected concentration of [emim][BF_4] + 1-butanol solution at T = 298.15 K. The estimated uncertainty of the measured values of conductivity was 1%.

Densities were measured with an Anton Paar DMA 5000 M oscillating U-tube densimeter equipped with a thermostat with a temperature stability within ±0.001 K. The densimeter was calibrated with extra pure water, previously degassed ultrasonically. The estimated uncertainty of density is $\pm 2 \cdot 10^{-4}$ g · cm^{-3}.

3. Results and discussion

The physical properties of 1-butanol are given in table 2. Viscosities and relative permittivities data were taken from literature. The measured density values of 1-butanol in the experimental temperatures are in a good agreement with the values reported in the literature (figure S2 in supporting information) [36–46]. As can be seen, only the results presented by Pura [46] differ significantly from the others, which is probably due to a less accurate pycnometric method used for measurements.

TABLE 2
Densities, ρ_o, viscosities, η, and relative permittivities, ε_r, of 1-butanol at different temperatures, at pressure p = 0.1 MPa.[a]

T/K	ρ_o/g · cm^{-3}	η/mPa · s	ε_r
283.15	0.817103	3.8727[b]	19.54[c]
288.15	0.813337	3.3713[b]	19.01[d]
293.15	0.809548	2.9458[b]	18.28[d]
298.15	0.805738	2.5772[b]	17.58[d]
303.15	0.801901	2.2263[b]	16.91[d]
308.15	0.798032	1.9950[b]	16.26[d]
313.15	0.794128	1.7630[b]	15.65[c]
318.15	0.790181	1.5645[b]	15.01[e]

[a] The standard uncertainties u are $u(T)$ = ±0.01 K, $u(p)$ = 0.05 · p, and the combined expanded uncertainties U_c are $U_c(\rho_o) = 2 \cdot 10^{-4}$ g · cm^{-3} (level of confidence = 0.95).
[b] Data calculated on the basis our density data and kinematic viscosity values from Ref. [47]
[c] From Ref. [48]
[d] From our data from Ref. [49]
[e] Interpolated from our data from Ref. [20] and data from Ref. [48].

To convert molonity, $\tilde{m}$, (moles of electrolyte per kilogram of solution) into molarity, c, the values of density gradients, b, have been determined independently and used in the equation

$$c/\tilde{m} = \rho = \rho_o + b \cdot \tilde{m} \quad (1a)$$

where ρ_o is the density of the solvent. Measured densities of 1-butanol + [emim][BF_4] and 1-butanol + [bmim][BF_4] binary solutions as a function of temperature are presented in table S2 in supporting information. Molar concentrations, c, were necessary to use the conductivity equation. The density gradients and the molar conductances of the ILs in solution, Λ, as a function of IL molality, m, (moles of electrolyte per kilogram of solvent) and temperature are presented in table 3. The relationship among m, $\tilde{m}$, and c is the following

$$\tilde{m} = c/\rho = m/(1 + m \cdot M) \quad (1b)$$

where M is the molar mass of electrolyte.

The plot of molar conductances, Λ, versus the square root of the molar concentration, $c^{1/2}$, for the investigated systems monotonically decreases as shown in figures 1 and 2, respectively over the temperature range from 283.15 to 318.15 K. The values of Λ for ionic liquids in 1-butanol are smaller than in DMF [28], water [26], and 1-propanol [27].

There are many equations used for conductivity data analysis. The most commonly used are: Pitts equation [50], developed by Fernandez-Print and Prue [51] (PFPP equation), Fuoss-Hsia/Fernandez-Prini [52] (FHFP equation), the Fuoss equation [53,54], the low concentration Chemical Model (lcCM) based on the

TABLE 1
Specification of chemical samples.

Chemical name	Source	Initial mass fraction purity	Purification method	Final mass fraction purity	Analysis method	Final water mass fraction purity
1-Ethyl-3-metylimidazolium tetrafluoroborate [emim][BF_4]	Fluka	0.990[a]	None			<0.0002[b] <0.00015[c]
1-Butyl-3-metylimidazolium tetrafluoroborate [bmim][BF_4]	Fluka	0.985[a]	None			<0.0005[b] <0.0004[c]
1-Butanol	POCh	0.995[a]	Redistillation	0.9997	GC[d]	0.0002[c]

[a] As stated by the supplier.
[b] Manufacturer's analysis.
[c] Our analysis (Karl Fischer coulometric titration).
[d] (Gas + liquid) chromatography.