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Conductance behavior of ionic liquids, 1-alkyl-3-methylimidazolium bromide, in aqueous D-xylose solutions

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ABSTRACT

The electrical conductivity of a number of ionic liquids, 1-propyl-3-methylimidazolium bromide ([PrMIm]Br), 1-hexyl-3-methylimidazolium bromide ([HMIm]Br), 1-octyl-3-methylimidazolium bromide ([OMIm]Br) and 1-decyl-3-methylimidazolium bromide ([DMIm]Br), in the aqueous d-xylose solutions at several concentrations, (0.2, 0.5 and 0.8) mol kg^{-1} have been measured at 298.15 K. The obtained data have been analyzed using low concentration Chemical Model (lcCM) of conductance equation in terms of ion association constant (K_a), limiting molar conductivity (Λ_0), Walden product ($\Lambda_0\eta$) and distance parameter (R). It was observed that the K_a values decrease with increase in both alkyl chain of ionic liquid and D-xylose concentration. Gibbs free energy of ion pair formation (ΔG_a^0) was estimated using the K_a values. It was found that the ΔG_a^0 values are negative and became more negative with shorter alkyl chain length of ionic liquids and low concentration of D-xylose.

1. Introduction

Aqueous biphasic systems (ABSs) are usually formed as a result of mutual incompatibility of two polymers or one polymer and one salt above a certain concentration. ABSs have been widely used as an important emerging technique for separation and purification of proteins [1,2], cell organelles [3], small organic molecules [4], heavy metal ions [5] and antibiotic [6–8]. In comparison with traditional liquid–liquid extraction, aqueous biphasic systems are free of toxic organic solvents which can address the increasing challenge of environmental protection and product safety.

Surprisingly, it was found that ionic liquids (ILs), as a new class of electrolytes and novel green solvents, can also form ABS [9–11]. Gutowski et al. [12] have demonstrated that the addition of potassium phosphate to an aqueous solution of a hydrophilic ionic liquid, 1-butyl-3-methylimidazolium chloride ([BMIm]Cl), produced aqueous two phase systems. Recently, Wu et al. [13,14] and Zhang et al. [15] have proposed new ABS, which are formed from an ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm]BF$_4$), along with concentrated solutions of saccharides such as fructose and glucose. These new ABS systems can be used to recycle or to concentrate the hydrophilic ionic liquids from aqueous solutions and are potentially more suitable to separate biological materials. Furthermore, the proposed systems are more environmentally benign than ILs/salt systems, since the latter inevitably introduce potassium and phosphate ions, complicating the recycling process as hydrophilic ionic liquids dissociate into ions in aqueous solution [13].

The rapid progress in this new type of aqueous biphasic systems and the increasing utilization of ionic liquids in chemical and separation processes requires reliable and systematic data of thermophysical properties. These properties must be available for process design and development in their applications. The transport properties (conductance, viscosity, and transference numbers) of such systems are important because the values provide useful and sensitive information about ion-solvent interaction, ion-ion association, and solvent structure. A considerable amount of conductivity data for pure ionic liquids and their aqueous solutions are available in literature [16–20]. However, data on the conductivity behavior of IL + saccharide + water systems in the aqueous medium are scarce [21].

As a part of our previous investigations on thermophysical properties of ionic liquids in presence of different solutes, in this work, precise conductivity measurements have been occurred for a number of ionic liquids, [C$_n$MIm]Br (n = 3, 6, 8 and 10), in aqueous D-xylose solutions with concentrations (0.2, 0.5 and 0.8) mol kg^{-1} at 298.15 K. The obtained data were used to calculate the ion association constant (K_a), limiting molar conductivity (Λ_0), Walden product ($\Lambda_0\eta$) and distance parameter (R) using the low concentration Chemical Model (lcCM). Gibbs free energy of ion pair formation (ΔG_a^0) was also estimated using K_a values.

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Table 1
Densities (d), viscosities (η) and dielectric constants (ε) of aqueous D-xylose solutions at $T = 298.15$ K.

m (mol kg^{-1})[a]	d (g cm^{-3})	η (mPa s)	ε
0.0000	0.99704	0.8949	78.3[b]
0.2000	1.00779	0.9689	77.7[c]
0.5000	1.02306	1.0751	76.4[c]
0.8000	1.03747	1.1952	75.4[c]

[a] m is the molality of D-xylose in water.
[b] Taken from Ref. [29].
[c] Taken from Ref. [30].

2. Experimental

2.1. Materials

N-methylimidazole, 1-bromopropane, 1-bromohexane, 1-bromooctane, 1-bromodecane, ethyl acetate, toluene and D-xylose were obtained from Merck. All the materials had purity greater than 99%. D-xylose was dried in vacuum over P_2O_5 at room temperature for at least 72 h. The other chemicals were used without further purification. The doubly distilled deionized water was used with a specific conductivity less than 1 μS cm^{-1} at 298.15 K.

2.2. Synthesis of ionic liquids

1-Alkyl-3-methylimidazolium bromide (C_nMImBr, $n = 3, 6, 8$ and 10) were synthesized analogously to the previously published procedures [22–25] by direct alkylation of *N*-methylimidazole with a 10% excess of 1-bromoalkane in toluene and in a round bottom flask under reflux and an argon atmosphere at nearly 353 K for 48 h. The crude product was separated from reagents and then washed triply with ethyl acetate until the non-reacted bromoalkane had been completely removed. The removal of residual volatile compounds in the ionic liquid was performed in high vacuum at about $T = 333$ K using a rotary evaporator for at least 4 h in the reduced pressure. The obtained ionic liquid has purity greater than mass fraction 0.98 and verified ^{1}H NMR spectroscopy. The ionic liquid was used after vacuum desiccated for at least 48 h to remove trace amount of moisture. Water content found by Karl Fischer method in the ionic liquids was less than 0.08%. The ionic liquids were checked by ^{1}H NMR (Brucker Av-300) and FT-IR (PerkinElmer, Spectrum RXI) spectra to confirm the absence of any major impurities.

2.3. Apparatus and procedure

2.3.1. Density and viscosity measurements

Solution densities were measured with a vibrating digital densimeter (DMA, 4500 M, Anton Paar, Austria). The uncertainty in density is estimated to be $\pm 3.0 \times 10^{-5}$ g cm^{-3}. The viscosities were measured by means of an Ubbelohde-type viscometer, calibrated at the experimental temperatures with doubly distilled water. The estimated uncertainty of experimental viscosities is ±0.002 mPa s. The experimental measurements have been described in detail by our previous paper [26]. Viscosities and densities of (D-xylose + water) mixtures at different concentrations are listed in Table 1.

2.3.2. Conductivity measurements

A conductivity meter (Metrohm model 712, Switzerland) with accuracy of ±0.5% and a dipping type conductivity cell with platinized electrodes were used to measure conductivities. The cell constant was calculated by repeated measurements of KCl solutions in 0.01 mol kg^{-1}. About 50 ml of solvent was placed in the conductivity cell and the cell was closed. All solutions were made up by weight and with an analytical balance (Sartrious, AG TE214S) with precision $\pm 1 \times 10^{-4}$ g. Weighed pure ionic liquid was added with a syringe to the cell containing solvent. To minimize the risk of the presence of concentration gradients in the cell, the solution was continuously stirred with a magnetic stirrer. The water from a thermostatically regulated bath was circled around the sample holder with double wall to maintain the temperature with an uncertainty of ±0.02 K. The measured specific conductivities of ionic liquid solutions were always corrected for the contribution of the pure solvent. The values of molar conductivity (Λ) obtained for all ionic liquids are given in Table 2.

3. Data analysis

The analysis of conductivity data is best performed on the basis of the low concentration Chemical Model (lcCM) using a set of equations [27]

$$\Lambda = \alpha[\Lambda_0 - S(c\alpha)^{1/2} + Ec\alpha \ln(c\alpha) + J_1 c\alpha + J_2 (c\alpha)^{3/2}] \quad (1)$$

$$K_a = \frac{1-\alpha}{\alpha^2 c \gamma_\pm^2} \quad (2)$$

$$\ln \gamma_\pm = -\frac{\kappa q}{1+\kappa R} \quad (3)$$

$$\kappa^2 = \frac{16,000 N_A z^2 e^2 \alpha c}{\varepsilon_0 \varepsilon k_B T} \quad (4)$$

$$q = \frac{z^2 e^2}{8\pi \varepsilon_0 \varepsilon k_B T} \quad (5)$$

In these equations, Λ and Λ_0 are the molar conductivities at ionic liquid molarity c and at infinite dilution, $(1-\alpha)$ is the fraction of oppositely charged ions acting as ion pairs, $\gamma_\pm$ is the corresponding mean activity coefficient of the free ions, κ is the Debye parameter, e is the electronic charge, z is the ionic charge, ε_0 is the permittivity of vacuum, ε is the relative dielectric constant of the solvent. The coefficients E, J_1, and J_2 required for calculations were taken from Ref. [27]. The parameter R represents the center-to-center distance between the ions in the ion pairs. At separations beyond this distance, the ions are considered to be unassociated. The other symbols have their usual meanings.

Three-parameter fits were used to obtain limiting values of the molar conductivity (Λ_0), the association constant (K_a) and the distance parameter (R) by non-linear least squares iterations. The calculation is made by finding the values Λ_0, K_a and R that minimized the standard deviation $\sigma(\Lambda)$. The standard deviation of the measured molar conductivities Λ_{exp} and the calculated one Λ_{cal} was computed as follows

$$\sigma(\Lambda) = \sqrt{\frac{\sum (\Lambda_{\text{exp}} - \Lambda_{\text{cal}})^2}{n-p}} \quad (6)$$

where n and p depict the number of the experimental data and parameters, respectively. The values of K_a, Λ_0 and R obtained by this procedure are summarized in Table 3.

4. Results and discussion

4.1. Limiting molar conductivities

Inspection of Table 3 indicates that the Λ_0 values of each ionic liquid decrease with increasing the concentration of D-xylose. This can be ascribed to the facts that with increase in D-xylose concentration (i) the microscopic viscosity of the mixtures increases thereby the mobility of ions decreases, and (ii) the solvated radii of ions become larger through an enhancement in the interactions between ionic liquid and D-xylose therefore, the mobility of ions decreases. On the other hand, the Λ_0 values