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Fluid Dynamics and Transport Phenomena

Electrical conductivities for four ternary electrolyte aqueous solutions with one or two ionic liquid components at ambient temperatures and pressure ☆

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ABSTRACT

This work provides a method to explore the transport property of the electrolyte aqueous solutions with one or two ionic liquids, especially focus on their electrical conductivity. The conductivities were measured for the ternary systems NaCl–[C_6mim][Cl] (1-hexyl-3-methylimidazolium chloride)–H_2O, [C_6mim][BF_4]–[C_6mim][Cl]–H_2O, $NaNO_3$–[C_6mim][BF_4](1-hexyl-3-methylimidazolium tetrafluoroborate)–H_2O, and [C_4mim][BF_4] (1-butyl-3-methylimidazolium tetrafluoroborate)–[C_6mim][BF_4]–H_2O, and their binary subsystems $NaNO_3$–H_2O, NaCl–H_2O, [C_6mim][BF_4]–H_2O, [C_6mim][Cl]–H_2O, and [C_4mim][BF_4]–H_2O, respectively. The conductivities of the ternary systems were also determined using generalized Young's rule and semi-ideal solution theory in terms of the data of their binary solutions. The comparison showed that the two simple equations provide good predictions for conductivity of mixed electrolyte solutions and the mixed ionic liquid solutions based on the conductivity of their binary subsystems.

1. Introduction

The transport properties of mixed aqueous solutions have always attracted considerable interest due to extensive applications in many fields such as chemistry and chemical engineering, separation process, wastewater treatment, pollution control, and oil recovery. Electrical conductivity is admittedly one of the principal transport properties of aqueous electrolyte systems not only for its intrinsic interest but also for technical and industrial applications such as batteries and plating [1].

A number of groups have reported the physical properties of binary electrolyte solutions [2–6]. However, it is still a considerable measurement work for the properties of the multicomponent solutions using the conventional testing method. Therefore, it is practically important to develop an efficient method to obtain more useful data of the multicomponent solutions according to the available information on the binary solutions [7–10]. Several attempts have been made using the Young's rule [11,12] and the semi-ideal solution theory [13,14] to obtain good predictions for the thermodynamic properties of the mixed electrolytes solutions from their binary subsystems [15,16]. Hu *et al.* have successfully verified and extended the applicability of the generalized Young's rule and the semi-ideal solution theory to the conductivity of mixed electrolytes solutions [17,18]. For example, the conductivities of the ternary systems NaCl–$LaCl_3$–H_2O can be predicted very well with the conductivities of its binary subsystems NaCl–H_2O and $LaCl_3$–H_2O at 298.15 K [17,18]. The measurement of the conductivities [1] were also made for the mixed electrolyte solution ternary systems $Y(NO_3)_3$–$Ce(NO_3)_3$–H_2O, $Y(NO_3)_3$–$Nd(NO_3)_3$–H_2O, and $Ce(NO_3)_3$–$Nd(NO_3)_3$–H_2O, $Y(NO_3)_3$–$La(NO_3)_3$–H_2O, $La(NO_3)_3$–$Ce(NO_3)_3$–H_2O, and $La(NO_3)$–$Nd(NO_3)_3$–H_2O, and their binary subsystems $Y(NO_3)_3$–H_2O, $Ce(NO_3)_3$–H_2O, and $Nd(NO_3)_3$–H_2O and $La(NO_3)_3$–H_2O, at (293.15, 298.15 and 308.15) K and up to $I_{max} \leq 24.4\ mol \cdot kg^{-1}$. With the equations of the generalized Young's rule and the semi-ideal solution theory, the predictions of conductivities for ternary systems based on the data of their binary subsystems are in good agreement with the measured values.

Ionic liquids (ILs) have been recognized as novel designable solvents which can be tuned/controlled by tailoring their cationic and anionic structures to optimize their physicochemical properties [1]. Thus, they are environmentally benign and non-flammable, and pose high thermal

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stability and a high solvation capacity [19,20]. These unique features suggest their potential application in a wide variety of industrial and chemical processes, such as absorption media in gas absorption, heat transfer fluids and working fluids in electrochemical processes [21–23].

In all these applications, the utilization of aqueous solutions of ILs, especially cognition of the basic properties for these systems, will be inevitable in a practical approach or in the design of industry process. One of the basic properties of interest for electrochemical applications is electrical conductivity. Moreover, the presence of water in ILs can dramatically affect their physicochemical properties [24–26]. Therefore, several groups [27–34] have studied the physical properties of aqueous solutions of ILs for the binary systems (water–IL). Up to now, the basic properties of aqueous solutions of IL mixtures are important not only for industrial applications, but also for the verification of the electrolyte theories although few measurements have been made on the electrical conductivities for ternary systems such as the aqueous solutions of IL mixtures and the mixed electrolyte solutions with IL.

Therefore, the experimental measurements of the conductivities of ternary systems NaCl–[C_6mim][Cl]–H_2O, [C_6mim][BF_4]–[C_6mim][Cl]–H_2O, $NaNO_3$–[C_6mim][BF_4]–H_2O, and [C_4mim][BF_4]–[C_6mim][BF_4]–H_2O, and their binary subsystems $NaNO_3$–H_2O, NaCl–H_2O, [C_6mim][BF_4]–H_2O, [C_6mim][Cl]–H_2O, and [C_4mim][BF_4]–H_2O were presented at room temperature, respectively. The above-mentioned predictive equations including generalized Young's rule and semi-ideal solution theory developed for the properties of mixed electrolyte solutions were extended to conductivities of mixed IL solutions and the mixed electrolyte solutions containing IL with lower concentration. On the other hand, the measured conductivities of the above ternary systems and their binary subsystems were also used to test the generalized Young's rule and the semi-ideal solution theory for electrical conductivity of multicomponent solutions containing ILs and electrolytes.

2. Experimental

Deionized water was distilled in a quartz still, and its conductivity was 0.8–1.2 × 10^{-6} S·cm^{-1}. All chemicals used in this study were of reagent grade with the claimed purity >99%. *N*-methylimidazole, *n*-C_4H_9Cl, *n*-$C_6H_{13}Cl$, and $NaBF_4$ were supplied by Shanghai Jiacheng Chemical Co., Ltd. These chemicals were refined by fractional distillation [35]. NaCl and $NaNO_3$ were dried under vacuum over $CaCl_2$ for 7 days at 423 K prior to their use [16]. All the ionic liquids present in this work were prepared using well-established procedures [36–38]. The chloride salts were prepared by reacting *N*-methylimidazole with RCl, where, R was *n*-C_4H_9 or *n*-C_6H_{13} The products were purified by repeated extractions of the remaining starting materials with ethyl acetate. After the last extraction, the remaining ethylacetate was removed at 343.15 K under vacuum [39]. The resulting [1-alkyl-mim][Cl] ([C_4mim][Cl] and [C_6mim][Cl]) were dried at 343.15 K under vacuum for 6 days. [C_4mim][Cl] and $NaBF_4$ were dissolved in acetone separately with equimolar amounts. Then, the two solutions gradually formed a mixture with stirring. The precipitated sodium chloride was removed from the liquid by filtration. The excess acetone was evaporated away and crude product [C_4mim][BF_4] was dried in vacuum for 48 h. The obtained [C_4mim][Cl] was white crystals at room temperature, and [C_6mim][Cl] and [C_6mim][BF_4] were liquid at room temperature. After purification, the ILs were dried under vacuum over $CaCl_2$ for several days at 70 °C and were then further dried with 0.3 nm molecular sieves for several days immediately before use. The water content after drying, measured by Karl Fisher titration, was within 0.012% (by mass).

All the samples were prepared by syringing weighed amounts of the pure liquids into stoppered bottles in a glove box. The binary aqueous solutions of $NaNO_3$, NaCl, [C_6mim][BF_4], [C_6mim][Cl] and [C_4mim][BF_4] were prepared by mass from double-distilled deionized water and the ILs using a Sartorius CT225D balance with a precision of ±5 × 10^{-5} g. The ternary systems were prepared by mixing the binary solutions with known mass concentration with uncertainty of ±5 × 10^{-5} mol·kg^{-1}. All solutions prepared in a glass flask were placed into stoppered bottles and stirred for 2 h. The measurements were made one week after preparation to assure complete dissolution and aggregation. Due to the low solubility of the ionic liquids, all the prepared samples was in a narrow concentration range of 0.0004–0.3000 mol·kg^{-1}.

The conductivities of prepared samples were measured with a METLER TOLEDO SevenEasyTM conductivity meter (cell constant = 0.57 cm^{-1}) calibrated with standard aqueous potassium chloride solutions [18]. The temperature of the cell was kept constant to within ± 0.005 K by circulating thermostated liquid and the temperature was measured with a calibrated calorimeter thermometer (±0.006 K).

3. Predictive Equations for Conductivity

3.1. Generalized Young's rule for conductivity

The generalized Young's rule for the conductivity of the ternary electrolyte solutions [40] can be expressed as

$$\sigma = y_1\sigma_1 + y_2\sigma_2 \tag{1}$$

with $y_i = I_i/(I_1 + I_2)$, where I is ionic strength. σ, σ_1 and σ_2 are the conductivities of the ternary solution $M_1X_1 - M_2X_2 - H_2O$ and its binary subsystems $M_iX_i - H_2O$ (i = 1 or 2) of equal ionic strength.

3.2. Semi-ideal solution theory for conductivity

The semi-ideal solution theory for the conductivity of the ternary electrolyte solutions can be expressed as [18,41,42]

$$\ln\sigma = z_1 \ln\sigma_1 + z_2 \ln\sigma_2 \tag{2}$$

where σ_i is the conductivity of the binary solution of salt i and water, $M_iX_i - H_2O$ (i = 1 or 2), having the same water activity as that of the ternary solution $M_1X_1 - M_2X_2 - H_2O$. z_i is the ratio of the mole fraction of $i \cdot H_2O_{(Li)}$(i = 1 or 2) in the ternary ideal solution $1 \cdot H_2O_{(L1)} - 2 \cdot H_2O_{(L2)} - H_2O$ to the mole fraction of $i \cdot H_2O_{(Li)}$ in the binary ideal solution $i \cdot H_2O_{(Li)} - H_2O$ *i.e.*,

$$z_i = x^{\text{ideal}}_{i\cdot H_2O_{(Li)}} / x^{\text{o,ideal}}_{i\cdot H_2O_{(Li)}} \tag{3}$$

with

$$x^{\text{o,ideal}}_{i\cdot H_2O_{(Li)}} = \nu_i m_i^{\text{o}} / (55.51 - c_i \nu_i m_i^{\text{o}} + \nu_i m_i^{\text{o}}) \tag{4}$$

and

$$x^{\text{ideal}}_{i\cdot H_2O_{(Li)}} = \nu_i m_i / [55.51 - \text{c}(\nu_1 m_1 + \nu_2 m_2) + \nu_1 m_1 + \nu_2 m_2] \tag{5}$$