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Physicochemical properties of binary mixtures of 1,1,3,3-tetramethylguanidine imidazolide ionic liquid with water and alcohols

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ABSTRACT

In this work, densities and viscosities of aqueous solution of 1,1,3,3-tetramethylguanidine imidazolide ([TMG]IM) ionic liquid were measured at temperatures from $T = (293.15 \text{ to } 313.15)$ K. Volumetric properties including excess molar volumes V^E, apparent molar volumes, partial molar volumes, and excess partial molar volumes were calculated from the experimental density. Viscosity deviations $\Delta\eta$, Gibbs energy and excess Gibbs energy of activation for viscous flow were deduced from the viscosity. Moreover, electrical conductivities κ and refractive indices of binary mixtures of [TMG]IM with water and alcohols were determined at 298.15 K. The results show that V^E values of {[TMG]IM (1) + water (2)} mixture are negative over the whole composition range, while $\Delta\eta$ and refractive index deviations Δn_D values exhibit positive deviations, indicating that the hydrogen bonding interaction between [TMG]IM and water is dominant. The absolute values of V^E and $\Delta\eta$ of the mixture decrease with the increasing temperature. The V^E, $\Delta\eta$, and Δn_D can be fitted by the Redlich–Kister equation with satisfactory results. The concentration-dependent κ of the studied systems are fitted to Casteel–Amis equation, showing that the κ values of {[TMG]IM (1) + water (2)} mixture are much higher than those of {[TMG]IM (1) + ethanol (2)} mixture.

1. Introduction

Ionic liquids (ILs) have attracted considerable attention in the chemical engineering processes such as synthesis and separation [1–4], due to their unique characteristics (*e.g.*, extremely low vapor pressure, excellent thermal and chemical stability, and designer solvents). Physicochemical properties of ILs are very important for engineering applications, industrial processes and complete design of new products [5]. Among these properties, viscosity and density are two important physical quantities for chemical engineering design. For example, viscosity as a transport property characterizes the inner friction of ILs has a significant impact on the rate of mass transfer. In many processes contain ILs, they always be mixed with one or more solvents to enhance their properties, which will affect physicochemical properties of pure ILs significantly [6,7]. In this regard, investigating the physicochemical properties of mixtures of ILs with other solvents seems very crucial for industrial application. Moreover, some physicochemical properties of mixtures containing IL can be used to study the intermolecular interaction information between IL and solvent. Therefore, investigating the physicochemical properties of the mixtures containing IL is crucially important for both the industrial and the academic communities.

During the last ten years, the measurements of the physicochemical properties of mixtures of ILs involving imidazolium, pyridinium, pyrrolidinium, piperidinium, phosphonium, and ammonium with water or molecular solvents [7–13], such as viscosity, density, electrical conductivity, refractive index, and surface tension have increased profoundly, but they are not fully enough for some newly-synthesized functionalized ILs. This work is a continuation of our systematic research on physicochemical properties of aqueous solutions of functionalized ILs [14–16]. Recently, 1,1,3,3-tetramethylguanidine imidazolide ([TMG]IM) IL has been reported as an efficient absorbent to capture acid gases such as sulfur dioxide (SO_2) and carbon dioxide (CO_2) [17,18]. Density and viscosity of pure [TMG]IM and its binary mixtures with alcohols were studied in our previous work [19], the effect of the alkyl chain

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length and polarity of alcohols on the interaction between [TMG]IM and alcohols were also discussed. In particular, in view of the potential use of ILs as solvents or catalysts, it is important to know the properties of ILs mixed with water due to their hydrophilicity [20,21]. For instance, there is a certain amount of water or moisture in flue gas, which will not only affect the physicochemical properties, but also the absorption ability of ILs [22,23]. The influence of moisture on CO_2 absorption of [TMG][IM] was investigated in our previous work [17], showing that the absorption capacity of [TMG]IM decreased slightly with the increasing of the moisture of CO_2. Therefore, it is desirable to study the effect of water on the physicochemical properties of [TMG]IM in more detail.

To this end, densities, viscosities, and corresponding excess properties of {[TMG]IM (1) + water (2)} mixture at wide range of temperature and composition are presented. According to the experimental results, the derived properties such as excess volumes, apparent molar volumes, partial molar volumes, excess partial molar volumes, Gibbs energy and excess Gibbs energy of activation for viscous flow are deduced. Moreover, electrical conductivities of binary mixtures of [TMG]IM with water and ethanol are determined at $T = 298.15$ K. Refractive indices of binary mixtures of [TMG]IM with water and alcohols including methanol, ethanol, 1-propanol, and 1-butanol, are measured at $T = 298.15$ K. Based on the measured and derived properties, the intermolecular interaction or structural factors between [TMG]IM and water are discussed. Furthermore, the effect of water and alcohols on physicochemical properties or intermolecular interaction of [TMG]IM is compared and discussed according to the results obtained from the present work and reported in our previous work [19].

2. Experimental

2.1. Chemicals

Imidazole (CAS NO. 288-32-4), 1,1,3,3-tetramethylguanidine (CAS NO. 80-70-6), methanol (CAS NO. 67-56-1), ethanol (CAS NO. 64-17-5), 1-propanol (CAS NO. 71-23-8), and 1-butanol (CAS NO. 71-36-3) are analytical Reagent grade (AR grade) and obtained from Aladdin Reagent Co. Ltd., Shanghai, China. Alcohols were distilled through a 1 m fractionating column and checked by gas chromatography using a SHIMADZU GC-2014 equipped with an FID detector. 1,1,3,3-Tetramethylguanidine was purified by vacuum distillation. Imidazole was used without additional purification. The deionized water used in the experiment was doubly distilled over $KMnO_4$ according to the literature [24]. The purity of materials is listed in table 1. The density, viscosity, and refractive index of water, as well as the refractive index of alcohols were determined and compared with literature values listed in table 2. The density and viscosity of pure [TMG]IM were measured in previous work [19] and used in the present work.

[TMG]IM was previously prepared from 1,1,3,3-tetramethylguanidine and imidazole through the neutralization reaction [19]. The detailed preparation and purification processes were described in our previous work [17,19]. The water content of [TMG]IM determined by Karl Fischer titration (Mettler Toledo DL32, Switzerland) was less than 200 ppm. [TMG]IM was analysed by ^{1}H NMR and ^{13}C NMR spectroscopy to confirm the absence of any major impurities, which were recorded on a Bruker AVANCE III 400 MHz NMR spectrometer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as an internal reference as follows, ^{1}H NMR: $\delta = 2.62$ (12H, s, N-C$\mathbf{H}_3$), 7.12 (2H, s, anion N-C**H**-C**H**-N), 7.79 (1H, s, anion N-C**H**-N), 9.79 (2H, s, cation C = N$\mathbf{H}_2$) ppm (see figure S1 in the supplementary); ^{13}C NMR: $\delta = 39.0$ (N-$\mathbf{C}H_3$), 121.9 (anion N-**C**H-**C**H-N), 135.7 (anion N-**C**H-N), 167.0 (cation **C** = NH_2) ppm (see figure S2 in the supplementary). According to the water content and NMR spectroscopy, the purity of [TMG]IM is greater than 98.0% in mass fraction.

2.2. Apparatus and procedure

2.2.1. Density and viscosity measurements

Binary mixtures of [TMG]IM with water and alcohols were prepared by mass using a Mettler Toledo AL204 analytical balance with a stated precision of ±0.0001 g. The standard uncertainty in mole fractions of the binary mixtures was less than $5 \cdot 10^{-4}$. All of the samples were prepared immediately prior to measurements into special stoppered glass bottles. The [TMG]IM used in the experiment was not recycled and reused. The atmospheric pressure was measured by Fortin mercury barometer with an uncertainty of 2.0 kPa.

A vibrating-tube densimeter (model DMA 5000 M, Anton Paar GmbH) was employed to measure the density values of the {[TMG]IM (1) + water (2)} mixture. The measurement procedure of density was similar to our previous work [14–16,19]. In a typical run, the densimeter was checked by itself, and then it was calibrated with doubly distilled deionised water and dried air. The measurement cell temperature was controlled and provided by two integrated Pt 100 platinum thermometers (uncertainty: ±0.05 K) together with Peltier elements. The uncertainty claimed by the manufacture was $\pm 5 \cdot 10^{-5}$ g · cm^{-3}. Considering the contribution of sample impurity to the uncertainty [29], the relative standard uncertainty for densities of a sample containing [TMG]IM with 98.0% purity was estimated to be ±0.2%. The V^E values of

TABLE 1
Purities and sources of the samples used in this work.

Chemical name	Source	Initial mass fraction purity	Purification method	Finial mass fraction purity	Analysis method	Water content	Electrical conductivity/ (μS · cm^{-1})
Methanol	Aladdin Reagent	>0.995	Distilled through a 1 m fractionating column	>0.998	Gas chromatography		
Ethanol	Aladdin Reagent	>0.995		>0.998	Gas chromatography		
1-Propanol	Aladdin Reagent	>0.995		>0.998	Gas chromatography		
1-Butanol	Aladdin Reagent	>0.995		>0.998	Gas chromatography		
1,1,3,3-Tetramethylguanidine	Aladdin Reagent	>0.990	Vacuum distillation	>0.998	Gas chromatography		
Imidazole	Aladdin Reagent	>0.990	No further purification				
[TMG]IM	Synthesis		Vacuum desiccation	>0.980[a]		<200 · 10^{-6}	
Water			Double distillation				<1.0

[a] According to the water content and NMR spectroscopy.