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Densities and viscosities of binary liquid mixtures of 1-ethyl-3-methylimidazolium tetrafluoroborate with acetone, methyl ethyl ketone, and *N*-methyl-2-pyrrolidone

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ABSTRACT

In this study, the densities and viscosities of three binary liquid mixtures of 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim][BF_4]) with acetone, methyl ethyl ketone, and *N*-methyl-2-pyrrolidone were measured at 303.15, 313.15, 323.15, and 333.15 K under atmospheric pressure. A vibrating-tube digital density meter and a capillary viscometer were used for density and viscosity measurements, respectively. The trends in densities and viscosities with respect to composition and temperature were compared. In addition, excess molar volumes and viscosity deviations were calculated to investigate the molecular interaction between an ionic liquid and an organic solvent. The ability of hydrogen bonding formation and interstitial accommodation were investigated to clarify the influence of excess molar volumes and viscosity deviations. In addition, the obtained excess molar volumes and viscosity deviations were fitted using a four-parameter Redlich–Kister equation. The optimally fitted parameters are presented. The correlated results were consistent with the experimental data.

1. Introduction

An ionic liquid, a compound entirely composed of ions and with a melting temperature of ≤373 K, has been demonstrated to be crucial in the pharmaceutical industry owing to its unique physiochemical properties [1,2]. For example, Smith et al. recrystallized an active pharmaceutical ingredient (API), paracetamol, by using two ionic liquids and determined the metastable zone width for designing the crystallization protocol. Their results demonstrated that an ionic liquid can be a media to manipulate the crystal properties of APIs and should be explored more widely for crystallizing APIs [3]. Weber et al. used an ionic liquid to purify an API, acetaminophen, by using an antisolvent crystallization approach and demonstrated that the extent of purification in the crystallization process depended on the hydrogen bond strength of the impurity [4]. In addition, the design and development of novel analytical methods involving ionic liquids are currently underway in the pharmaceutical industry. Frink et al. designed a headspace gas chromatography method involving an ionic liquid and introduced a rapid, accurate, and versatile analytical method for detecting and quantifying water in solid-phase APIs [5]. In addition, an ionic liquid with biological activity can be produced through an appropriate salt-formation process; this new method has been adopted to produce APIs with novel performance enhancement and delivery options. Several articles have reviewed the design and development of APIs in ionic liquids [6–8].

To design and develop a novel process by using an ionic liquid in the pharmaceutical industry, understanding the fundamental physical and chemical properties of the ionic liquid is essential. Several physical and chemical characteristics have been reported for ionic liquids. For example, Faria et al. measured the solubilities of pharmaceutical and bioactive compounds, such as *N*-acetyl-L-cysteine, isoniazid, pyrazine-2-carboxamide, coumarin, 4-hydroxycoumarin, 4'-isobutylacetophenone, ibuprofen, and thymoquinone, in an ionic liquid by using a synthetic method [9]. Salinas et al. measured the viscosities, densities, and speeds of sound of three separate binary mixtures of ionic liquids 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Emim][NTf2]), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Bmim][NTf2]), and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Hmim][NTf2]) with ethanol [10]. Cao et al. measured the densities, viscosities, and electrical conductivities of separate binary systems of an ionic liquid with three protic solvents: water, methanol, and ethanol [11]. In our previous

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Table 1
Information of pure fluids used in this study.

Name	Formula	CAS no.	Supplier	Product number	Lot number	Purity (%)	Analytical method
[Emim][BF4]	$C_6H_{11}BF_4N_2$	143314-16-3	Sigma-Aldrich Co.	711721	STBD4510V	Min. 98.0	H-NMR
Acetone	C_3H_6O	67-64-1	Merck Co.	1.00014.1000	K42947014	99.9	GC
MEK	C_4H_8O	78-93-3	Sigma-Aldrich Co.	34861	SZBC208AV	99.9	GC
NMP	C_5H_9NO	872-50-4	Sigma-Aldrich Co.	328634	STBC2115V	99.79	GC

study, we reported the densities and viscosities of binary mixtures of 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]) with several pharmaceutical industry-acceptable organic solvents [12,13].

More experimental studies are required to extend the applicability of ionic liquids in the pharmaceutical industry. In this study, the densities and viscosities of three separate binary liquid mixtures of 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim][BF_4]) with acetone, methyl ethyl ketone (MEK), and N-methyl-2-pyrrolidone (NMP) were measured at 303.15, 313.15, 323.15, and 333.15 K under atmospheric pressure. [Emim][BF_4] is a relatively low-cost ionic liquid and is commonly used in the chemical industry. According to the ICH Q3C guidelines, the three solvents used in this study, namely acetone, MEK, and NMP, are Class 2 and Class 3 solvents. These solvents are relatively safe and acceptable for practical use in the pharmaceutical industry. For these three binary mixture system, only density data of [Emim][BF4] with acetone [14] and NMP [15] have been published. However, the published densities data were measured at a narrow temperature interval from 293.15 to 308.15 K. In this paper, in addition to providing experimental density and viscosity data of new binary mixtures, the molecular interaction between the ionic liquid and the organic solvent is discussed using excess molar volumes and viscosity deviations. The calculated excess molar volumes and viscosity deviations were correlated with the composition by using Redlich–Kister polynomials.

2. Experimental section

Ionic liquid [Emim][BF_4] with a minimum purity of 98.0% was purchased from Sigma–Aldrich Co. Acetone with a purity of 99.9% was purchased from Merck Co. MEK and NMP with purities of 99.9% and 99.79%, respectively, were purchased from Sigma–Aldrich Co. The information of pure fluids used in this study is summarized in Table 1. Before density and viscosity measurements, pure fluids, including ionic liquid and solvents, were dried using 3 Å molecular sieves. The water content of the solvents and [Emim][BF_4] was measured through Karl–Fischer titration (Metrohm Ltd., 851 Titrando). The measured water contents for [Emim][BF_4], acetone, MEK and NMP are 272, 226, 92 and 332 ppm, respectively. Ionic liquid mixtures of various compositions (by mass) were prepared using an electronic balance (Shimadzu Corp., AUW220D) with an accuracy of ±0.01 mg, and the mole fractions of the ionic liquid mixtures were subsequently calculated. The uncertainty in the calculated mole fractions was estimated to be 0.001. Each liquid mixture was used immediately after it was well mixed using a vortexer and degassed in an ultrasonic water bath.

Density data were measured using a vibrating-tube digital density meter (Anton Parr DMA 5000 M), which was calibrated and validated using double-distilled water and air at atmospheric pressure. The uncertainty and relative standard uncertainty in the reported temperature and density were 0.01 K and 0.1%, respectively. The density data reported in this study are an average of at least three runs. In addition, the effect of the viscosity on the vibrating-tube density meter was automatically corrected. The viscosity correction of the density meter was examined using density measurements using several certified viscosity oil standards with known densities.

A semiautomatic instrument (PMT Tamson Co., TV2000AKV) and four Cannon–Fenske routine viscometer tubes were used for viscosity measurements. The size numbers of these four viscometer tubes were 25, 50, 75, and 150, and their corresponding kinematic viscosity measurement ranges were 0.4–2, 0.8–4, 1.6–8, and 7–35 cSt. The calibration constant for each viscometer tube was obtained after calibrating using certified viscosity oil standards and double-distilled water. Each viscometer tube was filled with the prepared liquid sample and was installed in the measuring head. The viscometer tube was then immersed vertically in a thermostatic water bath, the temperature of which was regulated within 0.01 K. The kinematic viscosity of the sample was determined by measuring the time required, automatically recorded using two optical infrared sensors in the measuring head, for the sample to travel along a defined length of the capillary. The accuracy of time measurement was 0.01 s. The kinematic viscosities of the samples were calculated using the measured flow time and calibration constants, following which the dynamic viscosities were calculated using these data and the corresponding densities of the mixtures at the same composition. The reported dynamic viscosities are the average values of at least three runs. The relative standard uncertainty or the coefficient of variance of viscosity measurement is defined as the ratio of standard deviation to average viscosity. In this study, the average relative standard uncertainty for viscosity measurements was estimated to be 0.5%. Table 2 shows the measured density and viscosity data of the pure fluids used in this study at 303.15, 313.15, 323.15, and 333.15 K. In Table 2, the example of pure density and viscosity data reported in literature are also presented. The averaged deviations of density and viscosity measurement of pure fluids listed in Table 2 were about 0.4% and 1.6%, respectively. The density and viscosity values of pure fluids are consistent with those reported in literature. These results illustrate that our measurement methods are reliabile. In addition, in our supplementary material, a complete comparison of pure densities and viscosities for [Emim][BF4] at 303.15, 313.15, 323.15, and 333.15 K was also presented (Table S1 and S2). The variance of pure density and viscosity measurements of [Emim][BF4] might be owing to the effect of trace impurity such as water content in ionic liquid.

3. Results and discussion

3.1. Density

The experimental densities of the three binary liquid mixtures of [Emim][BF_4] with acetone, MEK, and NMP at 303.15, 313.15, 323.15, and 333.15 K are listed in Tables 3–5, respectively. The trends of the measured density data with respect to temperature at various compositions are presented in Figure S1 in the supplementary material. According to Tables 3–5 and Figure S1, the density of the pure ionic liquid was higher than those of the organic solvents, and the densities decreased with increasing temperature and organic solvent content. To discuss the molecular interaction between ionic liquids and organic solvents, excess molar volumes (V^E) were calculated:

$$V^E = [x_1M_1 + (1-x_1)M_2]/\rho_m - [x_1M_1/\rho_1 + (1-x_1)M_2/\rho_2] \quad (1)$$