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Lithium *bis*(trifluoromethylsulfonyl)imide-added ionic liquid 1-ethyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide mixture: Densities and dynamic viscosities in the temperature range (298.15–358.15) K



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ARTICLE INFO

Article history:

Received 13 June 2017

Received in revised form 10 August 2017

Accepted 27 August 2017

Available online 15 September 2017

Keywords:

Ionic liquid

Li salts

Density

Dynamic viscosity

Temperature dependence of density

Temperature dependence of dynamic viscosity

ABSTRACT

Lithium salt-added ionic liquid mixtures have shown promise as alternate electrolyte media for Li-ion batteries. Densities and dynamic viscosities of lithium *bis*(trifluoromethylsulfonyl)imide (LiTf_2N) mixed with 1-ethyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide ($[\text{emim}][\text{Tf}_2\text{N}]$) for $0 \leq x_{\text{LiTf}_2\text{N}} \leq 0.4$ in the temperature range (298.15–358.15) K are presented. Decrease in density with increasing temperature is found to follow a simple linear expression. The density of $([\text{emim}][\text{Tf}_2\text{N}] + \text{LiTf}_2\text{N})$ mixtures increases with increasing $x_{\text{LiTf}_2\text{N}}$ quadratically. The temperature dependence of the dynamic viscosity of the $([\text{emim}][\text{Tf}_2\text{N}] + \text{LiTf}_2\text{N})$ mixtures follows Vogel–Fulcher–Tamman (VFT) model as opposed to an Arrhenius expression. The dynamic viscosity of $([\text{emim}][\text{Tf}_2\text{N}] + \text{LiTf}_2\text{N})$ mixture at a given temperature increases exponentially with $x_{\text{LiTf}_2\text{N}}$; the exponential increase being more prominent at lower temperatures ($T \leq 328.15$ K). The exponential increase in dynamic viscosity with $x_{\text{LiTf}_2\text{N}}$ is attributed to the well-documented formation of $[\text{Li}(\text{Tf}_2\text{N})_2]^-$ anionic aggregates that are less favored at higher temperatures.

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1. Introduction

In the fast growing world with the ever increasing need for alternative solvents, ionic liquids are being explored widely in almost all areas of chemistry [1–8]. Ionic liquids are room-temperature molten salts, composed of ions with notable physicochemical properties, such as, good thermal stability, high solubility, negligible vapor pressure, and non-flammability, among others [7,9–14]. Several research groups have carried out numerous studies on physicochemical properties of ionic liquid-based systems, and hence, a huge database of the physical properties of ionic liquids and related systems are available in the literature [15–21]. However, novel emerging applications of ionic liquids modified by other chemical systems render measuring and reporting of physical properties of such systems essential.

In the current energy scenario, lithium-ion batteries have proven to be a promising choice for mobile applications. But in order to expand its applications to large-scale, such as, in sustainable transportation (e.g., electric vehicles), we have to cope-up with

some of the limitations [22–25]. Thermal stability is a major issue in the currently used electrolytes, such as, lithium salt, LiPF_6 , dissolved in organic solvents - ethyl carbonates and diethyl carbonates, in lithium ion batteries [26]. Investigations were carried in order to overcome these limitations in past few years by using different permutation and combinations of salts and solvents [27–29]. While the organic solvents had their own limitations, ionic liquids, because of their low vapor pressure, desirable thermal and electrochemical stabilities, and most importantly, high ionic conductivities, have drawn much attention from researchers as an alternative electrolyte for lithium-ion batteries [26,30–34]. In order to further develop and improve this new alternative class of (ionic liquid + Li salt) electrolyte system for industrial and commercial purpose, knowledge of important physical properties of such systems and their temperature and composition dependence become of utmost importance. Density and dynamic viscosity are two such physical properties. Knowledge of the temperature/composition dependence of density and dynamic viscosity of important (ionic liquid + Li salt) systems will play an essential role in exploiting these systems further for industrial and academic uses.

In this paper, we report densities and dynamic viscosities of Li salt lithium *bis*(trifluoromethylsulfonyl)imide (LiTf_2N) mixed with

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ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf₂N]) up to 0.4 LiTf₂N mole fraction ($x_{\text{LiTf}_2\text{N}}$) in the temperature range (298.15–358.15) K at 15 K interval. For $x_{\text{LiTf}_2\text{N}} > 0.4$, ([emim][Tf₂N] + LiTf₂N) mixture showed difficulty in miscibility. The lithium salt and the ionic liquid selected have the same anion [Tf₂N⁻]. We believe this selection of the ionic liquid and the Li salt for the electrolyte system may afford information on the solvation aspects of lithium salt in the ionic liquid through density and dynamic viscosity and their temperature/composition dependence.

2. Experimental

2.1. Materials

Ionic liquid [emim][Tf₂N] used is of electrochemical grade (>99.0% by mass purity) and was purchased from Covalent Associates, Inc. [emim][Tf₂N] was stored under argon in an Auto Secador desiccator cabinet. Before use, [emim][Tf₂N] was rigorously dried under vacuum for at least 72 h. Karl-Fisher titrator was used next to assess water content of the ionic liquid prior to its use. Ionic liquid was dried till the water content became less than 100 ppm. LiTf₂N with 99.95% purity was purchased from Sigma-Aldrich and stored in the Auto Secador desiccator cabinet. The water content of the [emim][Tf₂N] and ([emim][Tf₂N] + LiTf₂N) samples was also assessed after data acquisition using Karl-Fisher titrator and was found to be <100 ppm. The description of the chemicals used together with their sources is provided in Table 1.

2.2. Methods

Densities (ρ) of [emim][Tf₂N] and ([emim][Tf₂N] + LiTf₂N) mixtures were measured using a Mettler Toledo, DE45 delta range density meter. The density measurement with the above-mentioned density meter was based on electromagnetically-induced oscillations of a U-shaped glass tube. The measurements were performed at 15 degree intervals in the temperature range (298.15–358.15) K. The standard deviation associated with the density measurement of ionic liquid and (ionic liquid + salt) mixtures in the entire temperature range of investigation is estimated to be $\pm 0.005 \text{ g cm}^{-3}$. The dynamic viscosities (η) were measured with a Peltier-based (resolution of 0.01 K and accuracy <0.05 K) automated Anton Paar microviscometer (model AMVn) having calibrated glass capillaries of different diameters (1.6, 1.8, 3.0, and 4.0 mm). This instrument is based on the rolling-ball principle, where the steel ball rolls down the inside of inclined, sample-filled calibrated glass capillaries. The deviation in η of ionic liquid and (ionic liquid + salt) mixtures in the entire temperature range of investigation is estimated to be $\pm 2\%$. Although the densities and viscosities of the ([emim][Tf₂N] + LiTf₂N) mixtures investigated at the temperatures in this report are scarce in literature, the ones that could be estimated from different parameters are compared with those available in literature [17,18]. The densities and viscosities of the neat ionic liquid [emim][Tf₂N] were compared with those provided in the literature, and outcomes are presented in Tables 2 and 3 and in Figs. 1 and 2 [35–46]. It is clear that for [emim][Tf₂N] at certain temperatures, our density and dynamic viscosity values deviate from those reported earlier. This is

attributed to the inherent hygroscopic nature of the ionic liquid [emim][Tf₂N]; the moisture content of this ionic liquid can be different in different reports. Thus, the differences can be tentatively attributed to the differences in the purification and the drying procedures used for the ionic liquid [emim][Tf₂N]. While we have used highest purity ionic liquids in this investigation, further drying was carried out rigorously and Karl-Fisher titrator was used to estimate water content within the ionic liquid-based system both before and after data acquisition. The water content was found to be less than 100 ppm. Possibility of the presence of other impurities in the ionic liquid samples reported in literature resulting in deviations in density and dynamic viscosity values reported in this work may not be ruled out either.

3. Results and discussion

3.1. Density of ([emim][Tf₂N] + LiTf₂N) mixture: Temperature dependence

Densities of the ([emim][Tf₂N] + LiTf₂N) mixtures were measured in the temperature range 298.15–358.15 K for $x_{\text{LiTf}_2\text{N}} = 0-0.4$ and are reported in Table 4. Density of ([emim][Tf₂N] + LiTf₂N) mixture at a given $x_{\text{LiTf}_2\text{N}}$ is found to decrease with increase in temperature. Thermal expansion usually results in decreased density of a substance as the temperature is increased. It is to be noted that the experimentally-measured densities are found to vary linearly with the absolute temperature and were fitted to the following linear equation:

$$\rho = \rho_0 + aT \quad (1)$$

where $\rho/\text{g cm}^{-3}$ is the density of the ([emim][Tf₂N] + LiTf₂N) mixture. The values of the parameters ρ_0 and a along with the associated standard deviations are listed in Table 5. Fig. 3 shows the linear temperature dependence according to Eq. (1) of the densities of ([emim][Tf₂N] + LiTf₂N) mixtures (solid lines are the result of linear regression analysis at each $x_{\text{LiTf}_2\text{N}}$). It is clear from the recovered values of r^2 listed in Table 5 as well as an examination of Figure 3 that the temperature-dependence of the densities can be appropriately depicted by a simple linear equation in the temperature range (298.15–358.15) K. Tsuzuki et. al. have also reported the density dependence on temperature for neat [emim][Tf₂N] and ([emim][Tf₂N] + 0.32 mol kg⁻¹ LiTf₂N) mixture to be linear [34]. This, however, is in contradiction with the temperature dependence of ([emim][Tf₂N] + LiTf₂N) mixtures. It is reported that for the LiTf₂N mole fraction from 0.03 to 0.38, decrease in the density with increasing temperature follows a non-linear relationship where a second-order polynomial is required to fit the density versus temperature data at a given $x_{\text{LiTf}_2\text{N}}$ in the temperature range (298.15–348.15) K [47]. We believe the longer butyl chain on imidazolium cation of the ionic liquid is responsible for this observation. Imidazolium ionic liquids possessing butyl or longer alkyl chain(s) are known to have inherent nano-heterogeneous regions that may result in non-linear temperature dependence of certain physical properties [17].

As expected, parameter ρ_0 , which depicts density at $T = 0 \text{ K}$, increases with increasing $x_{\text{LiTf}_2\text{N}}$. It is interesting to note that the temperature sensitivity of the density, reflected via slope a , of ([emim][Tf₂N] + LiTf₂N) mixtures, also appear to follow the same

Table 1
Description of the chemicals used in this work. the purity of the studied ionic liquid is shown in certificate of analysis given by covalent associates (see Supporting Information).

Chemical	Molar Mass (g/mol)	Source	Purity (%mass)	Purification done	Water Content (ppm)
[emim][Tf ₂ N]	391.30	Covalent Associates	$\geq 99.0\%$	Vacuum Drying	<100
LiTf ₂ N	287.09	Sigma Aldrich	99.95%	None	

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