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# Investigation of the rheological properties of two imidazolium-based ionic liquids

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ABSTRACT

The shear- and temperature-dependency of the viscosity of two imidazolium-based ionic liquids namely, 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][$PF_6$] and 1-butyl-3-methylimidazolium nitrate, [bmim][$NO_3$], has been studied in this work. The experimental results showed that the viscosity of these fluids decreases with increasing temperature. The results also showed that these ionic liquids are non-Newtonian over a wide range of shear rate ((14 to 56.0) $s^{-1}$) in the temperature range of (283.15 to 343.15) K and their shear viscosity depends strongly on temperature. The activation parameters, namely, $\Delta H^*$ (enthalpy of activation), $\Delta G^*$ (free energy of activation), $\Delta S^*$ (entropy of activation), and $\Delta C_p{}^*$ (change in heat capacity of activation) values for their viscous flow were evaluated. The magnitudes of the parameters were fairly large. The values of all these parameters decreased with temperature. The values of $\Delta H^*$ and $\Delta S^*$ nicely compensated each other. The temperature dependence of viscosities was fitted using the power law, Litovitz, Vogel–Fulcher–Tammann (VFT), and Ghatee et al. equations. Also, the law of corresponding states can be seen in the viscosity behavior of these ILs based on two different equations.



## 1. Introduction

Ionic liquids (ILs) are used as solvents for synthesis and catalysis [1], electrolytes [2], lubricants [3,4] and media for the formation and stabilization of nanoparticles [5–8]. Their physical, chemical and electrochemical properties make them suitable for an enormous range of applications [9–11], ranging from the petrochemical industry [12] to the nuclear industry [13] and in many diverse applications. There is a great interest in ILs because of their special properties. They are good solvents for both organic and inorganic liquids over a wide range of temperature, not volatile, highly negligible vapor pressure, thermally stable, non-flammable, polar, weakly coordinating solvents and less toxic than usual organic solvents. Their low volatility makes ILs a serious alternative for volatile organic compounds (VOC) which contributes towards a clean and "green" chemistry. Ionic liquid chemistry is a very new area that is not only extremely interesting from a fundamental chemistry point of view but could also have a very large impact on industry [14].

Rheological and volumetric properties of ionic liquids are very interesting due to the growing number of industrial applications of such materials. These properties provide important information on molecular basis of these fluids as well as engineering aspects of them. Viscosity as a transport property has a great effect on the rate of mass transport and thus the solvent viscosity is an important factor in all chemical processes. ILs are highly conductive and moderate to highly viscous. Imidazolium-based ILs qualify as a higher priority in research and are used for their physicochemical versatility and easier availability. The structural differences between their cationic and anionic components also hinder easy flow of these liquids to make them viscous and often non-Newtonian. From the literature survey, it is found that the viscosity ($\eta$) of ILs usually falls between ~ (0.20 and 4.0) Pa s [15], whereas water at 298 K has $\eta = 0.0009$ Pa s. The study of $\eta$ of ILs alone and in mixed states with other solvents is considered important.

The [bmim]$PF_6$ and [bmim]$NO_3$ are halogen-free ILs and thus more environment friendly. There are some papers, which have studied some physical properties such as density, viscosity, surface tension, heat capacity, enthalpy of formation, etc. for [bmim]$NO_3$ [16–20] and [bmim]$PF_6$ [21–25]. Although the ILs are non-Newtonian fluids in which the viscosity depends on shear rate as well as temperature, in all of these measurements, the viscosity has been considered as a function of only temperature. In this work, we have studied the temperature ($T$) and shear rate (SR) dependent viscosities or shear viscosities ($\eta$) of two ionic liquids namely, [bmim]$PF_6$ and [bmim]$NO_3$. The collected data were used to estimate the activation thermodynamic parameters, i.e. $\Delta H^*$ (enthalpy of activation), $\Delta G^*$ (free energy of activation), $\Delta S^*$ (entropy of activation), and $\Delta C_p{}^*$ (change in heat capacity of activation) for the viscous flow of the studied ILs. To show the temperature dependence of measured viscosity data, the power law, Litovitz, Vogel–Fulcher–Tammann (VFT), and Ghatee et al. equations are used to fit the data. Also, the law of corresponding states can be seen in the viscosity behavior of these ILs based on two different equations.

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## 2. Experimental

All the ILs, namely, [bmim][$PF_6$] and [bmim][$NO_3$] have been taken from Kimiaexir Company, with purities in mass fraction >98% and were used without further purification. The purities of the components were verified by measuring the densities and viscosities which were in almost good agreement with the reference values [26–33] as have been shown in Table 1. In the present study, the rheological properties of these ILs were measured using a Brookfield Viscometer (LV DV-II + Pro) with a small sample adaptor. The adaptor consists of a cylindrical sample holder, a water jacket, and spindle. The viscometer drives the spindle immersed into the sample holder containing the test fluid sample. It measures viscosity by measuring the viscous drag of the fluid against the spindle when it rotates. The viscometer can provide a rotational speed that can be controlled to vary from 0.8 to 200 rpm yielding the shear rate from 0.22 to 56 $s^{-1}$. The spindle type and speed combinations will produce satisfactory results when the applied torque is between 10% and 100%. The spindle SC4-34 was used in these measurements. The sample holder can hold a small sample volume of 9 mL and the temperature of the test sample is monitored by a temperature sensor embedded into the sample holder. The experimental uncertainty for viscosity, shear stress, and shear rate was lower than $1 \times 10^{-2}$ mPa s, $1 \times 10^{-2}$ mPa and $1 \times 10^{-3}$ $s^{-1}$, respectively. Accurate temperature control is a fundamental requirement for the rheological measurements. In the current research, the water jacket was connected to a refrigerated/heating circulator (Julabo, F12-ED) to control the water temperature with a precision of ±0.1 K. The Anton Paar DMA-HPM densitometer was used for measuring the density with an experimental uncertainty of less than $\pm 1 \times 10^{-5}$ g $cm^{-3}$ and temperature was controlled using a circulating water bath (LAUDA ECO SILVER) with a precision of ±0.01 K.

## 3. Results and discussion

### 3.1. Analysis of the rheological data

Newtonian and non-Newtonian fluids have completely different rheological behaviors. For a non-Newtonian fluid, the viscosity depends on the shear rate. The equation governing Newtonian behavior of a fluid is given by:

$$\tau = \eta\gamma^0 \quad (1)$$

where $\tau$ is the shear stress, $\eta$ is the shear viscosity, and $\gamma^o$ is the shear rate. Fig. 1 shows the measured shear stress as a function of shear rate for [bmim]$PF_6$ and [bmim]$NO_3$ ionic liquids at different temperatures. This figure shows that the shear stress depends linearly on the shear rate. The values of the y-intercept and the slope obtained from these plots for two mentioned ILs were summarized in Table 2. The intercept represents the shear stress when the shear rate is zero. The viscosity of these ILs as a function of shear rate at different temperatures was measured and shown in Fig. 2. As this figure shows the viscosity of these ILs depends upon shear rate and hence they are non-Newtonian fluids. The non-Newtonian behavior of these ILs appears to be similar to that of observed for other ILs in some previous works [34,35]. As Fig. 2 shows, the measured viscosity of ILs decreases significantly with increasing fluid temperature at a fixed shear rate. The results also showed that the [bmim][$PF_6$] and [bmim][$NO_3$] have shear-thinning and shear-thickening behaviors, respectively. To give a better presentation of the shear-dependence of each studied IL, the variation of the viscosity versus shear rate has been shown in the figures at 25 °C as an example. While viscosity perceptibly decreased with temperature, both shear thinning and thickening behaviors were observed with increasing shear rate. It may be due to the orientation differences of the molecules of the ILs under the influence of stress. The viscosity of ILs

**Table 1**
Densities, $\rho$, and viscosities, $\eta$, as a function of temperature for [bmim]$PF_6$ and [bmim]$NO_3$. The given viscosity experimental values are the measurements at SR = 56 $s^{-1}$.

| $T$(K) | $\rho$ (g $cm^{-3}$) | | $\eta$ (m Pa s) | |
|---|---|---|---|---|
| | Exp. | Lit. | Exp. | Lit. |
| *[bmim]$NO_3$* | | | | |
| 298.15 | 1.15829 | 1.1550[a], 1.1565[b] | 156.3 | 165.27[b] |
| 303.15 | 1.15444 | 1.1497[a], 1.1534[b] | 119.4 | 123.51[a], 126.77[b] |
| 308.15 | 1.15084 | 1.1502[b] | 94.2 | 97.47[b] |
| 313.15 | 1.14390 | 1.1435[a], 1.1470[b] | 74.4 | 71.8[a], 82.80[b] |
| 318.15 | 1.14083 | 1.1439[b] | 57.9 | 54.79[b] |
| 323.15 | 1.13726 | 1.1372[a], 1.1407[b] | 48.9 | 45.63[a], 44.6[b] |
| *[bmim]$PF_6$* | | | | |
| 298.15 | 1.37614 | 1.3709[c], 1.3675[d] | 255.8 | 282.2[d], 273[e], 281[f], 269[g] |
| 303.15 | 1.37223 | 1.3626[a], 1.3666[c], 1.3633[d] | 191.4 | 209.2[d], 202[e], 199.7[g] |
| 308.15 | 1.3675 | 1.3592[d] | 147 | 159.1[d], 158.4[e], 153.9[g] |
| 313.15 | 1.36555 | 1.3565[a], 1.3579[c], 1.3551[d] | 114 | 123.4[d], 120.7[g], 119[h] |
| 318.15 | 1.35818 | 1.3510[d] | 90.6 | 97.78[d] |
| 323.15 | 1.35723 | 1.3473[a], 1.3469[d] | 72.9 | 78.77[d], 74.9[e] |

The literature data were taken from references.
[a] Ref. [26].
[b] Ref. [27].
[c] Ref. [28].
[d] Ref. [29].
[e] Ref. [30].
[f] Ref. [31].
[g] Ref. [32].
[h] Ref. [33].

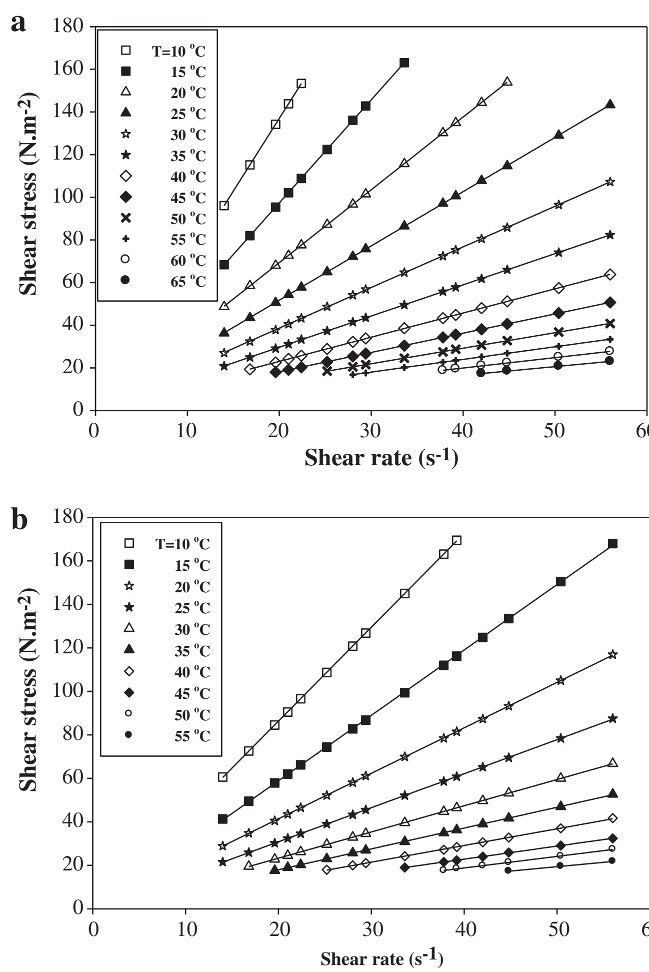


**Fig. 1.** Shear stress versus shear rate for (a) [bmim]$PF_6$ and (b) [bmim]$NO_3$ ionic liquids at different temperatures.