



Journal of Applied Sciences

ISSN 1812-5654

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Density and Viscosity Estimation of 1-hexyl-3-methyl Imidazolium Based Ionic Liquids with [BF₄] and [PF₆] Anions at High Pressures

A. Muhammad, M.I. Abdul Mutalib, T. Murugesan, Z. Man and A. Bustam
Department of Chemical Engineering, Universiti Teknologi Petronas,
Tronoh-31750, Perak, Malaysia

Abstract: The growing interest in exploring the physical properties of ionic liquids (ILs) could be attributed towards the design of industrial processes based on ILs (nonvolatile) to replace organic solvents (highly volatile). The densities and viscosities of imidazolium based ILs have been measured and reported by a number of researchers at ambient pressure. However, the experimental physical property data for most of the ILs at high pressure is quite scarce due to the difficulties involved in the treatment of natural gas to remove carbon dioxide (CO₂) at high pressures. Therefore, there is an immense need to apply correlations and thermodynamic Equation Of State (EOS) models to predict or estimate physical properties. The main objective of this work is to investigate the application of ‘Gardas and Coutinho method’ and ‘Modified Tait equation’ to estimate the densities and viscosities of two ILs: 1-hexyl-3-methyl imidazolium tetrafluoroborate; (C₆mim) (BF₄) and 1-hexyl-3-methyl imidazolium hexafluorophosphate; (C₆mim) (PF₆) at pressures up to 100 bar and at temperatures (298.15, 308.15, 318.15) K. The results show that these methods could be applied satisfactorily for estimating the density and viscosity of ionic liquids. The densities and viscosities of both ILs increased with the increase in pressure at all the studied temperatures. However, the effect of anion appeared to be significant on both physical properties for the studied ILs and found to be in decreasing order of (PF₆) > (BF₄).

Key words: Ionic liquids, density, viscosity, estimation, imidazolium

INTRODUCTION

Ionic liquids (ILs) are comprised of bulky/asymmetric N-containing organic cations (e.g., imidazole, pyrrole and pyridine) and anions (organic/inorganic) of wide variety ranging from simple ions: halides, to more complex species: triflates (Gardas and Coutinho, 2008). The potential applications for ILs are growing rapidly due to their unique properties such as negligible vapor pressure, wide liquidus range, high thermal stability and enormous recycling potential. Ionic liquids are also known as ‘designer solvents’ as their physicochemical properties can easily be tuned by combining various types of anions or cations. Most of the characterization of ILs has been performed for a wide temperature range but limited to ambient pressure (Huddleston *et al.*, 2001; Fredlake *et al.*, 2004; Pereira *et al.*, 2007; Nicolas *et al.*, 2007). It is necessary to accumulate a sufficient large data bank related to fundamental physical and chemical properties of ILs, for process/product design as well as for the development of predictive methods for the estimation of properties at wide ranges of temperature and pressure (Gardas *et al.*, 2007). The knowledge of densities and

viscosities of ILs is important to know the nature of compound which could be helpful for developing an understanding between their structure-property relationships. Moreover, the experimental data for density and viscosity of ILs at high pressures is still scarce due to the difficulty involved in maintaining high pressures conditions with great accuracy of measurement. Therefore, it is always encouraging to investigate some theoretical or empirical estimation methods to establish sufficient data for physical properties of newly developed materials.

In the present study, the densities and viscosities of two ILs: 1-hexyl-3-methyl imidazolium tetrafluoroborate; (C₆mim) (BF₄) and 1-hexyl-3-methyl imidazolium hexafluorophosphate; (C₆mim) (PF₆) have been estimated using ‘Gardas and Coutinho method’ and ‘modified Tait equation’ at pressures up to 100 bar and at three temperatures (298.15, 308.15, 318.15) K.

MATERIALS AND METHODS

Ionic liquids; (C₆ mim) (BF₄) containing both water and chloride contents = 100 ppm and (C₆ mim) (PF₆)

containing water = 100 ppm and chloride contents = 10 ppm, were purchased from Merck. The purchased ILs were of high purity grade with quoted purity of = 99.0%. Prior to their use, the ILs were dried in a vacuum drier at 313 K and 76 cm of Hg for 3 days. The chloride and water contents of treated ILs along with their methods of measuring densities and viscosities at ambient pressure and at wide temperatures can be found by Muhammad *et al.* (2008).

Theory

Gardas and coutinhos method: Ye and Shreeve (2007) proposed a simple estimation technique for the densities of ionic liquids and salts with a good accuracy but restricted to only ambient temperature and pressure conditions using Eq. 1 as follows:

$$\rho = \frac{M}{NV} \tag{1}$$

where, ρ is density (kg m^{-3}), M is molar mass (kg mole^{-1}), N is Avogadro's constant, V is molar volume ($\text{m}^3\text{molecule}^{-1}$). The proposed method was based on the fact that molar volumes of ionic salts are additive sum of the volume of their anions and cations. Most recently, Gardas and Coutinhos (2008) extended the application of Eq. 1 for a wide temperature range of s (273.15 to 393.15) K and pressures up to 10^3 bar. The dependence of molecular volume of materials on pressure (isothermal compressibility) and temperature (isobaric expansivity) was considered in Eq. 2 as follows:

$$\rho = \frac{M}{NV(a + bT + cP)} \tag{2}$$

where, ρ is density (kg m^{-3}), M is molar mass (kg mole^{-1}), N is Avogadro's constant (6.02214×10^{23}), V is molar volume ($^\circ\text{A}^3$), T is temperature (K) and P is pressure (bar). The constants of Eq. 2 were taken from Gardas *et al.* (2007) which were deduced after analyzing approximately 800 data points with 95% confidence level, i.e., $a = 8.005 \times 10^{-1}$, $b = 6.652 \times 10^{-4} \text{ K}^{-1}$ and $c = -5.919 \times 10^{-4} \text{ MPa}^{-1}$.

Modified 'Tait equation': The pressure-volume-temperature (PVT) relationships for most of the organic liquids and their mixtures are very well represented by an Eq. 3 known as 'Tait equation'.

$$\frac{V_0 - V}{PV_0} = \frac{A}{\pi + P} \tag{3}$$

where V_0 and V represent the molar volume at ambient pressure and under pressure P , A and π are constants.

The above 'Tait equation' was modified by Kashiwagi and Makita (1982) and fitted for viscosity data satisfactorily for twelve hydrocarbons at pressures up to (11×10^2) bar. In this study, Eq. 4 obtained after rearranging the modified 'Tait equation', was used to estimate the viscosities of two imidazolium based ILs at pressures up to 100 bar:

$$\eta_P = \eta_0 \left(\frac{D + P}{D + 1} \right)^E \tag{4}$$

where, η_P and η_0 are the viscosities at a pressure P and at 1 bar, respectively, D and E are fitting parameters which were obtained by their linear relationship with temperature represented as Eq. 5 and 6:

$$D = a + bT \tag{5}$$

$$E = c + dT \tag{6}$$

where, a , b , c and d are correlation coefficients and their values used for $(C_6\text{mim})(\text{BF}_4)$: 49668.8, -132.7, 73.83 and -0.2064 and for $(C_6\text{mim})(\text{PF}_6)$: 27177, -50.66, 82.11 and -0.2136 respectively (Ahosseini and Scurto, 2008; units of a and b (bar) and units of c and d (bar K^{-1})).

RESULTS AND DISCUSSION

The experimental densities and viscosities of both ILs are presented in Table 1 at ambient pressure and temperatures (298.15, 308.15, 318.15) K. The density and viscosity of $(C_6\text{mim})(\text{PF}_6)$ has been found to be higher than $(C_6\text{mim})(\text{BF}_4)$ which shows the significant effect of anion type as compared to the cation of imidazolium based ionic liquids. As expected the density and viscosity of both ILs decreased with an increase in temperature. Moreover, the imidazolium based ILs are considered to behave as 'physical solvents' because they are presumed important to know the effect of pressure on densities and viscosities of ILs in order to develop an understanding for to contain cavities in their structure. Therefore, it is their role in gases absorption behavior at high pressures.

Table 1: Experimental density and viscosity of ILs at ambient pressure and values for fitting parameters of Eq. 3

Temperature (K)	Density (kg m^{-3})	Viscosity (mPa.s)	D	E
$[C_6\text{mim}][\text{BF}_4]$				
298.15	1145.32	102	10104.3	12.3
308.15	1138.51	69	8777.3	10.2
318.15	1131.67	43	7450.3	8.16
$[C_6\text{mim}][\text{PF}_6]$				
298.15	1293.41	607	12072.7	18.4
308.15	1285.78	345	11566.1	16.3
318.15	1277.92	215	11059.5	14.2

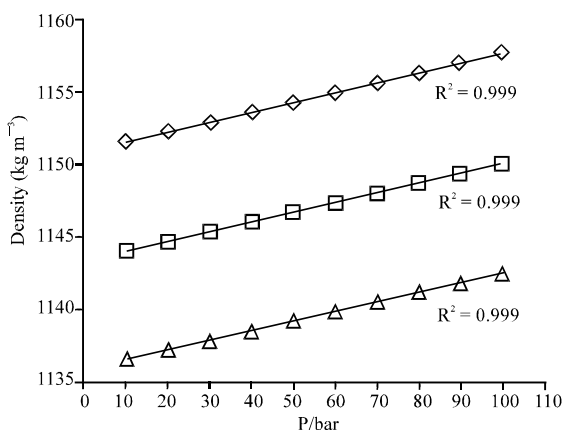


Fig. 1: Effect of pressure on the density of [C₆mim] [BF₄]: ◇; 298.15K, □; 308.15K, △; 318.15K

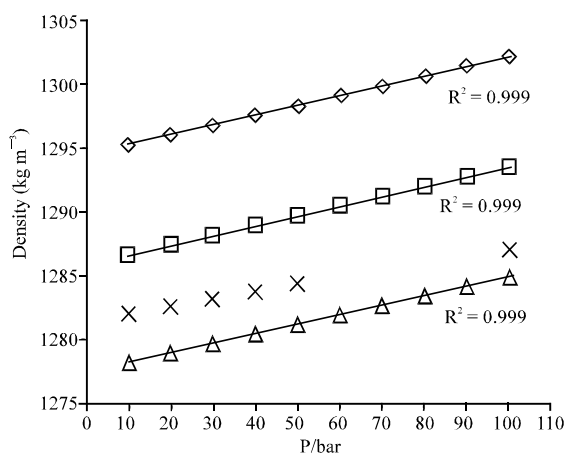


Fig. 2: Effect of pressure on the density of [C₆mim] [PF₆]: (this work) ◇; 298.15K, □; 308.15K, △; 318.15K and Gardas *et al.* (2007) ×; 313K

The densities of ILs; (C₆mim) (BF₄) and (C₆mim) (PF₆) were estimated using Eq. 2 at pressures up to 100 bar and at temperatures (298.15, 308.15, 318.15) K and are plotted in Fig. 1 and 2, respectively. In general, the densities of both ILs have shown a linear increase with the elevation of pressure at all the studied temperatures. However, the extent of density increment for (PF₆) containing anion was observed to be slightly higher than (BF₄) based ionic liquid. The estimated trend for the increase in density of IL: (C₆mim) (PF₆) (this work, at 308.15 K) at elevated pressures was also found to be in good agreement with its experimentally measured densities Gardas *et al.* (2007) at 313.15 K observed (Fig. 2) with a maximum deviations in their slope values of less than 1%.

The viscosities of ILs at pressures up to 100 bar and temperatures (298.15, 308.15, 318.15) K were estimated

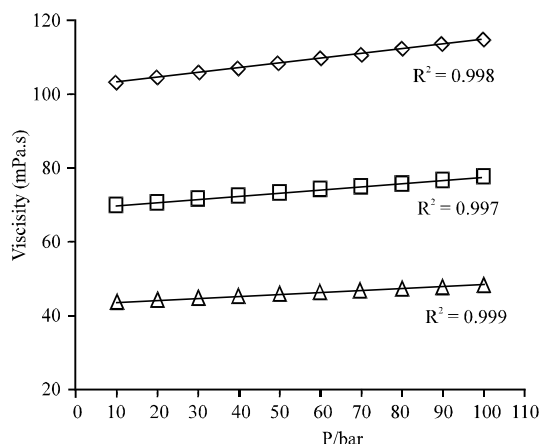


Fig. 3: Effect of pressure on the viscosity of [C₆mim] [BF₄]: ◇; 298.15K, □; 308.15K, △; 318.15K

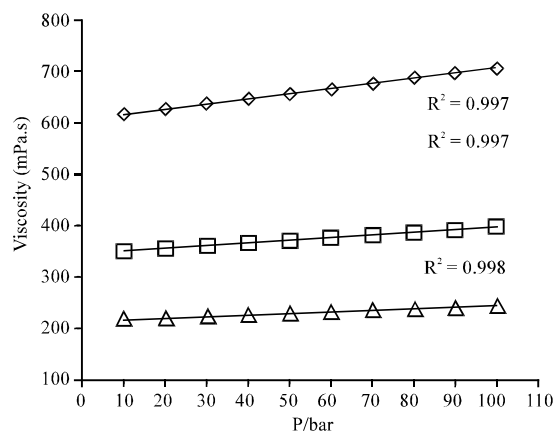


Fig. 4: Effect of pressure on the viscosity of [C₆mim] [PF₆]: ◇; 298.15K, □; 308.15K, △; 318.15K

using Eq. 3. The effect of pressure on the viscosities of (C₆mim) (BF₄) and (C₆mim) (PF₆) are plotted in Fig. 3 and 4 respectively. The fitting parameters (D and E) of Eq. 3 are presented in Table 1. It is obvious from the estimation trends of Fig. 3 and 4 that the viscosities of imidazolium based ILs present a linear increase with an increase in pressure at all the studied temperatures. However, the extent of viscosity increase of both ILs depends on the type of anion as well as on the temperature.

The increase in viscosity of IL with anion; (PF₆) was observed to higher as compared to IL with anion; (BF₄) with an increase in pressure from (10 to 100) bar at all the studied temperatures. On the other hand, the extent of increase in the viscosity of both ILs was found to be low with an increase in temperature. In other words, the value of change in the viscosity of (C₆mim) (BF₄) at 318.15 K was lower as compared to its increase at 298.15 K with elevation of pressure up to 100 bar i.e., 4 mPa.s < 11 mPa.s.

CONCLUSION

This study presents the application of two techniques to estimate the densities and viscosities of imidazolium based ILs: (C₆ mim) (BF₄) and (C₆ mim) (PF₆) using 'Gardas and Coutinho method' and 'modified Tait equation' at high pressures and at temperatures (298.15, 308.15, 318.15) K. The application of both methods for the estimation of density and viscosity of ILs at pressures up to 100 bar, seems to be satisfactory with high correlation coefficient values i.e., R²>0.97. The estimated density and viscosity values of both ILs have shown as linear increase with an increase in pressure. However, the extent of increase for both properties with pressure appeared to be highly dependent on the type of anion of ionic liquid.

ACKNOWLEDGMENT

The author (Ayyaz Muhammad) appreciatively acknowledges Universiti Teknologi Petronas for providing financial support through graduate assistantship (GA) scheme to pursue research work.

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