Journal of Molecular Liquids 219 (2016) 661–666

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Interactions of 1-butyl-3-methylimidazolium hexafluorophosphate with *N*,*N*-dimethylformamide: Density and viscosity measurements

V. Bennett [a], C.W. Dikio [b], S.S. Angaye [a], D. Wankasi [a], E.D. Dikio [b,*], I. Bahadur [c,*], E.E. Ebenso [c]

[a] Department of Chemical Sciences, Niger Delta University, Wilberforce Island, P.M.B, 071 Yenagoa, Bayelsa State, Nigeria
[b] Applied Chemistry and Nanoscience Laboratory, Department of Chemistry, Vaal University of Technology, P. O. Box X021, Vanderbijlpark, South Africa
[c] Department of Chemistry, School of Mathematical and Physical Sciences, Materials Science Innovation & Modelling (MaSIM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa

ARTICLE INFO

Article history:
Received 27 January 2016
Received in revised form 10 March 2016
Accepted 11 March 2016
Available online 18 April 2016

Keywords:
Thermodynamics
Intermolecular interactions
Ionic liquid
Excess Gibbs free energy
Excess molar volumes

ABSTRACT

Physico-chemical properties: density (ρ) and viscosity (η) at (303.15, 313.15 and 323.15) K were measured for the binary mixtures of synthesized and characterized ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF_6] with *N*,*N*-dimethylformamide (DMF) over the entire range of mixture composition. These data have been used to calculate the excess volume (V^E), deviations in viscosity ($\Delta\eta$) and excess Gibbs free energy of activation of viscous flow (ΔG^{*E}). These results are fitted to the Redlich-Kister polynomial equation to derive the binary coefficients and standard deviations. The experimental and calculated quantities are used to study the nature of the intermolecular interactions between the mixture components. The viscosities were correlated with single parameter Grunberg and Nissan model, Hind model, Frenkel model and Kendall and Monroe model.

1. Introduction

An ionic liquid (IL) is a salt that is liquid below 100 °C [1–7]. ILs is usually quaternary ammonium salts. Cations such as, tetraalkylammonium [R_4N^+] or cyclic amines (imidazolium, pyridinium, pyrrolidinium and Guanidinium) are known. Anions may be based on bromo group, cyano group, chloro group, hexafluorophosphate group [4]. Soon after the first reports on the synthesis and applications in organometallic catalysis of the air stable room temperature ionic liquids (RTIL), 1-*n*-butyl-3-methylimidazolium tetrafluoroborate, hexafluorophosphate and their analogues, in the middle of the 1990s a renaissance of the rich chemistry of molten salts has begun and continues to flourish [6]. There is then no doubt that research into the use of ILs as solvents, reagents, catalysts and materials will continue to grow. ILs possesses a unique array of physico-chemical properties that make them important candidates for a number of energy related task — specific applications. High polarity, high viscosity, low vapor pressure, non-flammability, low combustibility and excellent thermal stability [8–11]. However, mixtures of ILs have been known to have different properties from the properties of the pure liquids. In thermodynamics, various intermolecular interactions may take place between the component molecules. The types and strength of such interactions are most times evaluated through some thermodynamic excess functions which are usually described to be either positive or negative. This classification is used to develop statistical theories based on fluid models to interpret the deviations from ideal behaviors of the binary liquid systems. The thermodynamic functions are used to give a more quantitative understanding of the nature of intermolecular interactions of binary liquid systems. Density and viscosity of liquid mixtures are important in most engineering calculations and different analytical applications [12]. Hence, evaluation and prediction of these properties of solvent mixtures as functions of temperature and composition are of theoretical and practical importance because these mixtures are used in titration, calorimetry and reaction calorimetry [13]. In the chemical industry knowledge of the thermodynamic properties of liquids is essential in the designs involving chemical separation, heat transfer and fluid flow [14]. Moreover, thermodynamic properties of binary mixtures containing components capable of undergoing specific interactions exhibit significant deviations from ideality arising from differences in molecular size, shape and structural changes. The characterization of the mixtures through their thermodynamic and transport properties is important from the fundamental point of view to understand their molecular interactions as well as in practical applications [15].

An extensive literature survey showed that a limited number of research studies have been reported on the viscosity of DMF with [BMIM][PF_6] binary mixtures. 1-Butyl-3-methylimidazolium hexafluorophosphate ionic liquid [BMIM][PF_6] is one of the most important traditional ionic liquids and has been widely used in the fields of separation,

* Corresponding authors.
E-mail addresses: ezekield@vut.ac.za (E.D. Dikio), bahadur.indra@gmail.com (I. Bahadur).

http://dx.doi.org/10.1016/j.molliq.2016.03.072
0167-7322/

catalysis, synthesis, etc [16–18]. DMF is an aprotic polar solvent that is not able to self-organize hydrogen bonding [19]. It lacks hydrogen bond, large dipole moment and high dielectric constant [20]. It is a good donor acceptor compound [21]. These properties allow DMF to dissolve both polar and non-polar liquids and it is used in electrolytic capacitors [22].

Rebelo, et al., 2005 [23] analyzed the volumes of the mixtures of $[C_4C_1im][BF_4][NTf_2]$ and $[C_4C_1im][BF_4][PF_6]$. Yanwei, et al., 2007 [24] investigated binary mixtures formed by 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6] with aromatic compound (benzyl alcohol or benzaldehyde) over the full range of compositions at the temperature range from 298.15 K to 313.15 K and at atmospheric pressure. Hui, et al., 2012 [25] studied 1-butyl-3-methylimidazolium hexafluorophosphate with benzene, acetonitrile, and 1-propanol over the entire composition at 293.15 to 343.15 K. Wei, et al., 2009 [7] studied methyl methacrylate (MMA) and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) ionic liquid binary system, over the whole concentration range in the temperature range from (283.15 to 353.15) K. Shruti and Shiddhart 2010 [26] studied 1-Butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF_6] + Poly(ethylene glycol) [PEG 200] binary mixture.

This paper is a research of the thermodynamic properties of binary mixtures containing [BMIM][PF_6] and DMF. In this research, [BMIM][PF_6] was synthesized and the experimental measurements of density, viscosity and excess molar volume of their binary mixture were measured at three different temperatures ranging from (303.15 to 323.15) K. The density, corresponding viscosity deviation, excess molar volume, and excess Gibbs free energy of activation of viscous flow, were calculated. Further the excess Gibbs free energy of activation of viscous flow, and deviation functions were fitted to the Redlich and Kister type polynomial to estimate the coefficients and the standard deviations. The viscosities were correlated with single parameter Grunberg and Nissan model, Hind model, Frenkel model and Kendall and Monroe model. The present work is a part of our investigations on physicochemical properties of binary systems [27–39].

2. Experimental

2.1. Materials

DMF was purchased from Acros Organics and used without further purification. [BMIM][PF_6] was synthesized and characterized.

2.2. Density measurement

Density measurement of DMF and synthesized ionic liquid was carried out with an Anton Paar DMA-4500 M digital densitometer thermostatted at different temperatures. Two integrated Pt 100 platinum thermometers were used for good precision in temperature control internally ($T \pm 0.01$ K). The densimeter protocol includes an automatic correction for the viscosity of the sample. The apparatus is precise to within 1.0×10^{-5} g/cm^3, and the uncertainty of the measurements was estimated to be better than 1.0×10^{-4} g/cm^3. Calibration of the densimeter was performed at atmospheric pressure using doubly distilled and degassed water. A comparison of our measurements of density and viscosity with the data from literature [40–45] is shown in Table 1.

2.3. Viscosity measurement

Viscosity measurements were carried out using Anton Paar SVM 3000 Stabinger Viscometer. The viscometer has a dynamic viscosity range of (0.2–20,000) mPa·s, a kinematic viscosity range of (0.2–20,000) mm^2/s and a density range of (0.65 to 3) g/cm^3. The instrument is equipped with a maximum temperature range of 105 °C and a minimum of 20 °C below ambient. Instrument viscosity reproducibility is 0.35% of measured value and density reproducibility 0.0005 g/cm.

2.4. Infrared measurement

IR spectra of synthesized ionic liquid were recorded using Perkin-Elmer Spectrum 400 FT-IR/FT-NIR spectrometer in the range 400–4000 cm^{-1}.

2.5. NMR measurement

^{1}H NMR spectra of the ionic liquid in DMSO were measured using a Bruker Avariqance 400 NMR spectrometer operating at proton frequency of 300 MHz 75.48 MHz for ^{13}C proton chemical shifts were recorded relative to an internal TMS standard.

2.6. Thermogravimetric analysis

The thermal behavior of the ionic liquid was investigated using a Perkin Elmer Simultaneous Thermal Analyzer (STA 6000) under a nitrogen environment. The ionic liquid sample was heated in platinum crucibles with nitrogen gas flow rate of 19.7 ml/min and a gas pressure of 4.0 bars. The dynamic measurement was made from (30 to 950) °C with a ramp rate of (30 to 900) °C per minute.

2.7. Preparation of 1-Butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF_6]

81.89 g (1.0 mol) of 1-methylimidazole, 128.95 g (1.0 mol) of and 92.0 g (1.0 mol) of potassium hexafluorophosphate in a 500 ml three necked round bottom flask with a reflux condenser at 80 °C for 12 h. 1-bromobutane De-ionized water (100 ml) was added and a bi-phase was formed. The immiscible ionic liquid layer was separated from the water phase with a separating funnel. The ionic liquid was washed with de-ionized water (2×50 ml) until the water phase did not react with 0.001 M aqueous silver nitrate ($AgNO_3$). Diethyl ether (2×30 ml) was added to the ionic liquid and separated in a separating funnel. The ionic liquid was dried in vacuum for 2 h. A colorless liquid was obtained Yield (86%). The ionic liquid was characterized and by ^{1}H and ^{13}C NMR FTIR and by TGA.

^{1}H NMR of the ionic liquid sample (300 MHz, DMSO) contains peaks at δ: 9.05 (s, 1H-imidazole), 7.77 (s, 1H-imidazole), 7.65 (s, 1H-imidazole), 4.16 (s, N–CH_3), 3.8 (s, N–methyl), 1.8 (s, CH_2), 1.30 (s, CH_2), and 0.92 (t, methyl).^{13}C NMR in Fig. 4.4 (300 MHz, DMSO) δ: 19.2 (qt, CH_3), 32.3

Table 1
Comparison of experimental densities (ρ) and viscosities (η) with literature values.

Component		$T = 303.15$ K		$T = 313.15$ K		$T = 323.15$ K	
		ρ (g/cm^3)	η (mPa·s)	ρ (g/cm^3)	η (mPa·s)	ρ (g/cm^3)	η (mPa·s)
[BMIM][PF_6]	Experiment	1.3608	187.63	1.3524	129.67	1.3441	88.51
		1.36240[40]	202[42]	1.35430[41]	120.0[42]	1.34598[41]	74.9[42]
	Literature	1.36286[41]	199.7[43]	1.3550[42]	120.7[43]	1.3468[42]	
		1.36319[42]		1.35419[44]	119.0[40]		
				1.354[40]			
DMF	Experiment	0.9387	0.74	0.9291	0.66	0.9195	0.59
	Literature	0.9402[45]	0.82[45]	0.9307[45]	0.75[45]	–	–