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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*

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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,

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

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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
	Literature	1.36240[40]	202[42]	1.35430[41]	120.0[42]	1.34598[41]	74.9[42]
		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]	–	–

Table 2
Mole fraction (x_1) of DMF, density (ρ), viscosity (η), deviation in viscosities ($\Delta\eta$), molar volume (V_m), excess molar volume (V^E), excess Gibbs free energy of activation of viscous flow (ΔG^{*E}), Kendall-Monroe (Eηm) and Grunberg-Nissan (d′) parameters for binary mixture of DMF (x_1) + [BMIM][PF$_6$] (x_2) at (303.15, 313.15 and 323.15) K.

x_1	ρ (g/cm^3)	η/mPa·s	$\Delta\eta$/mPa·s	V_m (cm·mol^{-1})	V^E (cm·mol^{-1})	ΔG^{*E} (J·mol^{-1})	Eηm (mPa·s)	d′
T = 303.15 K								
0.0000	1.3524	187.63	0.000	208.7008	0.0000	0.00000	0.0000	0.0000
0.3028	1.2892	52.08	−78.989	168.8444	0.7675	3.72944	16.499	1.6999
0.4909	1.1818	15.21	−80.718	144.0856	7.5704	2.21065	9.6145	0.5898
0.6262	1.1718	6.21	−64.449	126.2766	2.3989	0.87728	4.7554	−0.0676
0.7227	1.1282	3.48	−69.152	113.5747	2.1204	0.32759	2.335	−0.3596
0.7963	1.0875	2.42	−36.463	103.887	1.9361	0.49193	1.1391	−0.2247
0.8543	1.0512	1.93	−26.118	96.25267	1.6479	1.07465	0.5466	0.4193
0.9012	1.0186	1.50	−17.791	90.07941	1.2949	0.90918	0.2513	0.5824
0.9399	0.9895	1.21	−10.85	84.98549	0.8715	0.70867	0.1046	0.8391
0.9724	0.9632	0.98	−5.0119	80.70764	0.4161	0.23568	0.0331	0.3645
1.0000	0.9387	0.83	0.0000	77.07477	0.0000	0.00000	0.0000	0.0000
T = T = 313.15 K								
0.0000	1.3441	129.67	0.000	209.99	0.0000	0.0000	0.000	0.0000
0.3028	1.3066	28.84	−617.786	169.98	−2.6542	1.2366	11.359	0.3600
0.4909	1.2175	5.03	−61.347	145.13	2.0377	−4.9696	6.7555	−2.8146
0.6262	1.1643	5.20	−43.735	127.25	2.2456	1.1315	3.4186	0.1046
0.7227	1.1017	3.33	−33.163	114.50	3.9846	1.4881	1.7195	0.3739
0.7963	1.0700	2.12	−24.881	104.77	2.7767	0.7745	0.8609	0.0193
0.8543	1.0441	1.70	−17.829	97.114	1.4433	1.2517	0.4249	0.6232
0.9012	1.0079	1.26	−12.224	90.917	1.4207	0.5998	0.2014	0.1963
0.9399	0.9797	1.05	−7.4474	85.805	0.9044	0.5583	0.0867	0.5502
0.9724	0.9530	0.83	−3.4675	81.509	0.4784	−0.0729	0.0285	−0.9880
1.0000	0.9291	0.74	0.0000	77.863	0.0000	0.0000	0.0000	0.0000
T = T = 323.15 K								
0.0000	1.3358	88.51	0.000	211.29	0.00000	0.0000	0.0000	0.0000
0.3028	1.2916	25.91	−35.997	171.13	−1.86158	2.8443	8.0848	1.2019
0.4909	1.2130	8.38	−37.005	146.19	1.516032	1.3498	4.900	0.1828
0.6262	1.1554	4.46	−29.039	128.24	2.245696	1.6373	2.5321	0.3314
0.7227	1.1117	2.20	−22.826	115.44	1.952655	−0.4077	1.3016	−0.7915
0.7963	1.0678	1.82	−16.738	105.68	2.078664	0.8889	0.6669	0.0798
0.8543	1.0279	1.51	−11.955	97.991	2.117521	1.5328	0.3373	0.8731
0.9012	0.9997	1.08	−8.2646	91.771	1.315201	0.4919	0.1641	0.0306
0.9399	0.9703	0.91	−5.033	86.638	0.901667	0.4950	0.0726	0.3967
0.9724	0.9450	0.77	−2.3176	82.328	0.340922	0.2731	0.0246	0.5453
1.0000	0.9195	0.66	0.0000	78.668	0.000000	0.0000	0.0000	0.0000

(q, CH$_2$), 35.69, (q, CH$_2$), 40.55 (tq, *N*-methyl), 48.5 (t, N–CH$_2$),0.120.3 (dm, imidazole CH), 122.5 (d, imidazole CH), 135.4 (d, imidazole CH).

3. Results and discussion

To investigate the molecular interaction between DMF and [BMIM][PF$_6$], excess molar volume (V^E) and deviation in viscosity, $\Delta\eta$ data of the binary mixtures were computed from measured density and viscosity data using the Eqs. (1) and (2), respectively.

$$V_m^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \qquad (1)$$

$$\Delta\eta = \eta_m - (x_1\eta_1 + x_2\eta_2) \qquad (2)$$

where x_1 and x_2 are the mole fractions calculated from mass fractions. M_1 and M_2 are molar masses, ρ_1 and ρ_2 are densities, η_1 and η_2 are the viscosities of pure component 1 DMF and 2 [BMIM][PF$_6$], respectively. ρ_m and η_m are the density and viscosity of the mixtures.

The excess Gibbs free energy of activation of viscous flow (ΔG^{*E}) for the mixtures was obtained from Eq. (3).

$$\Delta G^{*E} = RT\left[\ \ln\eta_m V_m - (x_1\ \ln\eta_1 V_1 + x_2\ \ln\eta_2 V_2)\right] \qquad (3)$$

where R is the universal gas constant, T is the absolute temperature. V_1 and V_2 are the molar volumes of component 1 and 2; V_m was obtained from Eq. (4). η_1 and η_2 and η_m are the viscosities of component 1 and 2 and mixture, respectively. The values of density, viscosity, excess molar volume, deviation in viscosity, excess Gibbs free energy of

Table 3
Coefficients A_i, and standard deviations, σ, obtained for the binary system DMF (x_1) + [BMIM][PF$_6$] (x_2) at different temperatures for the Redlich-Kister equation.

	T/K	A_0	A_1	A_2	A_3	A_4	σ
		DMF (x_1) + [BMIM][PF$_6$] (x_2)					
V^E/cm^{3}mol^{-1}	303.15	28.639	67.931	−92.232	−473.124	−345.242	0.3
	313.15	7.788	−22.431	−31.064	−77.759	−74.082	0.5
	323.15	6.528	−12.521	−29.839	−75.20	−49.047	0.2
$\Delta\eta$/mPa·s	303.15	−314.47	−39.194	−112.61	−406.763	−119.057	6.18
	313.15	−224.29	−1370.0	−7406.0	−13440.0	−7620.0	4.21
	323.15	−146.199	−85.812	10.093	100.368	72.682	0.2
ΔG^{*E}/(J·mol^{-1})	303.15	8.538	27.322	12.544	−49.364	−24.904	0.2
	313.15	−17.845	−83.426	103.158	512.336	373.531	0.4
	323.15	6.037	11.675	11.552	6.883	20.104	0.6

Table 4
Fitting parameters with Average Percentage Deviation (APD) for the binary mixtures at different temperatures.

Temperature	Frenkel		Hind	
K	η_{12}	APD	η_{12}	APD
303.15	65.207	8.2527	65.207	−7.4291
313.15	44.588	8.1669	44.588	−5.8805
323.15	26.958	8.018	26.958	−4.6577

activation of viscous flow, the Grunberg and Nissan constant (d') and modified Kendall-Monroe ($E\eta m$) for the system under study are presented in Table 2.

The values of V^E, $\Delta\eta$ and ΔG^{*E} were correlated by a Redlich-Kister [46] type polynomial Eq. (4).

$$X = x_1x_2\sum_{i=1}^{k} A_i\,(1\text{-}2x_1)^{\,i-1}. \tag{4}$$

The values of parameter A_k were obtained by fitting the equation to the experimental values with the Least Square method and are given in Table 3.

The standard deviations σ(X) was calculated from Eq. (5).

$$\sigma(X) = \left[\frac{\sum_{i=1}^{N}\left(X_{expt} - X_{calc}\right)^2}{(N-k)}\right]^{1/2} \tag{5}$$

where X is the excess volume (V^E), deviation in viscosity ($\Delta\eta$) and excess Gibbs free energy of activation of viscous flow (ΔG^{*E}).The subscripts expt. and calc. represent the experimental and calculated values respectively. N and k are the number of experimental data points and the number of coefficients in the Redlich-Kister, 1948 [46] polynomial equation.

Kendall and Monroe derived Eq. (6) for analyzing the viscosity of binary mixtures based on zero adjustable parameter.

$$E\eta_m = x_1x_2\left(x_1\eta_1{}^{1/3} + x_2\eta_2{}^{1/3}\right)^3 \tag{6}$$

where $E\eta_m$ is a modified Kendall-Monroe equation.

The predictive ability of some selected viscosity models such as the one parameter model of Frenkel Eq. (7) and hind Eq. (8), apply to the investigated binary systems.

$$ln\eta = x_1{}^2 ln\eta 1 + x_2{}^2 ln\eta_2 + 2x_1x_2 ln\eta_{12} \tag{7}$$

$$\eta = x_1{}^2\eta_1\ x_2{}^2\eta_2 + 2x_1x_2\eta_{12} \tag{8}$$

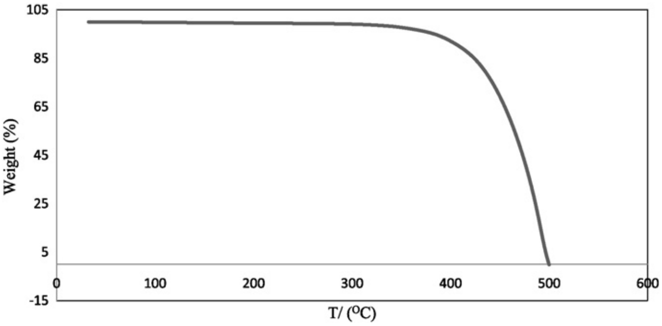

Fig. 1. Thermogravimetric analysis (TGA) spectrum of [BMIM][PF$_6$].

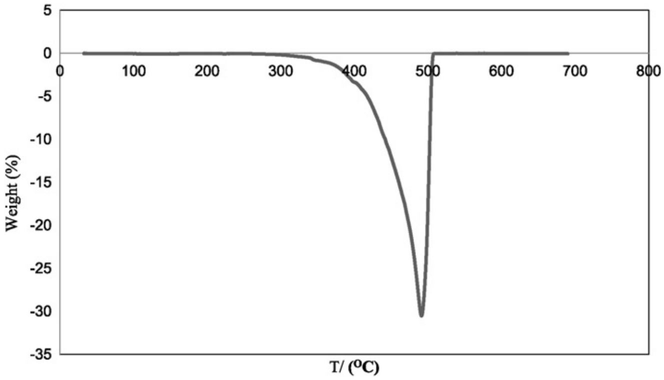

Fig. 2. Differential Thermogravimetric Analysis (DTG) of [BMIM][PF$_6$].

where η_{12} is a constant attributed to unlike pair interactions. Its value was obtained from Eq. (9).

$$\eta_{12} = 0.5\eta_1 + 0.5\eta_2 \tag{9}$$

Grunberg and Nissan, formulated Eq. (10) to determine the molecular interactions leading to viscosity changes.

$$ln\eta_m = x_1{}^2 ln\eta_1 + x_2{}^2 ln\eta_2 + 2x_1x_2 d' \tag{10}$$

where d′ is an interaction parameter which is a function of the composition and temperature of the binary liquid systems.

The correlating ability of Eqs. (6), (8), (9) and (10) were tested by calculating the average percentage deviations (APD) between the experimental and the calculated viscosities were calculated using (11)

$$APD = \frac{100}{N}\sum_{i=1}^{N}\left[\frac{\eta_{expt.} - \eta_{calc.}}{\eta_{expt.}}\right] \tag{11}$$

where $\eta expt$ and $\eta calc$ represent the viscosity of experimental and calculated data, N is the number of experimental data points. The APD values for the binary mixtures of DMF with [BMIM][PF$_6$] are presented in Table 4.

The TGA of the ionic liquid presented in Figs. 1 and 2 shows a single decomposition step. The decomposition of the *as*-synthesized ionic liquid started at 407 °C. This is an indication that the ionic liquid was thermally stable from (0–407) °C. This result is in line with the result of Truelove and Mantz [47]. Deviations in viscosity were found to be positive all through the composition range. The positive values of viscosity deviation for the binary mixtures investigated suggest that the viscosities of associates formed between unlike molecules were relatively less than those of the pure components [48]. Fig. 3 clearly

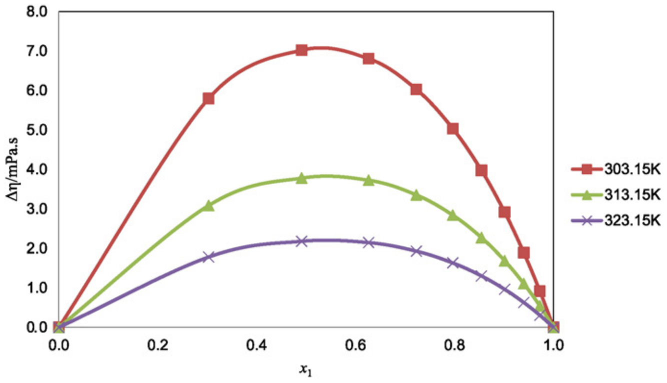

Fig. 3. Deviation in viscosity, $\Delta\eta$ with mole fraction (x_1) DMF in binary mixture of (DMF + [BMIM][PF$_6$]) at (303.15, 313.15 and 323.15) K.

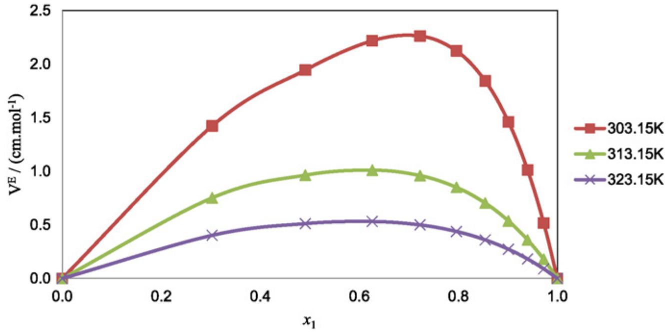

Fig. 4. Plots of excess molar volume (V^E) against mole fraction (x_1) DMF in binary mixture of (DMF + [BMIM][PF_6]) at (303.15, 313.15 and 323.15) K.

shows a deviation in viscosity to increase with increase in temperature. The plots of excess molar volume against mole fraction at (303.15, 313.15 and 323.15) K (DMF + [BMIM][PF_6]) are presented in Fig. 4. Excess parameters associated with a liquid mixture are a quantitative measure of deviation in the behavior of the liquid mixture from ideality. These functions are found to be sensitive towards the intermolecular forces and also on the difference in size and shape of the molecules. Excess volumes of liquid mixtures reflect the result of different contributions arising from structural changes undergone by the pure co-solvent. Positive contributions arise from breakup of interactions between molecules namely, the rupture of hydrogen bonded chains and the loosening of dipole interactions [49]. The values of V^E for the mixtures of (DMF + [BMIM][PF_6]) are positive all through the entire composition but negative at mole fraction 0.3028. The values of V^E are the result of contributions from several opposing effects. Positive excess volume values observed could be attributed to weak interactions between [BMIM][PF_6] and DMF molecules. Negative excess molar volume can be attributed to strong interactions between unlike molecules through hydrogen bonding as observed at mole fraction 0.3028. The plots of excess Gibbs free energy of activation of viscous flow against mole fraction at 303.15, 313.15 and 323.15 K for (DMF + [BMIM][PF_6]) are presented in Fig. 5. Excess properties provide information about the molecular interactions and macroscopic behavior of fluid mixtures which can be used to test and improve thermodynamic models for calculating and predicting fluid phase equilibria. The magnitude of ΔG^{*E} represents the strength of interaction between unlike molecules [50]. Excess Gibbs free energy of activation of viscous flow was found to be positive for all plots. In all plots, ΔG^{*E} increased with increase in temperature. The positive values of excess Gibbs free energy of activation of viscous flow indicate the presence of specific and strong interactions in the system under investigation [51]. The excess Gibbs free energy of activation of viscous flow attains a maximum at mole fraction 0.7227.

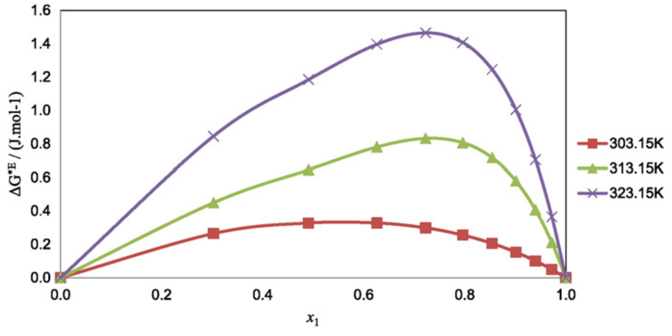

Fig. 5. Plots of excess Gibbs free energy of activation of viscous flow (ΔG^{*E}) against mole fraction (x_1) DMF in binary mixture of (DMF + [BMIM][PF_6]) at (303.15, 313.15 and 323.15) K.

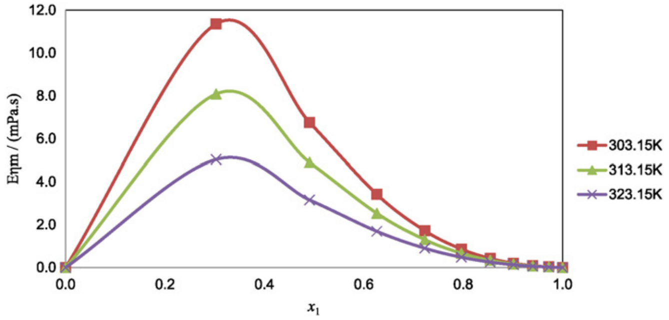

Fig. 6. Plots of modified Kendall and Monroe viscosity correlation Eηm (mPa.s) against mole fraction (x_1) DMF in binary mixture of (DMF + [BMIM][PF_6]) at (303.15, 313.15 and 323.15) K.

A comparison of experimental thermodynamic data of multicomponent mixtures with that calculated by means of various predictive methods is very useful from different points of view: (i) it suggests which model is more appropriate to the characteristics of the system, (ii) it may indicate which parameters should be improved when the model involves group contributions and (iii) it may allow the identification of some model as a convenient reference for the interpretation of the deviations observed. The viscosity data have been correlated with semi-empirical equations of modified Kendall and Monroe, Frenkel, Hind, and Grunberg-Nissan. Grunberg-Nissan interaction parameters are both positive and negative while the modified Kendall-Monroe viscosity correlation data are all positive as seen in Table 2. Plots for the modified Kendall-Monroe viscosity correlation are presented in Fig. 6. Plots of modified Kendall-Monroe viscosity correlation at different temperatures show decrease in viscosity with increase in temperature. The values of Frenkel and Hind are presented in Table 4.

4. Conclusions

Experimental data of density and viscosity for the mixture of (DMF + [BMIM][PF_6]) were measured over the entire range of compositions at atmospheric pressure from (303.15 to 323.15) K, from which the excess molar volumes, deviation in viscosity and excess Gibbs free energy of activation of viscous flow were calculated and the Redlich-Kister polynomial equation was applied successfully for the correlation of the excess/deviation properties. The estimated coefficients and standard deviation values were also presented. It was found that density and viscosity for pure components or mixtures decreased with increasing temperature and viscosity was more sensitive than density to temperature or composition change. It was found that all of these calculated quantities were positive, and the Redlich-Kister fitting curves were asymmetric. Positive V^E values suggest that the rupturing of hydrogen bonds and the cleavage of dipole-dipole interactions played a significant role in the mixing behavior which indicates weak interactions of the component molecules of the binary system. Positive $\Delta\eta$ indicates that there was a loss of dipolar association between unlike components because of the size and shape of the mixing components. Positive ΔG^{*E} suggests the formation of heterogeneous interaction between unlike components.

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