

# Interactions of Binary Mixtures of 1-Methyl-3-Phenylimidazolium Iodide [MPhIm][I] and Isopropyl Alcohol [C<sub>3</sub>H<sub>8</sub>O] at Varying Temperatures

Victoria Bennett<sup>1,\*</sup>, Nimibofa Ayawei<sup>2</sup>

<sup>1</sup>Department of Chemical Sciences, Faculty of Basic and Applied Sciences, University of Africa, Toru-Orua, Sagbama, Nigeria

<sup>2</sup>Department of Chemistry, Faculty of Science, Medical University, Yenagoa, Nigeria

## Email address:

vkalapai@gmail.com (Victoria Bennett), Victoria.bennett@uat.edu.ng (Victoria Bennett)

\*Corresponding author

## To cite this article:

Victoria Bennett, Nimibofa Ayawei. Interactions of Binary Mixtures of 1-Methyl-3-Phenylimidazolium Iodide [MPhIm][I] and Isopropyl Alcohol [C<sub>3</sub>H<sub>8</sub>O] at Varying Temperatures. *American Journal of Physical Chemistry*. Vol. 11, No. 3, 2022, pp. 45-51.

doi: 10.11648/j.ajpc.20221103.11

Received: July 9, 2022; Accepted: August 8, 2022; Published: August 17, 2022

**Abstract:** In potential engineering and process design applications of binary mixtures containing ionic liquids (ILs), the accurate determination of the physicochemical properties plays a pertinent role. Thermodynamic studies can provide an understanding into the nature of intermolecular interactions occurring between the solute and solvent in solutions. To this effect, thermodynamic properties of binary mixtures of 1-Methyl-3-Phenylimidazolium Iodide [MPhIm][I] + Isopropyl Alcohol [C<sub>3</sub>H<sub>8</sub>O] have been studied over the concentration range of mole fraction 0–1. Density and viscosity of the pure ionic liquid (IL) and the binary systems were measured and calculated. These data have been used to calculate excess molar volumes, V<sub>mE</sub>, Excess viscosity, Δη, excess Gibbs free energy of activation of viscous flow, ΔG<sup>\*</sup>E of each component in the mixtures. To derive the binary coefficients and the standard deviations, the results were fitted into the Redlich-Kister Polynomial equation. The experimental and calculated quantities were used to study the nature of intermolecular interactions between the binary mixtures of 1-Methyl-3-Phenylimidazolium Iodide [MPhIm][I] + Isopropyl Alcohol [C<sub>3</sub>H<sub>8</sub>O]. Several factors were discovered to have influenced the interactions. Positive excess molar volume (V<sub>mE</sub>) values reported were influenced by dipole-dipole and dipole-dipole induced interactions between unlike molecules, resulting in the contraction of the molar volumes of the mixtures. The viscosities were correlated with single parameter Grungberg-Nissan, Hind, Frenkel and Kendel- Monroe models.

**Keywords:** Molecular Interaction, Density, Excess Viscosity

## 1. Introduction

Ionic liquids (ILs) are compounds completely consisting of ions with melting point below 100°C [1-5]. The first reported ionic liquid was ethylammonium nitrate (C<sub>2</sub>H<sub>5</sub>)NH<sub>3</sub>·NO<sub>3</sub> with a melting point of 12°C [6]. Ionic liquids consist of salts derived from 1-methylimidazole and pyridine. In forming an ionic liquid, a huge organic cation is coordinately bonded to either Tetrafluoroborate (BF<sub>4</sub>), hexafluorophosphate (PF<sub>6</sub>), bis-trifluoromethanesulfonimide (NTf<sub>2</sub>), trifluoromethanesulfonate (OTf), dicyanamide (N(CN)<sub>2</sub>), hydrogen sulphate (HSO<sub>4</sub>), ethyl sulphate (EtOSO<sub>3</sub>), chloride (Cl<sup>-</sup>), Iodide (I<sup>-</sup>), AlCl<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, or [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>] [7-10]. Ionic

liquids are grouped into – room-temperature ILs (RTILs), task-specific ILs (TSILs), polyionic liquids (PILs) and supported IL membranes (SILMs) which include composites of ionic liquids supported on metal-organic frameworks (MOFs) [11-14]. Synthesis and application in organometallic catalysis of 1-n-butyl-3-methylimidazolium tetrafluoroborate, 1-n-butyl-3-methylimidazolium hexafluorophosphate and their counterparts was first reported in the mid 1990s, and soon after, a rejuvenation of the specific study of the properties and behaviour of molten salts as solvents, reagents, catalysts and materials started and has continued to thrive [15]. The properties of ILs are unique presenting them useful for a plethora of energy related task-specific

applications. High thermal stability, high solvation abilities, wide electrochemical windows, low vapour pressure, low volatility and low combustibility are some of the properties of ionic liquids that make them unique [16].

Nonetheless, binaries of ILs have been reported to have different properties from the properties of the pure ionic liquids. In thermodynamics, various intermolecular interactions may take place between the component molecules. The types and strength of intermolecular interactions are evaluated using thermodynamic excess functions which are usually described as positive or negative. Statistical theories are further developed based on fluid models to interpret the deviations from ideal behaviors of the components of the binary liquid systems. Density and viscosity of liquid mixtures are important in various analytical applications [17]. Hence, evaluating and predicting these properties of liquid mixtures as functions of temperature and composition is pertinent [18]. Knowledge of the thermodynamic properties of liquids is also essential in the chemical industry, in the designs pertaining to chemical separation, heat transfer and fluid flow [19]. Moreover, thermodynamic properties of binary mixtures exhibiting significant deviations from ideality were attributed to differences in molecular size, shape and structural changes. To understand their molecular interactions as well as in practical applications of binary mixtures, the characterization of the mixtures through their thermodynamic and transport properties is important [20]. Bennett and others [5] studied the interaction of 1-Butyl-3-methylimidazolium hexafluorophosphate with N, N-dimethylformamide at (303.15 – 323.15) K. Their results show a decrease in viscosity of the binary mixtures with increasing mole fractions of the cosolvent. Wei et al., [21] studied methyl methacrylate (MMA) and 1-butyl-3-methylimidazolium hexafluorophosphate [BMIm][PF<sub>6</sub>] ionic liquid binary system, over the whole concentration range in the temperature range from (283.15 – 353.15) K. They observed that the excess molar volume,  $V_m^E$  values were within the scope of research and were negative and became more negative with increasing temperature. Bennett et. al. [2] studied the interaction of 1-Butyl-3-methylimidazolium Bromide with Isopropyl Alcohol at (303.15 – 323.15) K. They observed 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. Conductance of 1-Butyl-3-methylimidazolium nitrate [BMIm][NO<sub>3</sub>] with N, N-dimethylformamide at T (293.15 – 323.15) K was investigated by Bennett et al. [3]. They observed that Conductivity measurement of the ionic liquid with N, N-dimethylformamide at different concentrations increased with increase in concentration. Shruti and Shiddhart [22] studied 1-Butyl-3-methylimidazolium hexafluorophosphate [BMIm][PF<sub>6</sub>] + Poly(ethylene glycol) [PEG 200] binary mixture and observed that excess molar volumes of the mixtures were negative throughout the entire temperature range. Bittencourt and others [23] studied the thermodynamic properties of binary mixtures of n-butylammonium-based ionic liquids with ethanol at T=(293.15–313.15) K. They observed that for all systems studied, the values of excess molar volume, ( $V_m^E$ )

and deviation in viscosity,  $\Delta\eta$  were negative over the entire composition range, whereas excess Gibbs energy of activation of viscous flow values were positive over the entire composition range and the results were attributed to structural effects and intermolecular interactions between like and unlike molecules.

This paper is a research of the thermodynamic properties of binary mixtures of 1-methyl-3-phenylimidazolium iodide [MPhIm][I] + Isopropyl alcohol [C<sub>3</sub>H<sub>8</sub>O], a polar protic solvent. 1-methyl-3-phenylimidazolium iodide [MPhIm][I] was synthesized, characterized and the experimental measurements of density, viscosity and excess molar volume of the liquid mixtures with isopropyl alcohol (C<sub>3</sub>H<sub>8</sub>O) were measured at four different temperatures (293.15 – 323.15) K.. The density ( $\rho$ ), corresponding viscosity deviation ( $\Delta\eta$ ), excess molar volume ( $V_m^E$ ), and excess Gibbs free energy of activation of viscous flow ( $\Delta G^*E$ ), were calculated. To estimate the coefficients, standard deviations and excess Gibbs free energy of activation of viscous flow, the results were fitted to the Redlich and Kister type polynomial [24]. Single parameter Grunberg and Nissan model, Hind model, Frenkel model and Kendall and Monroe model were employed in correlating the viscosities.

## 2. Experimental

### 2.1. Materials

All chemicals used were of analytical grades and obtained from BDH, Labtech chemicals, Ken Light Laboratories, Kermel and used without further purification.

### 2.2. Methods

#### 2.2.1. Synthesis of 1-Methyl-3-Phenylimidazolium Iodide [MPhIm][I]

1-Methyl-3-Phenylimidazolium Iodide [MPhIm][I] was synthesized according to method reported by Bennett and others [4]. 81.89 g (1.0 mol) of 1-methylimidazole and 204.01 g (1.0 mol) of iodobenzene were refluxed in a 500 mL three-necked round bottomed flask for 12 h at 80°C. 100 mL of ultra-pure water was added and washed twice with 50 mL ethyl acetate. A bi-phase was formed and the top phase, the crude ionic liquid phase was separated with a separating funnel. The crude ionic liquid was concentrated and dichloromethane (50 mL) was added and passed through silica gel mesh 60. The ionic liquid was dried in vacuum for 3 hrs. A yellow liquid with yield 83% was obtained. The ionic liquid was characterized by <sup>1</sup>H, <sup>13</sup>C, Nuclear Magnetic Resonance (NMR) Spectrometry, Fourier Transform Infrared (FTIR) Spectrometry and Thermal Gravimetric Analysis (TGA).

#### 2.2.2. Preparation of Binary Mixtures of [MPhIm][I] and Isopropyl Alcohol (C<sub>3</sub>H<sub>8</sub>O) at 293.15 – 323.15 K

Binary mixtures were prepared from calculated mole fractions and appropriate volumes (mL) of 1-Methyl-3-Phenylimidazolium Iodide and Isopropyl alcohol at the entire composition of 293.15 – 323.15 K.

### 3. Results and Discussion

The measurements of density and viscosity were compared with the data in the literature as presented in Table 1.

**Table 1.** Comparison of experimental densities ( $\rho$ ) and viscosities ( $\eta$ ) with literature value.

Component		T=293.15 K		T= 303.15 K		T = 313.15 K		T= 323.15 K	
		$\rho$ (g/cm <sup>3</sup> )	$\eta$ (mPa·s)	$\rho$ (g/cm <sup>3</sup> )	$\eta$ (mPa·s)	$\rho$ (g/cm <sup>3</sup> )	$\eta$ (mPa·s)	$\rho$ (g/cm <sup>3</sup> )	$\eta$ (mPa·s)
[MPhlM][1]	Experiment	1.030	4.375	1.037	3.153	1.026	2.388	1.015	1.882
	Literature	1.038 [4]	4.372 [4]	1.031 [4]	3.152 [4]	1.023 [4]	2.385 [4]	1.015 [4]	1.882 [4]
C <sub>3</sub> H <sub>8</sub> O	Experiment	0.787	2.198	0.779	1.648	0.7699	1.249	0.7607	0.9609
	Literature	0.7873 (N/A)	2.1975 [2]	0.7787 [2]	1.648 [2]	0.769 [2]	1.2492 [2]	0.7607 [2]	0.9609 [2]

N/A = Not available.

To study the molecular interaction between [C<sub>3</sub>H<sub>8</sub>O] and [MPhlM][1], 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 equations (1) and (2) respectively.

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho_m} \left( \frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right) \quad (1)$$

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

where  $x_1$  and  $x_2$  are the mole fractions calculated from mass fractions.  $M_1$  and  $M_2$  are molar masses,  $\rho_1$  and  $\rho_2$  are densities,  $\eta_1$  and  $\eta_2$  are the viscosities of pure component 1 and 2 [MPhlM][1] respectively.  $\rho_m$  and  $\eta_m$  are the density and viscosity of the binary mixtures. The excess Gibbs free energy of activation of viscous flow ( $\Delta G^{*E}$ ) for the mixtures was obtained using equation (3).

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

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 equation (4).  $\eta_1$  and  $\eta_2$  and  $\eta_m$  are the viscosities of component 1 and 2 and mixture respectively.

$$V_m = \frac{x_1 M_1 + x_2 M_2}{\rho_m} \quad (4)$$

The values of density, viscosity, excess molar volume, deviation in viscosity, excess Gibbs free energy of activation of viscous flow, the Grunberg and Nissan constant ( $d'$ ) and modified Kendall-Monroe ( $E\eta_m$ ) for C<sub>3</sub>H<sub>8</sub>O + [MPhlM][1] are presented in Table 2. The values of  $V^E$ ,  $\Delta\eta$  and  $\Delta G^{*E}$  were correlated using a Redlich-Kister type polynomial equations (5 and 6) [24].

**Table 2.** Mole fraction ( $x_1$ ) of C<sub>3</sub>H<sub>8</sub>O, density ( $\rho$ ), viscosity ( $\eta$ ), deviation in viscosities ( $\Delta\eta$ ), molar volume ( $V_m$ ), excess molar volume ( $V^E$ ), excess Gibbs free energy of activation of viscous flow ( $\Delta G^{*E}$ ), Kendall-Monroe ( $E\eta_m$ ) and Grunberg-Nissan ( $d'$ ) parameters for binary mixture of C<sub>3</sub>H<sub>8</sub>O ( $x_1$ ) + [MPhlM][1] ( $x_2$ ) at (293.15, 303.15, 313.15 and 323.15) K.

$x_1$	$\rho$ (g/cm <sup>3</sup> ) (cm <sup>3</sup> ·mol <sup>-1</sup> )	$\eta$ /mPa·s (cm <sup>3</sup> ·mol <sup>-1</sup> )	$\Delta\eta$ /mPa·s (J·mol <sup>-1</sup> )	$V_m$ (mPa·s)	$V_m^E$	$\Delta G^{*E}$	$E\eta_m$	$d'$
T= 293.15 K								
0.0000	1.0388	4.3729	0	275.44	0	0	0	0
0.3458	1.0105	4.1386	0.2070	206.59	0.3638	0.3745	0.7934	0.8084
0.5432	0.9807	4.113	0.2721	167.28	0.5041	0.6627	0.7614	1.2595
0.670	0.9512	3.9748	0.2924	141.85	0.5596	0.7507	0.6193	1.6586
0.7602	0.9237	3.7125	0.2815	124.07	0.5458	0.7217	0.4795	1.9714
0.8263	0.9858	3.3474	0.2503	110.91	0.4874	0.6322	0.3597	2.0995
0.0877	0.8718	2.9167	0.2069	100.80	0.4037	0.5139	0.2601	1.8420
0.9173	0.8479	2.6612	0.1574	92.786	0.3072	0.3844	0.1774	1.7753
0.9501	0.8275	2.2465	0.1049	86.256	0.2052	0.2525	0.1082	-0.2591
0.9772	0.8072	2.1966	0.0520	80.870	0.1019	0.1235	0.0498	-0.7226
1.0000	0.7873	2.1975	0	76.331	0	0	0	0
T = 303.15 K								
0.0000	1.0309	3.1516	0	277.55	0	0	0	0
0.3458	1.0064	2.9135	0.1391	208.26	0.2704	0.7438	0.5786	0.6514
0.5432	0.9704	2.9579	0.1818	168.71	0.3869	0.9855	0.5595	1.1637
0.6709	0.9404	2.8354	0.1945	143.12	0.4509	1.0664	0.4576	1.4912
0.7602	0.9151	2.6786	0.1867	125.23	0.4616	1.0312	0.3556	1.8117
0.8263	0.8856	2.4534	0.1655	111.98	0.4302	0.9194	0.2675	1.9877
0.0877	0.8614	2.1079	0.1368	101.80	0.3691	0.7620	0.1939	1.5441
0.9173	0.8391	2.0187	0.1039	93.734	0.2889	0.5803	0.1326	1.9693
0.9501	0.8180	1.7298	0.0692	87.173	0.1973	0.3874	0.0809	0.3394
0.9772	0.7988	1.6012	0.0343	81.742	0.0998	0.1922	0.0373	-1.9565
1.0000	0.7787	1.6430	0	77.174	0	0	0	0

x <sub>1</sub>	$\rho$ (g/cm <sup>3</sup> ) (cm <sup>3</sup> ·mol <sup>-1</sup> )	$\eta$ /mPa·s (cm <sup>3</sup> ·mol <sup>-1</sup> )	$\Delta\eta$ /mPa·s (J·mol <sup>-1</sup> )	V <sub>m</sub> (mPa·s)	V <sub>m</sub> E	$\Delta G^* E$	E <sub>ηm</sub>	d'
T = 313.15 K								
0.0000	1.0228	2.3851	0	279.75	0	0	0	0
0.3458	1.0027	2.1336	0.0911	210.01	0.0599	0.8232	0.4381	0.5984
0.5432	0.9898	2.2299	0.1195	170.19	0.1449	1.0945	0.4238	1.1416
0.6709	0.9325	2.1094	0.1283	144.43	0.2195	1.1902	0.3466	1.4068
0.7602	0.9033	1.9435	0.1234	126.42	0.2549	1.1567	0.2694	1.5879
0.8263	0.8752	1.8011	0.1097	113.09	0.2542	1.0361	0.2027	1.7666
0.0877	0.8521	1.6598	0.0907	102.84	0.2270	0.8622	0.1469	1.8991
0.9173	0.8288	1.4792	0.0689	94.725	0.1823	0.6589	0.1005	1.5239
0.9501	0.8080	1.3852	0.0459	88.120	0.1267	0.4412	0.0614	1.4990
0.9772	0.7883	1.2765	0.0228	82.654	0.0648	0.2195	0.0283	0.3085
1.0000	0.7699	1.2492	0	78.057	0	0	0	0
T = 323.15 K								
0.0000	1.0147	1.8825	0	281.98	0	0	0	0
0.3458	0.9855	1.7284	0.0543	211.79	0.0163	0.8203	0.3431	0.6504
0.5432	0.9522	1.6800	0.0718	171.72	0.0463	1.0950	0.3303	1.0134
0.6709	0.9268	1.5865	0.0776	145.80	0.0641	1.1958	0.2693	1.2685
0.7602	0.8924	1.4788	0.0749	127.67	0.0693	1.1663	0.2088	1.4801
0.8263	0.8665	1.3936	0.0668	114.25	0.0654	1.0476	0.1568	1.7757
0.0877	0.8421	1.2442	0.0553	103.94	0.0561	0.8739	0.1135	1.6299
0.9173	0.8193	1.1520	0.0421	95.775	0.0437	0.6691	0.0775	1.6585
0.9501	0.7982	1.0606	0.0281	89.128	0.0296	0.4488	0.0473	1.3736
0.9772	0.7789	1.0366	0.0139	83.627	0.0148	0.2236	0.0218	2.7135
1.0000	0.7607	0.9809	0	78.999	0	0	0	0

$$\Delta Y = x_1 x_2 \sum_{k=1}^N A_k (2x_1 - 1)^k \quad (5)$$

$$\Delta Y = x_1 x_2 [A_0 + A_1(2x_1 - 1) + A_2(2x_1 - 1)^2 + A_3(2x_1 - 1)^3 + A_4(2x_1 - 1)^4] \quad (6)$$

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

The standard deviations  $\sigma$  ( $\Delta Y$ ) were calculated from Equation (7)

$$\sigma(\Delta Y) = \left( \frac{\sum (Y_{\text{expt}} - Y_{\text{expt}})^2}{N - m} \right)^{1/2} \quad (7)$$

where  $x$  is the excess volume (VE), deviation in viscosity ( $\Delta\eta$ ) and excess Gibbs free energy of activation of viscous flow ( $\Delta G^* E$ ). The subscripts expt. and calc. are 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 polynomial equation [24]. Kendall and Monroe equation, equation 8, was used in analyzing the viscosity of the binary mixtures, based on zero adjustable parameter.

$$E_{\eta m} = x_1 x_2 (x_1 \eta_1^{1/3} + x_2 \eta_2^1) \quad (8)$$

**Table 3.** Coefficients  $A_i$  and standard deviations,  $\sigma$ , obtained for the binary system C<sub>3</sub>H<sub>8</sub>O (x<sub>1</sub>) + [MPhIm][I] (x<sub>2</sub>) at different temperatures for the Redlich-Kister equation.

	T/K	A0	A1	A2	A3	$\sigma$
C <sub>3</sub> H <sub>8</sub> O (x <sub>1</sub> ) + [MPhIm][I] (x <sub>2</sub> )						
VE / cm <sup>3</sup> mol <sup>-1</sup> n	293.15	-1.90	-2.75	0.97	0.14	-0.96
	303.15	1.44	2.41	0.81	-0.09	-0.68
	313.15	-2.59	0.51	0.72	-0.12	-0.505
	323.15	1.87	-2.79	1.04	-0.16	-0.003
$\Delta\eta$ /mPa·s	293.15	-1.04	1.19	-0.207	0.009	0.3835
	303.15	-0.696	0.78	-0.132	0.006	0.2565
	313.15	-0.457	0.52	-0.09	0.004	0.2298
	323.15	-0.274	0.33	-0.064	0.002	0.0020
$\Delta G^* E$ /(J·mol <sup>-1</sup> )	293.15	3.739	4.497	-0.746	0.033	2.5704
	303.15	-0.111	4.484	-0.144	0.056	2.2981
	313.15	-4.17	4.088	-1.009	0.072	2.2396
	323.15	-4.167	3.19	-1.099	0.088	2.2133

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 equation (9) and hind equation (10), apply to the studied binary mixtures.

$$\ln\eta = \chi_1^2 \ln\eta_1 + \chi_2^2 \ln\eta_2 + 2\chi_1 \chi_2 \ln\eta_{12} \quad (9)$$

$$\eta = \chi_1^2 \eta_1 + \chi_2^2 \eta_2 + 2\chi_1 \chi_2 \eta_{12} \quad (10)$$

where  $\eta_{12}$  is a constant attributed to unlike pair interactions. Its value was obtained from Equation (11).

$$\eta_{12} = 0.5\eta_1 + 0.5\eta_2 \quad (11)$$

Grunberg and Nissan formulated equation (12) to determine the molecular interactions leading to viscosity changes.

$$\ln \eta_m = \chi_1^2 \ln \eta_1 + \chi_2^2 \ln \eta_2 + 2\chi_1\chi_2 d' \quad (12)$$

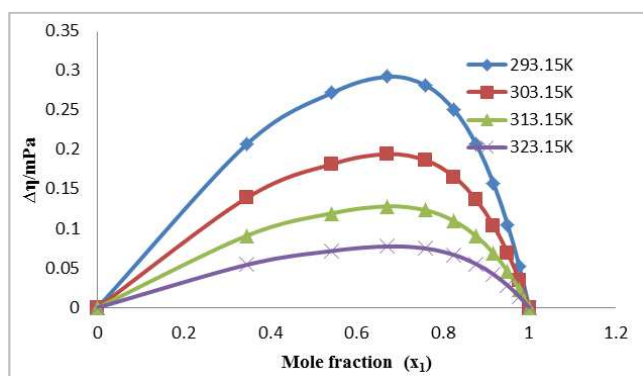
where  $d'$  is an interaction parameter which is a function of the composition and temperature of the binary liquid systems. The correlating ability of equations (8), (9), (10) and (12) were tested by calculating the average percentage deviations (APD) between the experimental and the calculated viscosities using equation (13).

$$\frac{APD}{N} = \frac{100 \sum_{i=1}^N [\eta_{\text{expt}} - \eta_{\text{calc}}]}{\eta_{\text{exp}}} \quad (13)$$

Where  $\eta_{\text{expt}}$  and  $\eta_{\text{calc}}$  represent the viscosity of experimental and calculated data,  $N$  is the number of experimental data points. The APD values for the binary mixtures of  $[C_3H_8O] + [MPhIm][I]$  are presented in Table 4.

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

Temperature	Frenkel		Hind	
K	$\eta_{12}$	APD	$\eta_{12}$	APD
293.15	3.285	6.515	285	1.809
303.15	2.403	6.969	2.40	2.115
313.15	1.817	8.016	1.82	2.372
323.15	1.422	9.755	1.42	2.522

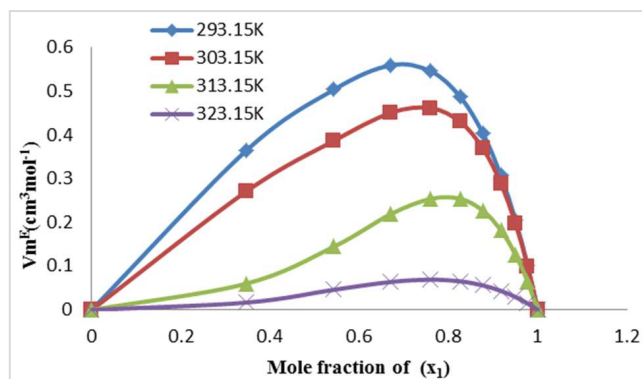


**Figure 1.** Plot of excess viscosity,  $\Delta\eta$  with mole fraction ( $x_1$ ) of Isopropyl alcohol in binary mixture for Isopropyl alcohol with  $[MPhIm][I]$  at 293.15, 303.15, 313.15 and 323.15 K.

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. Figure 1 clearly shows a deviation in viscosity with increase in temperature.

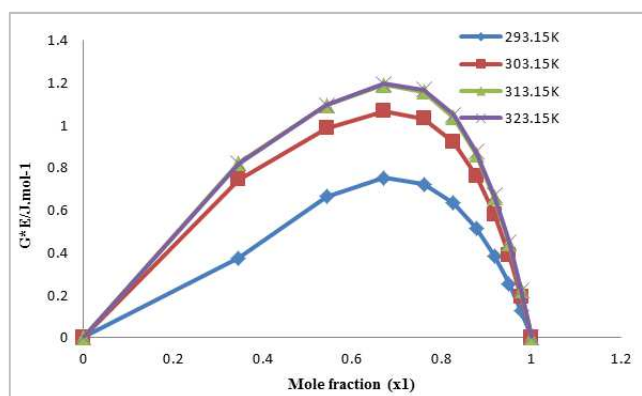
The plots of excess molar volume against mole fraction at (293.15, 303.15, 313.15 and 323.15) K of  $[C_3H_8O] + [MPhIm][I]$  are presented in Figure 2. Excess parameters associated with a liquid mixture are a quantitative measure of deviation in the behavior of the liquid mixture from ideality. These 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 attributed to rupture of hydrogen bonded chains and the loosening of dipole interactions [25].



**Figure 2.** Plot of excess molar volume,  $V_m^E$  with mole fraction ( $x_1$ ) of Isopropyl alcohol in binary mixture for Isopropyl alcohol with  $[MPhIm][I]$  at 293.15, 303.15, 313.15 and 323.15 K.

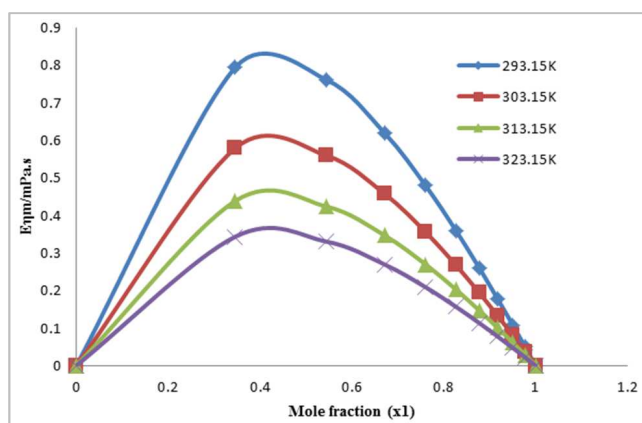
The values of VE for the mixtures of  $([C_3H_8O] + [MPhIm][I])$  are positive all through the entire composition. The values of VE are the result of contributions from several opposing effects. Positive excess volume values observed were attributed to weak interactions between  $[MPhIm][I]$  and  $[C_3H_8O]$  molecules. The plots of excess Gibbs free energy of activation of viscous flow against mole fraction at 293.15, 303.15, 313.15 and 323.15 K are presented in Figure 3. 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  $\Delta G^{*E}$  represents the strength of interaction between unlike molecules [26].



**Figure 3.** Plot of excess Gibbs free energy of activation of viscous flow,  $\Delta G^{*E}$ , with mole fraction ( $x_1$ ) Isopropyl alcohol in binary mixture for Isopropyl alcohol with  $[MPhIm][I]$  at 293.15, 303.15, 313.15 and 323.15 K.

Excess Gibbs free energy of activation of viscous flow was observed to be positive for all plots. In all plots,  $\Delta G^{*E}$  increased with increase in temperature. Positive values of excess Gibbs free energy of activation of viscous flow indicate the presence of specific and strong interactions in the binary system under study [27]. The excess Gibbs free energy of activation of viscous flow attains a maximum at mole fraction 0.6709. Comparing the experimental thermodynamic data of

binary mixtures with that calculated by means of various predictive methods is very useful because: (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 interaction parameters and are all positive while the modified Kendall-Monroe viscosity correlation data are both positive and negative as presented in Table 2. Plots for the modified Kendall Monroe viscosity correlation are presented in Figure 4.



**Figure 4.** Plot of Kendall – Monroe viscosity correlation,  $E\eta_m$  (mPa. s) with mole fraction ( $x_1$ ) Isopropyl alcohol in binary mixture for Isopropyl alcohol with [MPhIm][I] at 293.15, 303.15, 313.15 and 323.15 K.

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. Frenkel and Hind viscosity correlation at four different temperatures show decrease in viscosity with increase in temperature.

## 4. Conclusion

Experimental data of density and viscosity for the mixture of [C<sub>3</sub>H<sub>8</sub>O] + [MIPhM][I] were measured over the entire range of compositions at atmospheric pressure from (293.15 - 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 of pure components or mixtures decreased with increasing temperature. 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 VE values suggest that the rupturing of hydrogen bonds and the

cleavage of dipole-dipole interactions played a key role in the mixing behavior, indicating 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  $\Delta G^*E$  suggests the formation of heterogeneous interaction between unlike components.

## 5. Recommendation

This research investigated the interaction of the binary mixtures, 1-Methyl-3-Phenylimidazolium Iodide [MPhIm][I] and Isopropyl alcohol [C<sub>3</sub>H<sub>8</sub>O] at four temperatures (293.15 – 323.15 K). The study therefore, recommends the investigation of these binary mixtures at lower or higher temperatures.

## References

- [1] Bennett V., Abidemi S. A. and Dikio E. D. (2019). Effect of 1-Butyl-3-methylimidazolium hexafluorophosphate [BMIm][PF<sub>6</sub>] on N, N-dimethylformaldehyde: Conductivity Measurement at T (293.15 – 333.15) K Res. J. of Pure Sci and Tech. 2 (1), 1-12.
- [2] Bennett V., Ejidike I. P., Donbebe W. and Dikio E. D. (2018). Interactions of 1-Butyl-3-Methylimidazolium Bromide with Isopropyl alcohol binary system: Spectroscopic and volumetric measurements at T (303.15, 313.15 and 323.15) K. Int. J. of ChemTech Res. 11 (05).
- [3] Bennett V., Angaye S. S. and Dikio E. D. (2017). Conductance of 1-Butyl-3-methylimidazolium nitrate [BMIm][NO<sub>3</sub>] with N, N-dimethylformamide at T (293.15 – 323.15) K, Int. J. of Chem. and Chem. Proces. 3 (1) 23–34.
- [4] Bennett V., Ejidike I. P., Ayawei N., Wankasi D. and Dikio E. D. (2017). Synthesis, Characterization and Conductivity Study of 1-Methyl-3-Phenylimidazolium Iodide [MPhIm][I] at T (293.15-323.15) K. Res. J. of Pharm., Bio. and Chem. Sci. 8 (6), 365-374.
- [5] Bennett V., Dikio C. W., Angaye S. S., Dikio E. D., Bahadur I., Ebenso E. E. (2016). Interactions of 1-butyl-3-methylimidazolium hexafluorophosphate With N, N-dimethylformamide: Density and Viscosity Measurements J. of Mol. Lqs. 219, 661–666.
- [6] Zhigang L. B. C., Yoon-Mo K., Douglas R. M. (2017), Introduction: Ionic Liquids. Chem. Rev. 117, 10, 6633–6635.
- [7] Fraser J. K. and MacFarlane D. R. (2009). Phosphonium-Based Ionic Liquids: An Overview" Aust. J. of Chem. 62 (4): 309–321.
- [8] Luo J., Conrad O. and Vankelecom I. F. J. (2012). Physicochemical properties of phosphonium-based and ammonium-based protic ionic liquids. J. of Mater. Chem. 22 (38): 20574–20579.
- [9] Tripathi A. K. (2021). Ionic liquid-based solid electrolytes (ionogels) for application in rechargeable lithium battery. Mater. Today Energy. 20: 100643.
- [10] Fatemeh M. (2013) Ionic Liquids - New Aspects for the Future ISBN978-953-51-0937-2 DOI: 10.5772/53646.



- [11] Bara, J. E.; Carlisle, T. K.; Gabriel, C. J.; Camper, D.; Finotello, A.; Gin, D. L.; Nobel, R. D. Guide to CO<sub>2</sub> Separations in Imidazolium-Based Room-Temperature Ionic Liquids *Ind. Eng. Chem. Res.* 2009, 48, 2739–2751 DOI: 10.1021/ie8016237.
- [12] Lei, Z.; Dai, C.; Zhu, J.; Chen, B. Extractive Distillation with Ionic Liquids: A Review *AIChE J.* 2014, 60, 3312–3329 DOI: 10.1002/aic.14537.
- [13] Mai, N. L.; Koo, Y. M. Computer-Aided Design of Ionic Liquids for High Cellulose Dissolution *ACS Sustainable Chem. Eng.* 2016, 4, 541–547 DOI: 10.1021/acssuschemeng.5b00958.
- [14] Rojas, M. F.; Bernard, F. L.; Aquino, A.; Borges, J.; Dalla Vecchia, F.; Menezes, S.; Ligabue, R.; Einloft, S. Poly(ionic liquid)s as Efficient Catalyst in Transformation of CO<sub>2</sub> to Cyclic Carbonate *J. Mol. Catal. A: Chem.* 2014, 392, 83– 88 DOI: 10.1016/j.molcata.2014.05.007.
- [15] Davis J. H. and Fox P. A. (2003). From curiosity to commodities: ionic liquids begin the transition. *Chem Comm.* 11, 1209-1212.
- [16] Cinzia Chiappe, Marco Malvaldi, Christian Silvio Pomelli (2009) Ionic liquids: Solvation ability and polarity. *Pure and Applied Chemistry* 81 (4): 767-776 DOI: 10.1351/PAC-CON-08-09-08.
- [17] Suojlang Z., Ning S., Xuezhong H., Xingmel L., Xiangping Z. (2006). Physical properties of ionic liquids: Database and evaluation, China Acad, Sci, Beijing 10080.
- [18] Abbot M. M. and Vanness H. C. (1976). *Theories and Problems of Thermodynamics*. SI Ed. McGraw-Hill, Inc, 251259.
- [19] Mahajan A. R. and Mirgane S. R. (2013). Study of molecular interactions in binary liquid mixtures of n-alkanes with higher alkanol: An ultrasonic, volumetric and viscometric study. *Ind. J. of Chem.- Section A* 52A, 624-629.
- [20] Dikio E. D., Vilazi G., Ngoyi T. P. (2013). Density, dynamic and derived properties of binary mixtures of m-xylene, o-xylene and p-xylene, with pyridine at T = 293.15, 303.15, 313.15 and 323.15K, *J. Mol. Liqs.* 177, 190-197.
- [21] Wei F., Qing Z., Jian S., Suojlang Z. (2009). Density, excess molar volume, and viscosity for the methyl methacrylate + 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid binary system at atmospheric pressure, *J. of Chem. Eng. Data* 54, 2307-2311.
- [22] Shruti T. and Shiddhart P. (2010). Temperature dependent densities of mixtures of 1-Butyl-3-methylimidazoliumhexafluorophosphate+poly(ethylene glycol) *Ind. J. of Chem.* 49A, 731-735.
- [23] Bittencourt S. S., Hoga H. E.; Torres R. B. & Angelo J. V. H., (2019). Thermodynamic properties of binary mixtures of n-butylammonium-based ionic liquids with ethanol at T=(293.15–313.15) K. *J. Therm. Anal. Calor.* Vol. 135, 2519-2539.
- [24] Redlich O. and Kister A. T. (1948). Thermodynamics of nonelectrolyte solutions, algebraic representation of thermodynamic properties and the classification of solutions. *Ing. Eng. Chem.* 40, 345-348.
- [25] Canongia L. J. N., Cordeiro T. C., Esperança J. M. S. S., Guedes H. J. R., Huq S., Rebelo L. P. N., Seddon K. R. (2005). On the critical temperature, normal boiling point, and vapor pressure of ionic liquids *J. Phys. Chem. B* 109, 3519-3525.
- [26] Jereena S. S. (2014). *Ultrasonic, Volumetric and Viscometric Studies of Binary Mixtures of N-Alkyl Anilines at Different Temperatures*, PhD Thesis, Acharya Nagarjuna University, India.
- [27] Reed T. M. and Taylor T. E. (1959). Viscosities of liquid mixtures. *J. of Phys. Chem.* 63, 58.