JOURNAL OF CHEMICAL & ENGINEERING DATA

Article

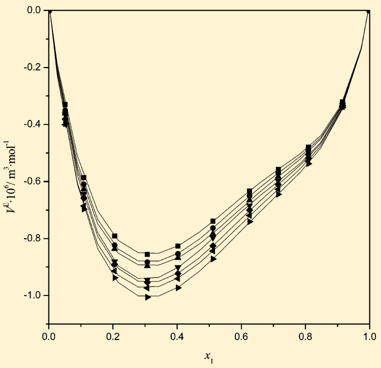
pubs.acs.org/jced

Volumetric and Acoustic Properties of Binary Mixtures of the Ionic Liquid 1-Butyl-3-methylimidazolium Tetrafluoroborate [bmim][BF_4] with Alkoxyalkanols at Different Temperatures

Amalendu Pal* and Bhupinder Kumar

Department of Chemistry, Kurukshetra University, Kurukshetra-136 119, India

ABSTRACT: Densities, ρ, and speeds of sound, u, of the solutions of the room temperature ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4] in ethylene glycol monomethyl ether (EGMME), diethylene glycol monomethyl ether (di-EGMME), and triethylene glycol monomethyl ether (tri-EGMME) have been measured over the whole composition range at T = (288.15 to 318.15) K. The density values have been used to calculate excess molar volumes, V^E, whereas speeds of sound results were used to calculate excess isentropic compressibilities, $K_{S,m}^E$. Excess properties are fitted to the Redlich–Kister polynomial equation to obtain the binary coefficients and the standard errors. The data obtained were analyzed to determine the effect of (i) temperature and (ii) the alkyl chain length of the alkoxyalkanols. Also, these results have been interpreted in terms of molecular interactions occurring in the binary mixtures of the present study.



■ INTRODUCTION

Room temperature ionic liquids (RTILs) are salts that are liquids at or near room temperature and are excellent solvents for both polar and nonpolar organic substances. They exhibit many interesting properties such as a negligible vapor pressure, low melting point, suitable viscosity, and stability up to high temperature. Due to their nonvolatile, nonflammable, thermally stable, and recyclable nature and favorable solvation properties, RTILs have been suggested as potentially green replacements for conventional volatile organic solvents, and hence these have been the focus of many scientific investigations.[1−20] Despite their importance and interest, detailed knowledge of the thermodynamic behavior of the mixtures of ionic liquids (ILs) with organic solvents, which is of immense importance for the design of any technological processes, is still limited. On the other hand, alkoxyalkanols which are amphiphilic organic solvents have been used in many chemical processes. To understand the mixing behavior and provide accurate physicochemical data for various industrial applications, thermodynamic studies on the binary mixtures of RTILs in the organic solvents are of great importance. Further, the addition of a cosolvent can improve the properties of ILs for their effective use in various chemical processes. In recent years, a number of workers have determined the various thermodynamic properties of binary mixtures of ILs in organic solvents;[21−26] 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4] was selected for this study. It is the most commonly used IL for which some physicochemical properties with other organic solvents have been studied. Its density, speed of sound, and heat capacity in organic solvents,[27−29] volumetric and viscosity study in organic solvents,[30] and thermophysical properties in organic solvents[31,32] have been reported. Volumetric properties of binary liquid mixtures containing alkoxyalkanols have also been studied to understand the nature and extent of various intermolecular interactions present in mixtures.[33]

In present work, we report density and speed of sound measurements on the mixture of 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF_4] with ethylene glycol monomethyl ether (EGMME), diethylene glycol monomethyl ether (di-EGMME), and triethylene glycol monomethyl (tri-EGMME) ether at temperatures T = (288.15 to 318.15) K. The excess molar volume, V^E, and isentropic compressibilities, $K_{S,m}{}^E$, were reported for every system investigated. The results are discussed in terms of the molecular interactions between the IL and the alkoxyalkanols. Also, the composition and temperature dependence of the excess molar properties with an increase in the alkyl chain length of the alkoxyalkanols have been analyzed.

■ EXPERIMENTAL SECTION

Materials. The IL, 1-butyl-3-methylimidazolium tetrafluoroborate (>98.0 mol %), was purchased from Merck–Schuchardt. The IL was dried and degassed under vacuum at 60 °C for few days to remove moisture. A Karl–Fischer analysis of the samples indicated that the water content was reduced to less than 100 ppm. Analytical grade ethylene glycol monomethyl ether (EGMME) from SD Fine Chemicals, diethylene glycol monomethyl ether (di-EGMME) (>98 mol %) from Merck–Schuchardt, and triethylene glycol monomethyl ether (tri-EGMME) (>97 mol %) for GC from Fluka were obtained. All of the organic liquids were used after drying

Received: January 27, 2011
Accepted: February 1, 2012
Published: February 13, 2012

Table 1. Experimental Densities ρ^*, Speeds of Sound u^*, and Isobaric Heat Capacities $C_{p,\mathrm{m}}$ of Pure Components

		$\rho^*\cdot10^{-3}$/kg·m^{-3}		u^*/m·s^{-1}		$C_{p,\mathrm{m}}$
component	T/K	exptl.	lit.	exptl.	lit.	J·K^{-1}·mol^{-1}
[bmim][BF$_4$]	288.15	1.206508		1589	1591.1[38]	360.2[39]
	293.15	1.202952	1.2046[34] 1.19571[35]	1577	1578.0[38]	362.5[39]
	298.15	1.199387	1.19207[35] 1.19[36]	1565	1565.1[38]	364.8[39]
	303.15	1.195818	1.1984[34] 1.18837[35]	1554	1555.5[28] 1552.6[38]	367.2[39]
	308.15	1.192266	1.1954[34] 1.18472[35]	1542	1543.9[28] 1540.3[38]	369.5[39]
	313.15	1.188723	1.1922[34] 1.18143[35]	1531	1532.5[28] 1528.5[38]	371.9[39]
	318.15	1.185171	1.1890[34] 1.19[37]	1520	1521.2[28] 1516.5[38]	374.3[39]
EGMME	288.15	0.969794	0.96926[40]	1380		173.68[a]
	293.15	0.965063	0.96458[41]	1367		175.04[a]
	298.15	0.960447	0.96024[41] 0.960978[42]	1351		176.40[43]
	303.15	0.955825	0.95545[41]	1337		177.76[a]
	308.15	0.951214	0.95129[40]	1321		179.12[a]
	313.15	0.946562		1304		180.48[a]
	318.15	0.941864		1287		181.84[a]
di-EGMME	288.15	1.024599		1451		268.38[a]
	293.15	1.020202	1.0196[44]	1434	1432.37[47]	269.74[a]
	298.15	1.015787	1.0154[44] 1.01591[45]	1416	1415.98[46] 1415.21[47]	271.10[48]
	303.15	1.011360	1.0112[44]	1399	1397.93[47]	272.46[a]
	308.15	1.006918	1.0065[44]	1382		273.82[a]
	313.15	1.002467	1.0022[44]	1366		275.18[a]
	318.15	0.998009		1349		276.54[a]
tri-EGMME	288.15	1.050097		1470		355.28[a]
	293.15	1.045749	1.0476[49]	1452		356.64[a]
	298.15	1.041315	1.0414[50]	1436		358.0[51]
	303.15	1.036842	1.0387[49]	1421		359.36[a]
	308.15	1.032267	1.03262[52]	1408		360.72[a]
	313.15	1.027763	1.02908[52]	1393		362.08[a]
	318.15	1.023296		1376		363.44[a]

[a] By the group additive method.

over the 0.4 nm molecular sieves and under vacuum at ambient conditions. The purity of the compounds was also monitored by a comparison of density and speed of sound measurements with the literature data[28,34−52] as shown in Table 1.

Density and Speed of Sound Measurements. The densities and speeds of sound of the pure liquids and their binary mixtures were measured with an Anton Paar (model DSA 5000) vibrating-tube densimeter. Both the speed of sound and the density are extremely sensitive to temperature, so it was controlled to ± $1\cdot10^{-2}$ K by a built-in solid state thermostat. Before each series of measurements, the densimeter was calibrated with doubly distilled, degassed water and with dry air at atmospheric pressure. The reproducibility of the instrument corresponded to a precision in density and speed of sound measurements of $1\cdot10^{-3}$ kg·m^{-3} and $1\cdot10^{-2}$ m·s^{-1}. The uncertainty of the density and speed of sound estimates was found to be within ± $5\cdot10^{-3}$ kg·m^{-3} and lower than ± 2 m·s^{-1}, respectively. The reproducibility of the results was confirmed by performing the measurements in triplicate.

The mixtures were prepared by mass and were kept in airtight stoppered glass bottles to minimize the absorption of atmospheric moisture and CO$_2$. Binary mixtures were prepared by mass, using an A&D Co. limited electronic balance (Japan, model GR-202) with a precision of ± 0.01 mg. The probable error in the mole fraction was estimated to be less than ± $1\cdot10^{-4}$. All molar quantities were based on the International Union of Pure and Applied Chemistry (IUPAC) relative atomic mass table.[53]

RESULTS AND DISCUSSION

Experimental density, ρ, and speed of sound, u, results of binary mixtures of 1-butyl-3-methylimidazolium tetrafluoroborate + alkoxyalkanols as a function of mole fraction, x_1, of 1-butyl-3-methylimidazolium tetrafluoroborate ($0 \le x_1 \le 1$) at different temperatures are listed in Table 2.

The excess molar volumes, V^E, were calculated by using the following equation

$$V^{\mathrm{E}} = \sum_{i=1} x_i M_i(\rho^{-1} - \rho_i^{*-1}) \tag{1}$$

Table 2. Density, ρ, and Speed of Sound, u, of [bmim][BF_4] (1) + EGMME (2), Di-EGMME (2), or Tri-EGMME (2) at Different Temperatures

	T/K = 288.15		T/K = 293.15		T/K = 298.15		T/K = 303.15		T/K = 308.15		T/K = 313.15		T/K = 318.15	
x_1	$\rho\cdot10^{-3}$ / $kg\cdot m^{-3}$	u / $m\cdot s^{-1}$	$\rho\cdot10^{-3}$ / $kg\cdot m^{-3}$	u / $m\cdot s^{-1}$	$\rho\cdot10^{-3}$ / $kg\cdot m^{-3}$	u / $m\cdot s^{-1}$	$\rho\cdot10^{-3}$ / $kg\cdot m^{-3}$	u / $m\cdot s^{-1}$	$\rho\cdot10^{-3}$ / $kg\cdot m^{-3}$	u / $m\cdot s^{-1}$	$\rho\cdot10^{-3}$ / $kg\cdot m^{-3}$	u / $m\cdot s^{-1}$	$\rho\cdot10^{-3}$ / $kg\cdot m^{-3}$	u / $m\cdot s^{-1}$
[bmim][BF_4] (1) + EGMME (2)														
0.0509	1.000596	1411	0.996158	1394	0.991715	1378	0.987145	1361	0.982765	1344	0.978381	1328	0.973683	1311
0.1092	1.030064	1438	1.025737	1422	1.021410	1406	1.017071	1391	1.012723	1375	1.008485	1359	1.004012	1343
0.2052	1.068448	1474	1.064328	1460	1.060084	1446	1.056148	1431	1.051854	1415	1.047681	1400	1.043461	1383
0.3071	1.099906	1500	1.095866	1486	1.091755	1472	1.087958	1457	1.083794	1443	1.079713	1430	1.075708	1415
0.4025	1.123356	1521	1.119424	1508	1.115423	1494	1.111592	1480	1.107663	1467	1.103682	1453	1.099790	1440
0.5116	1.145198	1539	1.141378	1527	1.137545	1514	1.133655	1501	1.129902	1488	1.126044	1475	1.122250	1461
0.6257	1.164110	1553	1.160347	1542	1.156586	1530	1.152840	1517	1.149096	1505	1.145367	1492	1.141633	1479
0.7153	1.176883	1565	1.173169	1554	1.169467	1542	1.165771	1530	1.162087	1517	1.158411	1505	1.154739	1492
0.8088	1.188610	1574	1.184963	1563	1.181307	1551	1.177657	1539	1.174007	1526	1.170376	1514	1.166724	1502
0.9155	1.199861	1582	1.196253	1571	1.192640	1560	1.189035	1548	1.185433	1536	1.181838	1525	1.178227	1513
[bmim][BF_4] (1) + Di-EGMME (2)														
0.0308	1.035125	1461	1.030688	1445	1.026512	1428	1.022021	1411	1.017503	1395	1.013137	1378	1.008896	1362
0.1053	1.059035	1490	1.054733	1473	1.050613	1457	1.046355	1441	1.042003	1425	1.037685	1409	1.033445	1393
0.2065	1.086982	1514	1.082851	1499	1.078494	1483	1.074577	1468	1.070558	1453	1.066486	1437	1.062001	1422
0.3137	1.110842	1533	1.106708	1517	1.102508	1503	1.098601	1489	1.094685	1474	1.090915	1460	1.086381	1447
0.4002	1.126769	1544	1.122558	1531	1.118579	1518	1.114549	1504	1.110652	1490	1.107008	1477	1.102747	1464
0.5035	1.143125	1559	1.138991	1546	1.135225	1533	1.131183	1519	1.127295	1506	1.123645	1493	1.119786	1480
0.6083	1.158137	1568	1.154165	1555	1.150519	1543	1.146730	1530	1.142953	1517	1.139191	1505	1.135506	1494
0.7023	1.170822	1575	1.167068	1563	1.163463	1551	1.160076	1539	1.156362	1526	1.152492	1514	1.148843	1503
0.8291	1.187123	1580	1.183253	1572	1.179998	1560	1.176923	1546	1.173243	1534	1.169381	1523	1.165676	1512
0.9381	1.199908	1583	1.196014	1574	1.192920	1563	1.189623	1552	1.185913	1540	1.182201	1529	1.178569	1519
[bmim][BF_4] (1) + Tri-EGMME (2)														
0.0240	1.056872	1484	1.052518	1466	1.048151	1450	1.043758	1435	1.039370	1421	1.034901	1406	1.030535	1390
0.1070	1.076656	1510	1.072568	1492	1.068364	1475	1.064168	1458	1.060132	1444	1.055734	1431	1.051512	1415
0.2241	1.099666	1541	1.095948	1519	1.091873	1503	1.087794	1488	1.083757	1475	1.079586	1461	1.075427	1447
0.3275	1.118288	1555	1.114498	1539	1.110478	1524	1.106458	1509	1.102438	1494	1.098413	1483	1.094374	1468
0.4285	1.135349	1564	1.131412	1550	1.127421	1533	1.123478	1519	1.119544	1507	1.115625	1493	1.111735	1480
0.5067	1.147584	1570	1.143602	1555	1.139641	1541	1.135768	1528	1.131914	1516	1.128038	1503	1.124254	1490
0.6282	1.164468	1575	1.160738	1561	1.156883	1548	1.153121	1534	1.149372	1523	1.145628	1511	1.141801	1500
0.7072	1.174318	1581	1.170785	1568	1.166998	1555	1.163333	1543	1.159631	1530	1.155929	1518	1.151998	1506
0.8256	1.188107	1584	1.184682	1572	1.181027	1560	1.177388	1548	1.173678	1536	1.170128	1524	1.166141	1513
0.9130	1.197842	1585	1.194256	1573	1.190695	1560	1.186998	1549	1.183357	1538	1.179904	1527	1.175997	1516

where ρ is the density and x_i and M_i are the mole fraction and molar mass of component i in the mixture, respectively.

The isentropic compressibility, κ_S, and the molar isentropic compressibility, $K_{S,m}$, have been calculated from the relations

$$\kappa_S = (\rho\cdot u^2)^{-1} = V(M\cdot u^2)^{-1} \tag{2}$$

$$K_{S,\mathrm{m}} = -(\partial V/\partial p)_S = V\cdot\kappa_S = \sum x_iM_i/(\rho\cdot u)^2 \tag{3}$$

where V is the molar volume.

The excess molar quantities were calculated from

$$K_{S,\mathrm{m}}^{\mathrm{E}} = K_{S,\mathrm{m}} - K_{S,\mathrm{m}}^{\mathrm{id}} \tag{4}$$

where:

$$K_{S,\mathrm{m}}^{\mathrm{id}} = \sum x_i[K_{S,i}{}^* - TA_{P,i}{}^*\{(\sum x_iA_{P,i}{}^*/\sum x_iC_{P,i}{}^*) - (A_{P,i}{}^*/C_{P,i}{}^*)\}] \tag{5}$$

where ρ and ρ^* are the density of the mixture and the density of the pure components and x_i and M_i are the mole fraction and molar mass of component i in the mixture, respectively. The $A_{P,i}{}^*$, is the product of the molar volume, $V_i{}^*$, and the isobaric expansivity, $\alpha_{P,i}{}^*$, $C_{P,i}{}^*$, is the isobaric molar heat capacity, $K_{S,i}{}^*$, the product of the molar volume, $V_i{}^*$, and the isentropic compressibility, $\kappa_{S,i}{}^*$ and T is the temperature. The isobaric expansivity ($\alpha_{P,i}{}^*$) of IL and alkoxyalkanols was calculated from density data as given in Table 1.

The calculated values of V^{E} and $K_{S,\mathrm{m}}^{\mathrm{E}}$ of the binary mixtures, at each investigated temperature, were fitted to a Redlich–Kister type polynomial equation:

$$Y^{\mathrm{E}} = x_1x_2\sum_{i=0} a_i(x_1 - x_2)^i \tag{6}$$

The values of coefficients a_i for all of the mixtures are listed in Table 3, along with the standard deviation, $\sigma(Y^{\mathrm{E}})$, calculated using the relation

$$\sigma(Y^{\mathrm{E}}) = [\sum\{Y_{\mathrm{exptl}}^{\mathrm{E}} - Y_{\mathrm{calcd}}^{\mathrm{E}}\}^2/(p - n)]^{1/2} \tag{7}$$

where p is the total number of experimental points and n is the number of parameters. Y^{E} stands for V^{E} or $K_{S,\mathrm{m}}^{\mathrm{E}}$. Results on V^{E} and $K_{S,\mathrm{m}}^{\mathrm{E}}$ are shown graphically in Figures 1 to 6.

For all mixtures, V^{E} is negative over the whole mole fraction range and at all temperatures. Figures 1 to 6 show the values of the excess molar volume and excess molar isentropic compressibility. The negative V^{E} indicates that a more efficient packing or attractive interaction occurred between the IL and the amphiphile molecules which results in a contraction in

Table 3. Redlich–Kister Coefficients, a_i, and Standard Deviations, $\sigma(Y^E)$ (eq 6) for the Binary Mixtures at Different Temperatures

	T/K	a_0	a_1	a_2	a_3	a_4	σ
			[bmim][BF$_4$] (1) + EGMME (2)				
$V^E \cdot 10^6/\mathrm{m^3 \cdot mol^{-1}}$	288.15	−3.002	1.809	−2.171	−0.707	−1.559	0.003
	293.15	−3.097	1.875	−2.188	−0.579	−1.729	0.002
	298.15	−3.169	1.843	−2.107	−0.398	−1.942	0.003
	303.15	−3.245	2.080	−2.688	−0.658	−1.113	0.003
	308.15	−3.350	2.029	−2.297	−0.455	−1.762	0.003
	313.15	−3.424	1.966	−2.338	−0.161	−1.939	0.003
	318.15	−3.536	2.103	−2.438	−0.290	−1.636	0.003
$K_{S,m}^E/\mathrm{mm^3 \cdot mol^{-1} \cdot MPa^{-1}}$	288.15	−12.049	7.695	−8.010	4.371		0.073
	293.15	−12.730	7.630	−7.243	2.048		0.072
	298.15	−13.456	8.478	−7.955			0.085
	303.15	−13.982	8.390	−7.510			0.128
	308.15	−14.861	8.765	−6.224			0.128
	313.15	−15.799	9.595	−7.225			0.112
	318.15	−16.662	10.311	−6.691			0.104
			[bmim][BF$_4$] (1) + Di-EGMME (2)				
$V^E \cdot 10^6/\mathrm{m^3 \cdot mol^{-1}}$	288.15	−3.270	5.503	−2.966	−3.213	2.129	0.003
	293.15	−3.181	5.442	−3.906	−2.589	3.960	0.003
	298.15	−3.309	5.289	−3.056	−2.982	1.383	0.003
	303.15	−3.282	5.296	−4.987	−3.677	3.178	0.003
	308.15	−3.345	5.455	−5.628	−3.756	4.483	0.003
	313.15	−3.542	5.864	−4.978	−4.033	4.118	0.003
	318.15	−3.604	5.303	−4.161	−2.837	2.752	0.002
$K_{S,m}^E/\mathrm{mm^3 \cdot mol^{-1} \cdot MPa^{-1}}$	288.15	−13.023	8.058	−8.268	5.966	7.869	0.130
	293.15	−13.985	8.425	−6.311	2.914		0.128
	298.15	−15.061	9.412	−6.922			0.104
	303.15	−15.936	10.024	−7.676			0.104
	308.15	−16.891	9.968	−7.914	2.438		0.101
	313.15	−18.167	11.232	−7.814			0.095
	318.15	−19.448	10.745	−8.450	1.972		0.086
			[bmim][BF$_4$] (1) + Tri-EGMME (2)				
$V^E \cdot 10^6/\mathrm{m^3 \cdot mol^{-1}}$	288.15	−6.723	1.169	1.950	3.563	−6.732	0.003
	293.15	−6.763	1.292	0.119	3.552	−4.416	0.001
	298.15	−6.841	1.417	−0.124	3.510	−4.447	0.001
	303.15	−6.981	1.379	−0.416	3.949	−4.142	0.002
	308.15	−7.164	1.364	−0.403	4.726	−4.740	0.003
	313.15	−7.325	1.468	−0.417	4.371	−4.922	0.002
	318.15	−7.511	1.574	0.371	5.020	−5.600	0.002
$K_{S,m}^E/\mathrm{mm^3 \cdot mol^{-1} \cdot MPa^{-1}}$	288.15	−19.586	11.362	−9.081	8.166		0.188
	293.15	−20.547	10.990	−8.052	7.184		0.238
	298.15	−21.258	10.601	−8.428	8.728		0.261
	303.15	−22.101	11.100	−8.269	6.871		0.307
	308.15	−22.978	11.073	−7.790	7.163		0.251
	313.15	−24.066	12.143	−9.135	6.957		0.250
	318.15	−25.630	12.318	−9.605	9.091		0.261

volume. As temperature increases, V^E decreases for all of the systems. For the investigated systems at any particular temperature, the V^E values decrease in the order: EGMME< di-EGMME< tri-EGMME. The minimum in V^E shifts from $x_1 = 0.30$ for EGMME to $x_1 = 0.40$ for tri-EGMME. In fact, we observe similar characteristics for V^E as in the mixture of [bmim][PF$_6$] with di-EGMME[54] but with a marked decrease in the values of V^E at lower temperatures here. Further, this behavior may be compared with the results for [bmim][BF$_4$] with ethylene glycol (EG):[55] a large negative value of V^E for alkoxyethanol is evident here, and the behavior is indifferent from EG. Figures 1 to 3 show that V^E decreases with the increase of the polar group of EGMME. That is, the strength of the interaction increases due to increased molecular weight and size of the alkoxyethanol molecules.

For all of the mixtures studied, $K_{S,m}^E$ (Figures 4 to 6) is negative over the entire range of composition and at all of the temperatures and shows a minimum in the sequence EGMME < di-EGMME < tri-EGMME. Also, the curves are symmetrical, the position of the minimum being at $x_1 > 0.2$. As the concentrations of the IL increase and large portions of the solvent alkoxyethanol molecules are solvated, the amount of bulk solvent decreases, causing a decrease in the compressibility. The negative $K_{S,m}^E$ values of IL in alkoxyethanols also attributed to the strong interactions due to the solvation of the ions in these solvents. Negative values of $K_{S,m}^E$ mean that the

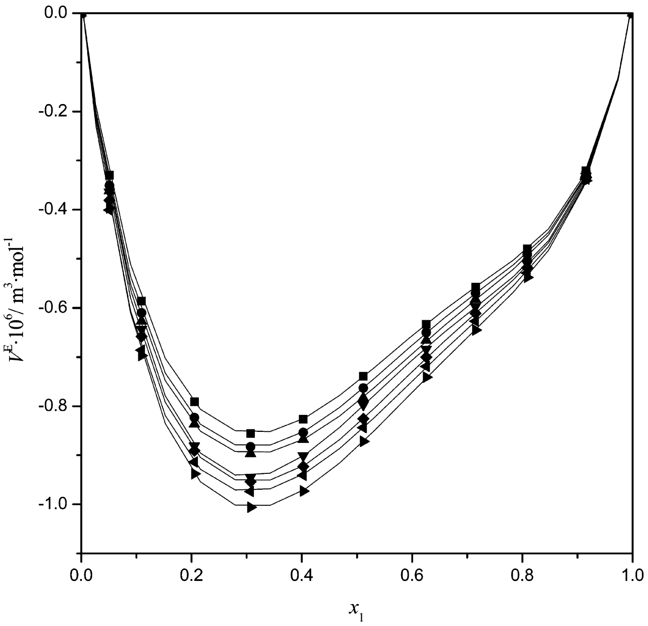


Figure 1. Excess molar volume (V^E) measured over the entire range of composition for the binary mixture of [bmim][BF_4] (1) with EGMME at ■, 288.15 K; ●, 293.15 K; ▲, 298.15 K; ▼, 303.15 K; ♦, 308.15 K; ◀, 313.15 K; ▶, 318.15 K.

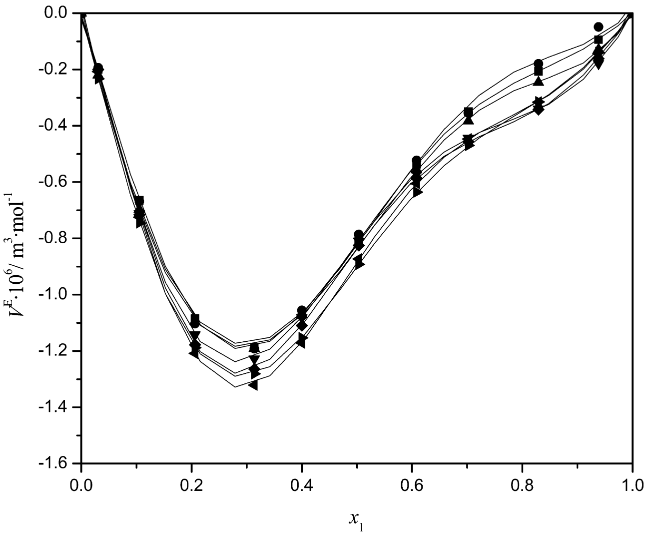


Figure 2. Excess molar volume (V^E) measured over the entire range of composition for the binary mixture of [bmim][BF_4] (1) with di-EGMME at ■, 288.15 K; ●, 293.15 K; ▲, 298.15 K; ▼, 303.15 K; ♦, 308.15 K; ◀, 313.15 K; ▶, 318.15 K.

solvent alkoxyethanol molecules around the IL are less compressible than the solvent molecules in the bulk solution, suggesting strong attractive interactions with alkoxyalkanols. The behavior of excess molar volumes seems to be consistent with a minimum value of $K_{S,m}^E$ of [bmim][BF_4] with alkoxyalkanols. The more negative V^E and $K_{S,m}^E$ values as shown in Figures 1 to 6 suggest that the interactions between the unlike molecules are strong and they increase with the introduction of the OC_2H_4 group in the alkoxyethanol. Further, the V^E and $K_{S,m}^E$ values decrease with an increase in temperature.

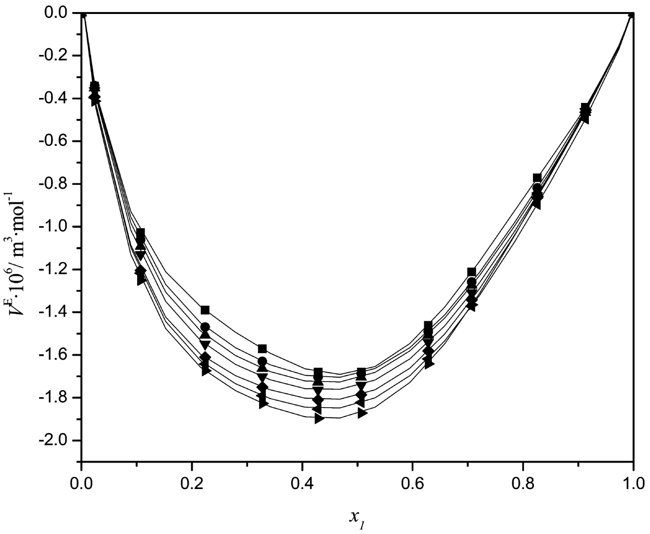


Figure 3. Excess molar volume (V^E) measured over the entire range of composition for the binary mixture of [bmim][BF_4] (1) with tri-EGMME at ■, 288.15 K; ●, 293.15 K; ▲, 298.15 K; ▼, 303.15 K; ♦, 308.15 K; ◀, 313.15 K; ▶, 318.15 K.

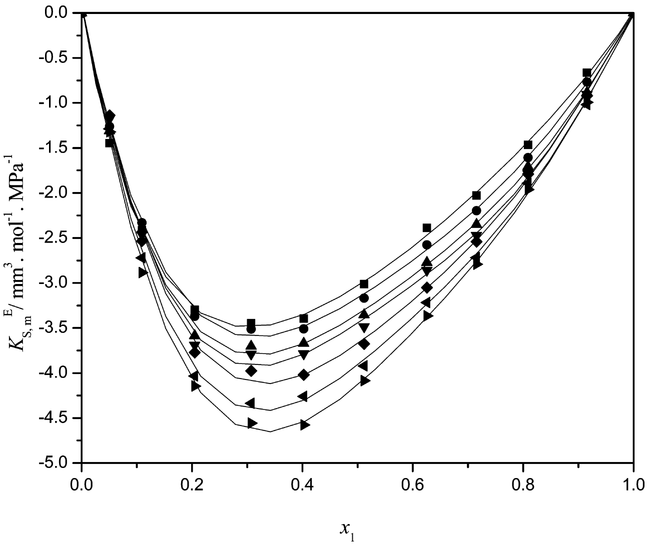


Figure 4. Excess molar isentropic compressibility ($K_{S,m}^E$) measured over the entire range of composition for the binary mixture of [bmim][BF_4] (1) with EGMME at ■, 288.15 K; ●, 293.15 K; ▲, 298.15 K; ▼, 303.15 K; ♦, 308.15 K; ◀, 313.15 K; ▶, 318.15 K.

■ CONCLUSIONS

New experimental data of density and speed of sound for the binary mixture of [bmim][BF_4] + alkoxyalkanols were measured over the whole composition range at atmospheric pressure from (288.15 to 318.15) K, from which the excess molar volumes V^E and excess molar isentropic compressibilities $K_{S,m}^E$ were calculated and the Redlich–Kister polynomial equation was applied successfully for the correlation of these excess properties. The estimated coefficients and standard deviation values were also presented. It was found that the excess molar volumes are negative over the whole composition range. The V^E values in these mixtures become more negative with the introduction of the OC_2H_4 group in the alkoxyalkanol molecule and are in the order EGMME > di-EGMME > tri-EGMME. It suggests very strong specific [bmim][BF_4]–

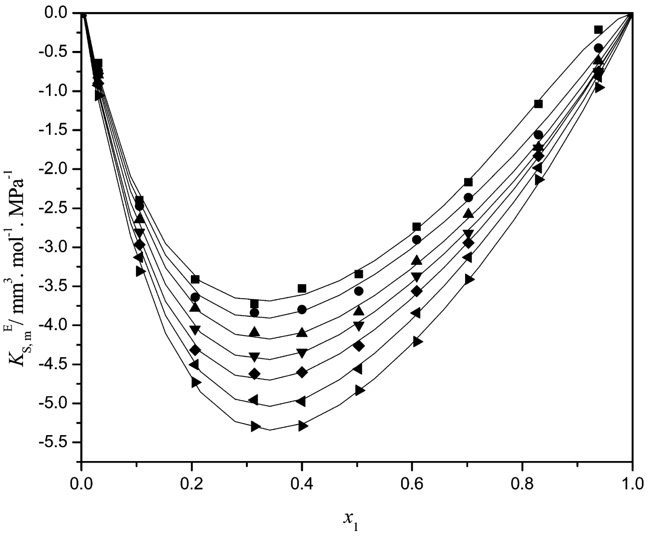


Figure 5. Excess molar isentropic compressibility ($K^{E}_{S,m}$) measured over the entire range of composition for the binary mixture of [bmim][BF_4] (1) with di-EGMME at ■, 288.15 K; ●, 293.15 K; ▲, 298.15 K; ▼, 303.15 K; ♦, 308.15 K; ◀, 313.15 K; ▶, 318.15 K.

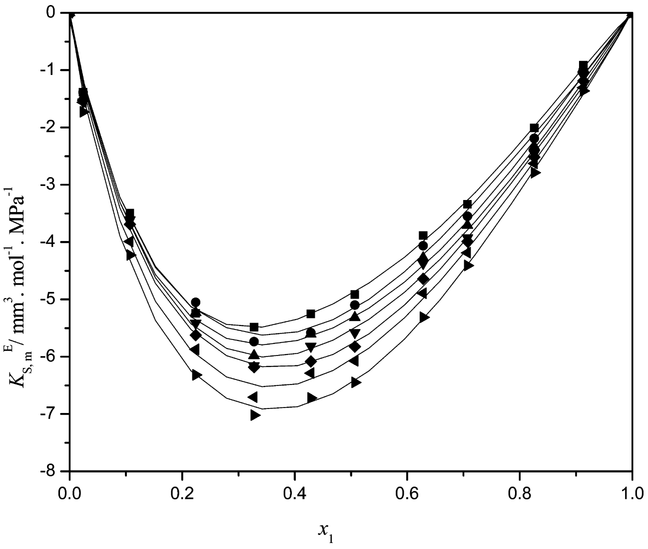


Figure 6. Excess molar isentropic compressibility ($K^{E}_{S,m}$) measured over the entire range of composition for the binary mixture of [bmim][BF_4] (1) with tri-EGMME at ■, 288.15 K; ●, 293.15 K; ▲, 298.15 K; ▼, 303.15 K; ♦, 308.15 K; ◀, 313.15 K; ▶, 318.15 K.

alkoxyalkanol interaction. $K^{E}_{S,m}$ is also negative over the whole composition range, and it increases as the increase in the chain length of alkoxyalkanol. The negative $K^{E}_{S,m}$ of [bmim][BF_4] with alkoxyalkanols was also attributed to the strong attractive interactions due to the solvation of the ions in the solvents. Both V^E and $K^{E}_{S,m}$ increase with the increase in temperature for all the mixtures.

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: +91 1744-239765. Fax: +91 1744-238277. E-mail address: palchem@sify.com.

Funding

Financial support for this project (Grant No. SR/S1/PC-55/2008) by the Government of India through the Department of Science and Technology (DST) is gratefully acknowledged.

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Zakrzewska, M. E.; Bogel-Łukasik, E.; Bogel-Łukasik, R. Solubility of carbohydrates in ionic liquids. *Energy Fuels* **2010**, *24*, 737−745.

(2) Bogel-Łukasik, R.; Matkowska, D.; Zakrzewska, M. E.; Bogel-Łukasik, E.; Hofman, T. The phase envelopes of alternative solvents (ionic liquids, CO_2) and building blocks of biomass origin (lactic acid, propionic acid). *Fluid Phase Equilib.* **2010**, *295*, 177−185.

(3) Bogel-Łukasik, E.; Santos, S.; Bogel-Łukasik, R.; Nunes da Ponte, M. Selectivity enhancement in the catalytic heterogeneous hydrogenation of limonene in supercritical carbon dioxide by an ionic liquid. *J. Supercrit. Fluids* **2010**, *54*, 210−217.

(4) Zaitsau, D. H.; Kabo, G. J.; Strechan, A. A.; Paulechka, Y. U.; Tschersich, A.; Verevkin, S. P.; Heintz, A. Experimental vapor pressures of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imides and a correlation scheme for estimation of vaporization enthalpies of ionic liquids. *J. Phys. Chem. A* **2006**, *110*, 7303−7306.

(5) Earle, M. J.; Esperanca, J. M. S. S.; Gilea, M. A.; Lopes, J. N. C.; Rebelo, L. P. N.; Magee, J. W.; Seddon, K. R.; Widergren, J. A. The distillation and volatility of ionic liquids. *Nature* **2006**, *439*, 831−834.

(6) Zakrzewska, M. E.; Bogel-Łukasik, E.; Bogel-Łukasik, R. Ionic liquid-mediated formation of 5-hydroxymethylfurfural-A promising biomass-derived building block. *Chem. Rev.* **2011**, *111*, 397−417.

(7) Heintz, A.; Lehmann, J. K.; Wertz, C. Thermodynamic properties of mixtures containing ionic liquids. 3. liquid−liquid equilibria of binary mixtures of 1-ethyl-3-methylimidazolium Bis-(trifluoromethylsulfonyl)imide with propan-1-ol, butan-1-ol, and pentan-1-ol. *J. Chem. Eng. Data* **2003**, *48*, 472−474.

(8) Zhang, J.; Wu, W.; Jiang, T.; Gao, H.; Liu, Z.; He, J.; Han, B. Conductivities and viscosities of the ionic liquid [bmim][PF_6] + water + ethanol and [bmim][PF_6] + water + acetone ternary mixtures. *J. Chem. Eng. Data* **2003**, *48*, 1315−1317.

(9) Forte, A.; Lukasik, E. B.; Lukasik, R. B. Miscibility phenomena in systems containing polyhydroxy alcohols and ionic liquids. *J. Chem. Eng. Data* **2011**, in press.

(10) Xu, H.; Zhao, D.; Xu, P.; Liu, F.; Gao, G. Conductivity and viscosity of 1-allyl-3-methyl-imidazolium chloride + water and + ethanol from 293.15 to 333.15 K. *J. Chem. Eng. Data* **2005**, *50*, 133−135.

(11) Vasiltsova, T. V.; Verevkin, S. P.; Bich, E.; Heintz, A.; Bogel-Lukasik, R.; Domanska, U. Thermodynamic properties of mixtures containing ionic liquids. Activity coefficients of ethers and alcohols in 1-methyl-3-ethylimidazolium bis(trifluoromethyl-sulfonyl)imide using the transipiration method. *J. Chem. Eng. Data* **2005**, *50*, 142−148.

(12) Zafarani-Moattar, M. T.; Shekaari, H. Volumetric and speed of sound of ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate with acetonitrile and methanol at T = (298.15 to 318.15) K. *J. Chem. Eng. Data* **2005**, *50*, 1694−1699.

(13) Harris, K. R.; Kanakubo, M.; Woolf, L. A. Temperature and pressure dependence of the viscosity of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate. *J. Chem. Eng. Data* **2005**, *50*, 1777−1782.

(14) Wang, J.; Zhu, A.; Zhao, Y.; Zhuo, K. Excess molar volumes and excess logarithm viscosities for binary mixtures of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate with some organic compounds. *J. Solution Chem.* **2005**, *34*, 585−596.

(15) Pereiro, A. B.; Tojo, E.; Rodriguez, A.; Canosa, J.; Tojo, J. Properties of ionic liquid HmimPF_6 with carbonates, ketones and alkyl acetates. *J. Chem. Thermodyn.* **2006**, *38*, 651−661.

(16) Pereiro, A. B.; Tojo, E.; Rodriguez, A.; Canosa, J.; Tojo, J. Hmim PF_6 ionic liquid that separates the azeotropic mixture ethanol + heptanes. *Green Chem.* **2006**, *8*, 307−310.

(17) Zafarani-Moattar, M. T.; Shekaari, H. Volumetric and compressibility behavior of ionic liquid, 1-*n*-butyl-3-methylimidazolium hexafluorophosphate and tetrabutylammonium hexafluorophosphate in organic solvents at $T = 298.15$ K. *J. Chem. Thermodyn.* **2006**, *38*, 624−633.

(18) Pereiro, A. B.; Rodríguez, A. Thermodynamic properties of ionic liquids in organic solvents from (293.15 to 303.15) K. *J. Chem. Eng. Data* **2007**, *52*, 600−608.

(19) Pereiro, A. B.; Rodríguez, A. Study on the phase behavior and thermodynamic properties of ionic liquids containing imidazolium cation with ethanol at several temperatures. *J. Chem. Thermodyn.* **2007**, *39*, 978−989.

(20) Zhong, Y.; Wang, H.; Diao, K. Densities and excess volumes of binary mixtures of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate with aromatic compound at T = (298.15 to 313.15) K. *J. Chem. Thermodyn.* **2007**, *39*, 291−296.

(21) Li, Y.; Ye, H.; Zeng, P.; Qi, F. Volumetric properties of binary mixtures of the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate with aniline. *J. Solution Chem.* **2010**, *39*, 219−230.

(22) Zhang, S.; Li, X.; Chen, H.; Wang, J.; Zhang, J.; Zhang, M. Determination of physical properties for the binary system of 1-ethyl-3-methylimidazolium tetrafluoroborate + H_2O. *J. Chem. Eng. Data* **2004**, *49*, 760−764.

(23) Kim, K. S.; Shin, B. K.; Lee, H.; Ziegler, F. Refractive index and heat capacity of 1-butyl-3-methylimidazolium bromide and 1-butyl-3-methylimidazolium tetrafluoroborate and vapor pressure of binary systems for 1-butyl-3-methylimidazolium bromide + trifluoroethanol and 1-butyl-3-tetrafluoroborate + trifluoroethanol. *Fluid Phase Equilib.* **2004**, *218*, 215−220.

(24) Heintz, A.; Klasen, D.; Lehmann, J. K.; Wertz, C. Excess molar volumes and liquid- liquid equilibria of the ionic liquid 1-methyl-3-octylimidazolium tetrafluoroborate mixed with butan-1-ol and pentan-1-ol. *J. Solution Chem.* **2005**, *34*, 1135−1144.

(25) Arce, A.; Rodil, E.; Soto, A. Physical and excess properties for binary mixtures of 1-methyl-3-octylimidazolium tetrafluoroborate, [Omim][BF_4], ionic liquid with different alcohols. *J. Solution Chem.* **2006**, *35*, 63−78.

(26) Shekaari, H.; Zafarani-Moattar, M. T. Osmotic coefficients of some imidazolium based ionic liquids in water and acetonitrile at temperature 318.15 K. *Fluid Phase Equilib.* **2007**, *254*, 198−203.

(27) Shekaari, H.; Zafarani-Moattar, M. T. Volumetric properties of the ionic liquids 1-butyl- 3-methylimidazolium tetrafluoroborate in organic solvents at $T = 298.15$ K. *Int. J. Thermophys.* **2008**, *29*, 534−545.

(28) Garcia-Miaja, G.; Troncoso, J.; Romani, L. Excess molar properties for binary systems of alkylimidazolium-based ionic liquids + nitromethane. Experimental results and ERAS-model calculations. *J. Chem. Thermodyn.* **2009**, *41*, 334−341.

(29) Zafarani-Moattar, M. T.; Shekaari, H. Applications of Prigogine-Flory-Patterson theory to excess molar volumes and speed of sound of 1-n-butyl-3-methylimidazolium hexafluorophosphate or 1-n-butyl-3-methylimidazolium tetrafluoroborate in methanol and acetonitrile. *J. Chem. Thermodyn.* **2006**, *38*, 1377−1384.

(30) Wang, J.; Tian, Y.; Zhuo, K. A volumetric and viscosity study for the mixtures of 1-n- butyl-3-methylimidazolium tetrafluoroborate ionic liquid with acetonitrile, dichloromethane, 2-butanone and N,N-dimethylformamide. *Green Chem.* **2003**, *5*, 618−622.

(31) Comminges, C.; Barhdadi, R.; Laurent, M.; Troupel, M. Determination of viscosity, ionic conductivity and diffusion co-efficient in some binary systems: Ionic liquids + molecular solvents. *J. Chem. Eng. Data* **2006**, *51*, 680−685.

(32) Malham, I. B.; Letellier, P.; Turmine, M. Evidence of a phase transition in water-1-butyl- 3-methylimidazolium tetrafluoroborate and water-1-butyl-2,3-dimethylimidazolium tetrafluoroborate mixtures at 298 K: Determination of the surface thermal co-efficient, $b_{T,P}$. *J. Phys. Chem. B* **2006**, *110*, 14212−14214.

(33) Singh, T.; Kumar, A. Physical and excess properties of a room temperature ionic liquid (1-methyl-3-octylimidazolium tetrafluoroborate) with n-alkoxyethanols (C_1E_m, m = 1 to 3) at T = (298.15 to 318.15) K. *J. Chem. Thermodyn.* **2008**, *40*, 417−423.

(34) Zhou, Q.; Wang, L.-S.; Chen, H.-P. Densities and viscosities of 1-butyl-3-methylimidazolium tetrafluoroborate + H_2O binary mixtures from (303.15 to 353.15) K. *J. Chem. Eng. Data* **2006**, *51*, 905−908.

(35) Huo, Y.; Xia, S.; Ma, P. Densities of ionic liquids, 1-butyl-3-methylimidazolium hexafluorophosphate and 1-butyl-3-methylimidazolium tetrafluoroborate, with benzene, acetonitrile, and 1-propanol at T = (293.15 to 343.15) K. *J. Chem. Eng. Data* **2007**, *52*, 2077−2082.

(36) Zhang, S.; Sun, N.; He, X.; Lu, X.; Zhang, X. Physical properties of ionic liquids: database and evolution. *J. Phys. Chem. Ref. Data* **2006**, *35*, 1475−1517.

(37) Kim, K.-S.; Park, S.-Y.; Choi, S.; Lee, H. Vapor pressures of the 1-butyl-3-methylimidazolium bromide + water, 1-butyl-3-methylimidazolium tetrafluoroborate + water, and 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate + water systems. *J. Chem. Eng. Data* **2004**, *49*, 1550−1553.

(38) Kumar, A. Estimates of internal pressure and molar refraction of imidazolium based ionic liquids as a function of temperature. *J. Solution Chem.* **2008**, *37*, 203−214.

(39) Waliszewski, D.; Stepniak, I.; Piekarski, H.; Lewandowski, A. Heat capacities of ionic liquids and their heats of solution in molecular liquids. *Thermochim. Acta* **2005**, *433*, 149−152.

(40) Pal, A.; Kumar, A. Apparent molar volumes of tetrabutylammonium bromide and tetrabutylammonium iodide in 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol at different temperatures. *Phys. Chem. Liq.* **2003**, *41*, 423−430.

(41) Nishsimoto, M.; Tabata, S.; Tamura, K.; Murakami, S. Thermodynamic properties of the mixture of methoxyetanol and cyclohexane: measurements at the temperatures 293.15, 298.15 and 303.15 K above and below UCST. *Fluid Phase Equilib.* **1997**, *136*, 235−247.

(42) Dubey, G.; Kumar, K. Volumetric and viscometric properties of binary liquid mixtures of ethylene glycol monomethyl ether + 1-hexanol, 1-octanol and 1-decanol at temperatures of T = (293.15, 298.15, 303.15 and 308.15) K. *J. Chem. Eng. Data* **2010**, *55*, 1700−1703.

(43) Roux, G.; Perron, G.; Desnoyers, E. J. Model systems for hydrophobic interactions; volumes and heat capacities for *n*-alkoxyethanols in water. *J. Solution Chem.* **1978**, *7*, 639−654.

(44) Li, X.-X.; Zhou, W.-D.; Li, X.-Y.; Sun, J.-L.; Jiang, W. Density, viscosity, and excess properties of the binary mixture of diethylene glycol monomethyl ether + water at T = (293.15, 303.15, 313.15, 323.15, 333.15) K. *J. Mol. Liq.* **2009**, *148*, 73−76.

(45) Venkatesulu, D.; Vankatesu, P.; Rao, M. V. P. Viscosities and densities of trichloroethylene or tetrachloroethylene with 2-alkoxyethanols at 303.15 and 313.15 K. *J. Chem. Eng. Data* **1997**, *42*, 365−367.

(46) Douheret, G.; Lajoie, P.; Davis, M. I.; Ratliff, J. L.; Ulloa, J.; Hoiland, H. Volumetric properties of binary mixtures of water with methoxy(ethoxy)$_n$ ethanols. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2291−2298.

(47) Mozo, I.; Garcia de la Funte, I.; Gonzalez, J. A.; Cobos, J. C.; Reisco, N. Thermodynamics of mixtures containing alkoxyethanols. Part XXVI. Densities, excess molar volumes, speeds of sound at (293.15, 298.15, and 303.15) K, and isentropic or isothermal compressibilities at 298.15 K for 2-methoxyethanol + alkoxyethanol or 2-propoxyethanol + dibutylether systems. *J. Chem. Eng. Data* **2008**, *53*, 1404−1414.

(48) Riddick, J. A.; Bunger, W. B.; Sakano, F. K. *Organic Solvents, Physical Properties and Method of Purification*, 4th ed.; Wiley-Interscience: New York, 1986.

(49) Li, X.-X.; Fan, G.-C.; Wang, Y.-W.; Zhang, M.; Lu, Y.-Q. Volumetric and viscometric properties of the binary mixture of triethylene glycol monomethyl ether + water at T = (293.15, 303.15, 313.15, 323.15, 333.15) K under atmospheric pressure. *J. Mol. Liq.* **2010**, *151*, 62−66.

(50) Aznarez, S.; de Ruiz Holgado, M. M. E. F.; Arancibia, E. L. Viscosimetric behavior of n-alkanols with triethylene glycol mono-

methyl ether at different temperatures. *J. Mol. Liq.* **2008**, *139*, 131–137.

(51) Pal, A.; Kumar, A. Speeds of sound and isentropic compressibilities of mixtures containing triethylene glycol monomethyl ether and n-alkanols at 298.15 K. *Acoust. Lett.* **1999**, *22*, 168–175.

(52) Henni, A.; Tontiwachwuthikul, P.; Chakma, A.; Mather, E. A. Densities and viscosities of triethylene glycol monomethyl ether + water solutions in the temperature interval 25 °C–80 °C. *J. Chem. Eng. Data* **1999**, *44*, 101–107.

(53) IUPAC. Commission on atomic weights and isotopic abundances 1985. *Pure Appl. Chem.* **1986**, *58*, 1677–1692.

(54) Pal, A.; Gaba, R.; Singh, T.; Kumar, A. Excess thermodynamic properties of binary mixtures of ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate) with alkoxyalkanols at several temperatures. *J. Mol. Liq.* **2010**, *154*, 41–46.

(55) Singh, T.; Kumar, A.; Kaur, M.; Kaur, G.; Kumar, H. Non-ideal behavior of imidazolium based room temperature ionic liquid in ethylene glycol at T = (298.15 to 318.15) K. *J. Chem. Thermodyn.* **2009**, *41*, 717–723.