Determination of Physical Properties for the Binary System of 1-Ethyl-3-methylimidazolium Tetrafluoroborate + H_2O

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Experimental data of densities and viscosities are presented for 1-ethyl-3-methylimidazolium tetrafluoroborate + H_2O binary systems over the entire range of their compositions at (293.15, 298.15, 303.15, 308.15, 313.15, 318.15, and 323.15) K. Excess molar volumes V^E and viscosity deviations $\Delta\eta$ have been obtained and fitted to the Redlich−Kister equation. The results show that the densities and viscosities are dependent strongly on water content and weakly on temperature. Comparatively, the viscosity deviation $\Delta\eta$ is more sensitive to temperature than the excess molar volume V^E.

Introduction

Room-temperature ionic liquids (ILs) are organic salts composed of cations and anions that are liquids at conditions near room temperature. Known as environmentally benign solvents, ILs are attracting a great deal of attention as possible a replacement for traditional volatile organic solvents. Their application involves many fields, such as organic synthesis, catalytic reactions, and multiphase separations. The key functions of ILs are their possiblity to be tuned by varying the nature of the cations and anions.[1] Two important cation groups are those based on imidazolium and pyridinium. While the focus of research on ILs has predominantly been on their applicability as solvents for reactions and separations, the physicochemical properties of ILs and their mixtures with organic or inorganic solvents have been studied. The study of thermophysical properties is important in order to obtain sufficient information to predict properties and characteristics of ILs. The lack of physical property data and fundamental understanding of ILs prevent their further application to industry.[2]

A wide range of imidazolium-based ionic liquids have been prepared, incorporating many different anions in an effort to demonstrate the potential specifically to tailor the properties of the ILs for specific applications. For tetrafluoroborate salts, they are hydrophilic and miscible with water. The presence of water may have a rather dramatic effect on properties of such a kind of IL. Knowledge of the physicochemical and thermodynamic properties of binary liquid mixtures formed by one or two components associated through hydrogen bonds is important from both theoretical and process design aspects. Excess thermodynamic properties can give some information of the structural and energetic consequences of the interactions between ILs and water.

Several properties of some of 1-alkyl-3-methylimidazolium tetrafluoroborates have been reported in previous research.[3−5] Ohno[6] reported the viscosities of ILs prepared by the neutralization of several alkylimidazoles with several acids. It has been demonstrated that the viscosities of 1-alkyl-3-methylimidazolium salts can be decreased by using a highly branched alkyl chain but more importantly by changing the nature of the anion.[7] Huddleston et al.[2] examined the properties of different hydrophobic and hydrophilic 1-alkyl-3-methylimidazolium ILs. Recently, Seddon[8] and Heintz[9] presented some work on excess properties for water + [bmim][BF_4] (1-butyl-3-methylimidazolium tetrafluoroborate) and methanol + [mbpy][BF_4] (4-methyl-N-butylpyridinium tetrafluoroborate) mixtures, respectively.

In this work, data of densities and viscosities of mixtures consisting of water and [emim][BF_4] (1-ethyl-3-methylimidalozium tetrafluoroborate) were measured over the entire range of their compositions at (293.15, 298.15, 303.15, 308.15, 313.15, 318.15, and 323.15) K. The excess molar volume V^E and viscosity derivation $\Delta\eta$ of this binary system have been obtained and fitted to the Redlich−Kister equation. The effects of water content and temperature on the physical properties were analyzed, and the interactions and structures were discussed in terms of the behavior of excess molar volume V^E and viscosity derivation $\Delta\eta$ of an [emim][BF_4] + H_2O mixture.

Experimental Section

All chemicals were of analytical grade and used without further purification. All aqueous solutions were prepared with deionized water. The tetrafluoroborate salt was prepared by metathesis reactions from the corresponding bromide.

First, 1-ethyl-3-methylimidalozium bromide was synthesized similar to Dzyuba's description.[10] Equimolar amounts of 1-methylimidazole and ethyl bromide were mixed and heated to form a transparent, golden, slightly viscous solution. And the solution was dried under vacuum at (100 to 120) °C to produce 1-ethyl-3-methyl-imidazolium bromide in very high yield (99%).

Second, tetrafluoroboric acid was added slowly to a slurry of silver oxide in water and rapidly stirred until all the silver oxide had completely reacted to give a colorless solution. The reaction mixture was covered with aluminum foil to prevent photodegradation.

Third, a solution of 1-ethyl-3-methylimidalozium bromide in water was added to the reaction mixture and

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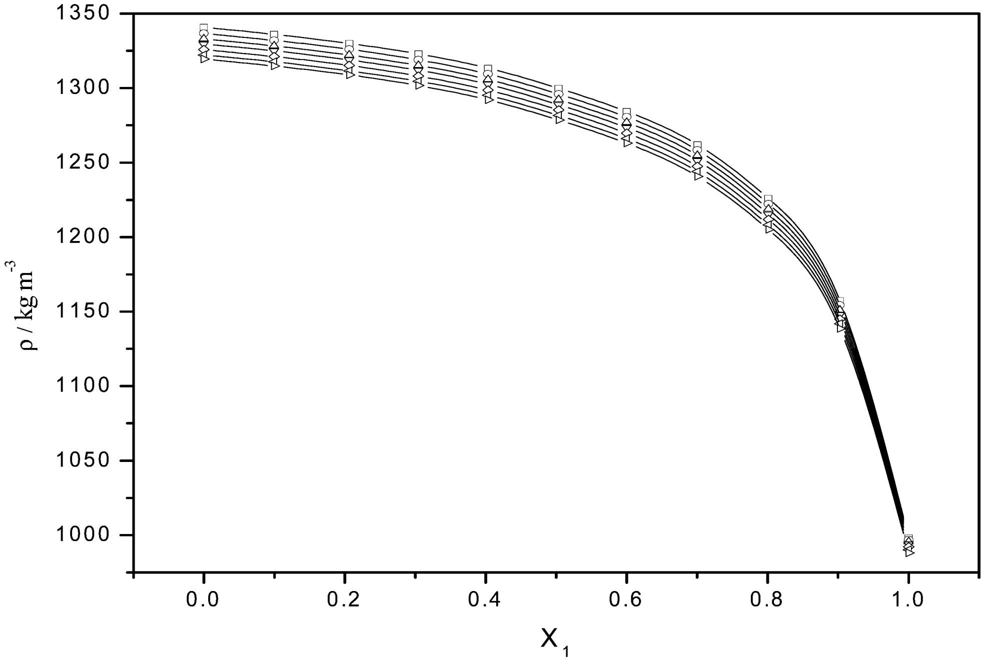

Figure 1. Variation of density vs mol fraction of water for H_2O (1) + [emim][BF_4] (2). □, 293.15 K; ○, 298.15 K; △, 303.15 K; ▽, 308.15 K; ◇, 313.15 K; triangle pointing left, 318.15 K; triangle pointing right, 323.15 K.

Table 1. Experimental Densities of the H_2O (1) + [emim][BF_4] (2) System

	ρ/kg·m^{-3}						
x_1	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K
0	1340.7	1336.7	1332.9	1329.6	1325.9	1322.2	1319.5
0.0995	1336.1	1332.1	1328.3	1324.9	1321.2	1317.6	1314.8
0.2062	1330.0	1326.0	1322.2	1318.9	1315.2	1311.6	1308.8
0.3047	1322.9	1318.9	1315.2	1311.9	1308.1	1304.5	1301.6
0.4034	1313.4	1309.5	1305.8	1302.5	1298.7	1295.0	1292.0
0.5034	1299.8	1296.0	1292.3	1288.9	1285.3	1281.6	1278.6
0.5998	1284.2	1280.6	1276.9	1273.5	1269.7	1266.0	1263.1
0.7005	1262.0	1258.4	1254.8	1251.4	1247.5	1243.9	1240.7
0.8011	1225.9	1222.3	1218.7	1215.4	1211.8	1208.2	1205.0
0.9027	1157.4	1154.2	1151.1	1148.0	1145.0	1141.8	1138.5
1[11]	998.2	997.0	995.7	994.0	992.2	990.1	988.0

Table 2. Experimental Viscosities of the H_2O (1) + [emim][BF_4] (2) System

	η/mPa·s						
x_1	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K
0	45.290	37.190	31.362	25.557	21.537	18.838	15.903
0.0995	34.431	29.025	24.800	20.533	17.964	15.927	13.743
0.2062	25.098	21.008	17.897	14.584	12.678	11.157	9.797
0.3047	19.252	15.965	13.577	10.931	9.634	8.324	7.470
0.4034	13.760	11.448	9.674	8.187	7.165	6.357	5.692
0.5034	10.365	8.597	7.384	6.409	5.465	4.979	4.522
0.5998	7.892	6.975	5.492	4.707	4.159	3.630	3.215
0.7005	5.797	4.822	3.896	3.531	3.133	2.584	2.512
0.8011	4.127	3.499	2.962	2.555	2.267	2.044	1.904
0.9027	3.035	2.584	2.189	1.898	1.689	1.530	1.439
1[11]	1.002	0.890	0.798	0.719	0.653	0.599	0.547

stirred. The resulting yellow precipitate of silver bromide was removed by filtration, and the solvent was removed from the supernatant liquor by heating at 70 °C, initially under reduced pressure and finally in vacuo, to yield [emim][BF_4] as a pale-yellow liquid.

The water content of pure [emim]BF_4 was determined to be about 30 ppm by the Karl Fischer titration; its density and viscosity are in a good agreement with those reported in the literature.[12] The densities of the mixtures were measured by using a pycnometer (10 mL, 298.15 K) provided by Beijing Chemical Reagents Company. Its capacities varied with the experiment temperature and were calibrated by pure water.[11] The temperature is controlled by a constant water bath with an accuracy of ±0.05 °C. The mixtures composed of [emim][BF_4] and water were prepared by mass. The balance was a Shanghai Precision Science Instrument Company with a precision of ±0.1 mg. The viscosities of the mixtures were determined by a Ubbelohde viscometer (Beijing Chemical Reagents Company); the viscometer was calibrated by the standard liquid of viscosity provided by Chinese National Research Center of Certified Reference Materials and pure water. The viscosity data of pure water was obtained from Lange's Handbook of Chemistry.[11]

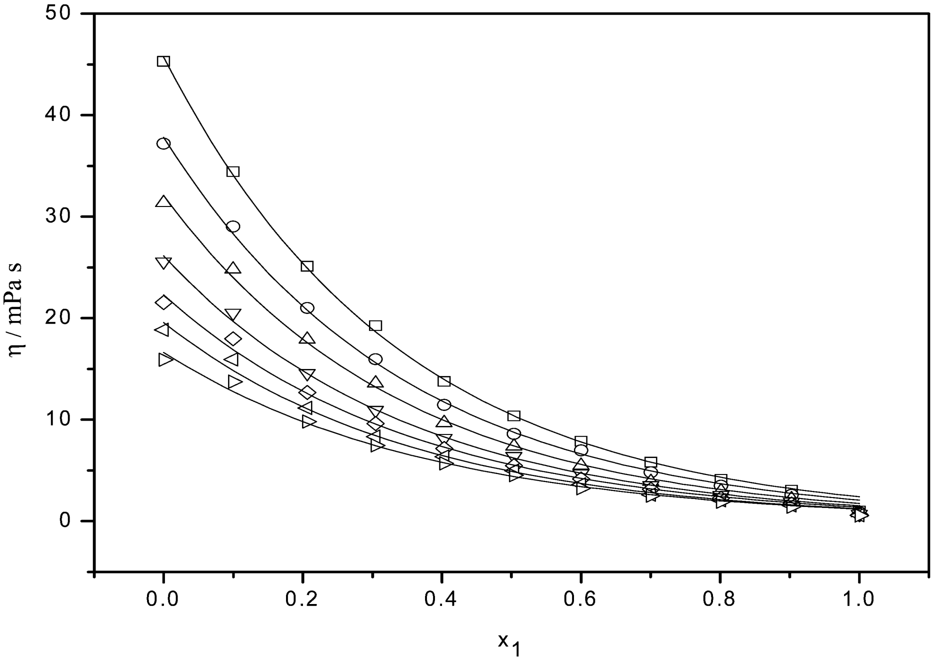

Figure 2. Variation of viscosity vs mol fraction of water for H_2O (1) + [emim][BF_4] (2). □, 293.15 K; ○, 298.15 K; △, 303.15 K; ▽, 308.15 K; ◇, 313.15 K; triangle pointing left, 318.15 K; triangle pointing right, 323.15 K.

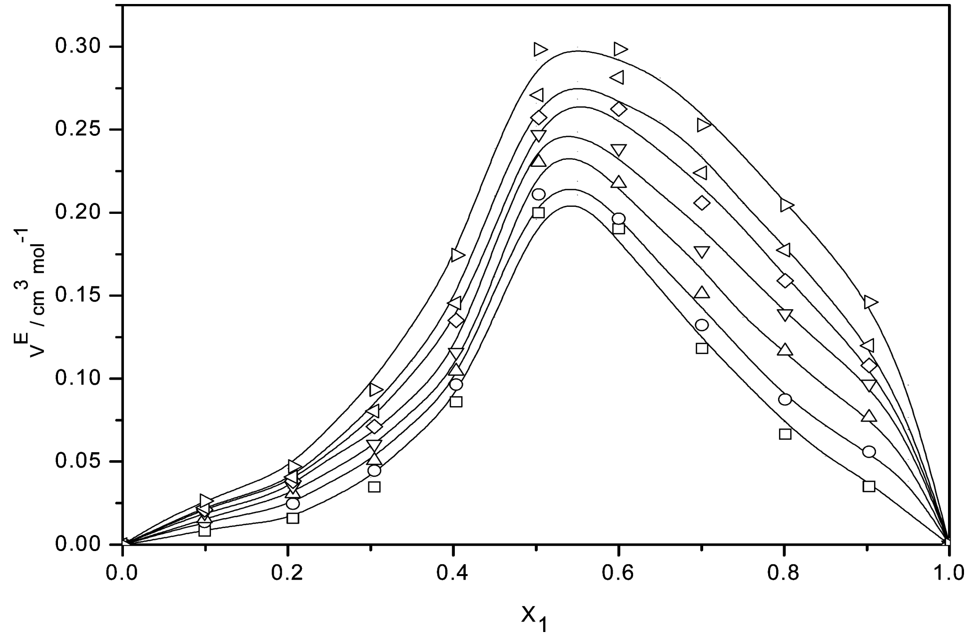

Figure 3. Molar excess volume V^E vs mol fraction of water for H_2O (1) + [emim][BF_4] (2). □, 293.15 K; ○, 298.15 K; △, 303.15 K; ▽, 308.15 K; ◇, 313.15 K; triangle pointing left, 318.15 K; triangle pointing right, 323.15 K; solid line, Redlich−Kister equation.

According to the precision of all experimental instruments, the experimental uncertainties of density and viscosity were estimated to be ±0.03% and ±0.1%, respectively. Accordingly, the deviations of V^E and $\Delta\eta$ were about ±0.05% and ±0.1%, respectively.

Results and Discussion

The densities and viscosities of the [emim][BF_4] + H_2O mixture, as a function of water content over the temperature range from (293.15 to 323.15) K are presented in Tables 1 and 2.

The viscosity of pure [emim][BF_4] is 1 or 2 orders of magnitude greater than that of traditional organic solvents and is more comparable to typical oil. Such viscosities, as observed here and in the literature,[6] will critically affect rates of mass transfer and power requirements for mixing in liquid reaction or separation process.

Further exploration of the nature of IL behavior was allowed by changing the experimental conditions. From the graphical representation of density and viscosity data in Figures 1 and 2, respectively, it can be readily observed that an increase in the content of water or temperature causes the density or viscosity to decrease and approach that of water. With the addition of water, the densities of mixtures declined sharply at the mol fraction of water lager than 0.6, while the viscosities of mixtures declined sharply at the mol fraction of water less than 0.5. Increasing in temperature causes both the density and viscosity to decrease slightly. Therefore the physical properties of ILs can be adjusted to meet the needs of applications for

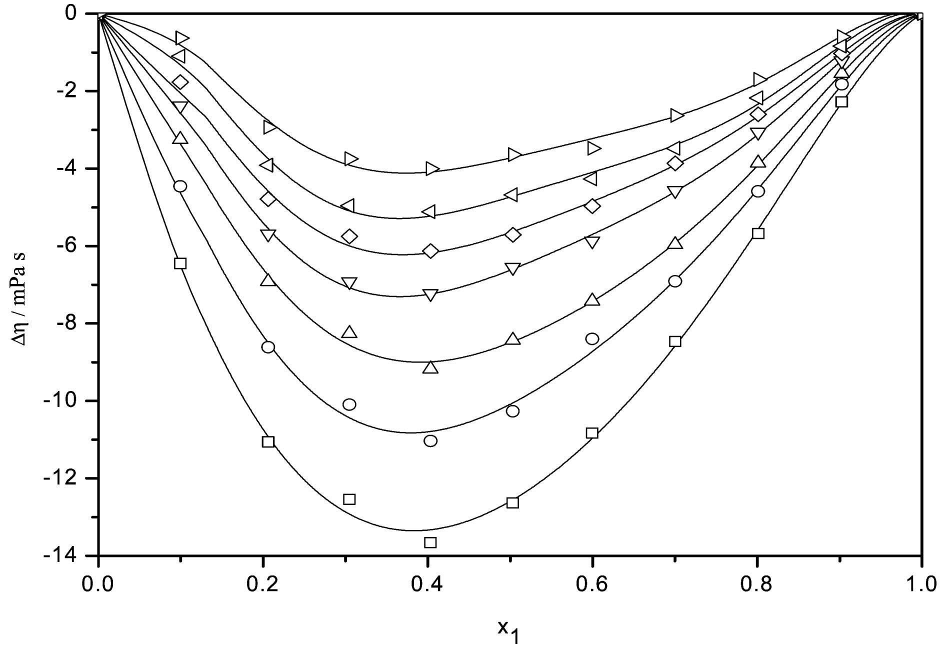

Figure 4. Viscosity derivation $\Delta\eta$ vs mol fraction of water for H_2O (1) + [emim][BF_4] (2). □, 293.15 K; ○, 298.15 K; △, 303.15 K; ▽, 308.15 K; ◇, 313.15 K; triangle pointing left, 318.15 K; triangle pointing right, 323.15 K; solid line, Redlich−Kister equation.

Table 3. Excess Molar Volume V^E of the H_2O (1) + [emim][BF_4] (2) System

	V^E/cm^3·mol^{-1}						
x_1	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K
0	0	0	0	0	0	0	0
0.0995	0.0081	0.0137	0.0156	0.0193	0.0210	0.0224	0.0263
0.2062	0.0159	0.0246	0.0308	0.0353	0.0383	0.0407	0.0471
0.3047	0.0348	0.0445	0.0507	0.0605	0.0711	0.0804	0.0933
0.4034	0.0861	0.0963	0.1046	0.1159	0.1350	0.1456	0.1743
0.5034	0.1999	0.2109	0.2304	0.2472	0.2573	0.2708	0.2982
0.5998	0.1902	0.1964	0.2176	0.2387	0.2624	0.2814	0.2984
0.7005	0.1182	0.1323	0.1510	0.1772	0.2059	0.2239	0.2528
0.8011	0.0666	0.0875	0.1166	0.1392	0.1590	0.1774	0.2045
0.9027	0.0351	0.0560	0.0767	0.0968	0.1079	0.1199	0.1461
1	0	0	0	0	0	0	0

Table 4. Viscosity Derivation $\Delta\eta$ of the H_2O (1) + [emim][BF_4] (2) System

	$\Delta\eta$/mPa·s						
x_1	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K
0	0	0	0	0	0	0	0
0.0995	−6.45	−4.46	−3.25	−2.38	−1.77	−1.10	−0.63
0.2062	−11.06	−8.62	−6.92	−5.69	−4.79	−3.92	−2.94
0.3047	−12.54	−10.10	−8.26	−6.92	−5.75	−4.96	−3.75
0.4034	−13.66	−11.04	−9.18	−7.23	−6.13	−5.12	−4.01
0.5034	−12.63	−10.27	−8.44	−6.55	−5.71	−4.68	−3.65
0.5998	−10.83	−8.40	−7.42	−5.87	−4.97	−4.27	−3.48
0.7005	−8.47	−6.91	−5.97	−4.57	−3.87	−3.48	−2.63
0.8011	−5.68	−4.59	−3.86	−3.06	−2.60	−2.18	−1.70
0.9027	−2.28	−1.83	−1.55	−1.22	−1.03	−0.84	−0.60
1	0	0	0	0	0	0	0

hydrophilic ILs, e.g., [emim][BF_4], by adding water or changing temperature.

Excess thermodynamic properties, which depend on the composition and/or temperature, are of great importance in understanding the nature of molecular aggregation that exists in the binary mixtures. From the measured densities and viscosities of H_2O (1) + [emim][BF_4] (2) mixture, the excess molar volume V^E and viscosity derivation $\Delta\eta$ were obtained by using the following equations

$$V^E = (M_1x_1 + M_2x_2)/\rho - (M_1x_1/\rho_1 + M_2x_2/\rho_2) \quad (1)$$

$$\Delta\eta = \eta - (\eta_1x_1 + \eta_2x_2) \quad (2)$$

where ρ and η are the density and viscosity of mixed solutions, ρ_i, η_i, and M_i are the density, viscosity, and molar mass of pure component i, where $i = 1$ or 2, and 1 and 2 denote water and [emim][BF_4], respectively.

The excess molar volume V^E and viscosity derivation $\Delta\eta$ have been fitted in the form of Redlich−Kister equation

$$V^E/\text{cm}^3\cdot\text{mol}^{-1} \text{ (or } \Delta\eta/\text{mPa}\cdot\text{s}) = x_1(1 - x_1)\sum A_i(1 - 2x_1)^i \quad (3)$$

It can be found that the fourth-order Redlich−Kister equation can represent well the experimental behavior as shown in Figures 1 and 2.

Table 5. Coefficients of the Redlich−Kister Equation for Excess Molar Volumes and Viscosity Derivations of the H_2O (1) + [emim][BF_4] (2) System

property	T/K	A_0	A_1	A_2	A_3	A_4	σ^a
V^E/cm^3·mol^{-1}	293.15	0.69172	−0.65122	−2.16273	0.76277	2.30622	0.011
	298.15	0.72631	−0.64332	−2.03712	0.57979	2.38855	0.010
	303.15	0.78601	−0.73032	−1.94271	0.50694	2.4132	0.014
	308.15	0.85579	−0.81751	−1.932	0.46537	2.5489	0.016
	313.15	0.92839	−0.92374	−1.86112	0.52355	2.43238	0.013
	318.15	0.98718	−0.99419	−1.84298	0.51315	2.44433	0.011
	323.15	1.09142	−1.02112	−1.96131	0.30511	2.78481	0.009
$\Delta\eta$/mPa·s	293.15	−50.382	−24.46211	−6.50275	−6.33459	12.87634	0.21
	298.15	−40.35758	−21.82192	−8.81539	6.1183	25.44632	0.21
	303.15	−33.99214	−16.61223	−6.71847	7.65057	27.14291	0.16
	308.15	−26.50121	−16.66409	−13.37543	13.44486	35.75198	0.13
	313.15	−22.60961	−14.50285	−11.01755	14.4682	33.42781	0.15
	318.15	−18.95302	−12.56668	−13.92509	16.48366	40.99544	0.15
	323.15	−14.91707	−9.59929	−9.54401	14.36353	33.98266	0.16

[a]

$$\sigma = \left(\frac{\sum_i (y_{\exp,i} - y_{\mathrm{cal},i})^2}{n - m} \right)^{1/2}$$

where y denotes V^E or $\Delta\eta$, n is the number of experimental data, and m is the number of coefficients of the Redlich−Kister equation. The units of A_i (i = 0−4) are cm^3·mol^{-1} for V^E and mPa·s for $\Delta\eta$.

The excess molar volume V^E increases with the molar fraction of water when $x_1 < 0.55$ or so, which is corresponding to the mass fraction of $W_1 = 0{-}0.1$, however, the excess volume V^E decreases with mol fraction of water when $x_1 > 0.55$ or so. There appears a peak between the water-rich region and the [emim][BF_4]-rich region, although it is not symmetrical at all. The similar phenomenon has been observed for [bmim][BF_4] (1-butyl-3-methylimidazolium tetrafluoroborate) + H_2O by Seddon et al.[8] Comparatively, V^E increases slightly with temperature.

The viscosity derivations $\Delta\eta$ are negative over the whole composition range and approach the minimum at $x_1 = 0.4$ or so within the whole region of the temperatures studied (Figure 4). As temperature increases, the values of $\Delta\eta$ become less negative.

The polynomial coefficients of the fourth-order Redlich−Kister equation for excess molar volumes and viscosity derivations of [emim][BF_4] + H_2O mixtures were summarized in Table 5.

Conclusions

The data of density and viscosity for the H_2O (1) + [emim][BF_4] (2) system were measured over the whole range of compositions at (293.15, 298.15, 303.15, 308.15, 313.15, 318.15, and 323.15) K. The excess molar volume V^E and viscosity derivation $\Delta\eta$ of this system have been measured and fitted to the Redlich−Kister equation. The results show that water content has significant influence on the properties such as density, viscosity, V^E, and $\Delta\eta$. The effect of temperature on viscosity derivation is stronger than that on excess molar volume. Therefore, it can be concluded that water content has stronger effects on the physical properties and excess thermodynamic properties of ILs for binary system of [emim][BF_4] + H_2O.

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