Densities and Viscosities of 1-Propyl-2,3-dimethylimidazolium Tetrafluoroborate + H_2O at T = (298.15 to 343.15) K

Ming-Lan Ge,*[,†] Xiao-Guang Ren,[†] Yong-Ji Song,[†] and Li-Sheng Wang[‡]

Department of Chemical Engineering, Beijing Institute of Petrochemical Technology, Beijing 102617, People's Republic of China, and School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing 100081, People's Republic of China

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Experimental data of densities and viscosities of 1-propyl-2,3-dimethylimidazolium tetrafluoroborate ([PDMIM][BF_4]) + H_2O binary mixtures were measured over the entire mole fraction range from (298.15 to 343.15) K at atmospheric pressure. Excess molar volumes and viscosity deviations as a function of mole fraction average have been obtained and fitted to the Redlich−Kister equation. Estimated coefficients of the Redlich−Kister equation and standard error calculated from the Redlich−Kister equation to the experimental data were also presented.

Introduction

Ionic liquids (ILs) have been receiving increasing interest as environmental friendly solvents recently because of their unique physical and chemical properties.[1−4] For ILs to be used effectively as solvents, it is essential to know the thermodynamic and thermophysical properties of ILs and, in particular, of mixtures containing ILs.[5,6] This work continues our studies on the determination of the densities and viscosities of IL + H_2O binary mixtures.[7,8]

1-Propyl-2,3-dimethylimidazolium tetrafluoroborate ([PDMIM][BF_4], CAS no. 157310-72-0) is one of the air- and water-stable hydrophilic ILs and is also thermally stable. The activity coefficient γ_i^∞ data of 34 organic solutes in [PDMIM][BF_4] from (303.15 to 363.15) K have been measured in our previous works.[9,10] However, no experimental density and viscosity data of the mixtures of [PDMIM][BF_4] and water have been reported in the previous literature. In this work, the densities and viscosities of mixtures consisting of [PDMIM][BF_4] and water were measured over the entire range of their compositions from (298.15 to 343.15) K. The excess molar volume, V^E, and viscosity deviation, $\Delta\eta$, of this binary system have been obtained and fitted to the Redlich−Kister equation.

Experimental Section

Materials. In this work, all of the aqueous solutions were prepared with deionized water, and the chemicals for preparation of [PDMIM][BF_4] were of analytical grade and used without further purification. [PDMIM][BF_4] was prepared via the traditional two steps.[11] First, 1-propyl-2,3-dimethylimidazolium bromide [PDMIM][Br] was prepared via the reaction of 1,2-dimethylimidazole (0.1 mol) and 1-bromopropane (0.11 mol). Second, [PDMIM][BF_4] was synthesized by metathesis reactions from [PDMIM][Br] and $NaBF_4$ in water. The NaBr precipitate was removed by filtration, and the remaining water was removed by rotary evaporation. The crude product was dissolved in dichloromethane, and the solution was washed with a small amount of cooled deionized water five times until the aqueous solution did not form any precipitate with $AgNO_3$ solution. The solvent dichloromethane was removed by rotary evaporation, and the [PDMIM][BF_4] was dried under high vacuum at 343 K for 8 h to remove volatile impurities. Water mass fractions analyzed by Karl Fischer analysis were less than 10^{-3}. The chemical shifts for the ^1H NMR spectrum (δ, D_2O) appear as follows: 7.245 [s, 1H, H(4)], 7.216 [s, 1H, H(5)], 3.997 [t, 2H, NCH_2], 3.670 [s, 3H, NCH_3], 2.487 [s, 3H, CH_3], 1.760 [m, 2H, $NCH_2{-}CH_2$], and 0.840 [t, 3H, $NCH_2CH_2{-}CH_2{-}CH_3$]. Impurity peaks were not observed in the ^1H NMR spectra. The purity of the IL was > 99 %. The change in the pH value of this IL between room temperature and 343 K was less than 1 %. This phenomenon showed that this IL will not hydrolyze at 343 K. Before use, the IL was subjected to vacuum evaporation at (323 to 333) K over 24 h to remove possible traces of solvents and moisture.

Table 1. Experimental Densities, ρ, for Binary Mixture of H_2O (1) + [PDMIM][BF_4] (2)

	T/K							
x_1	298.15	303.15	308.15	313.15	318.15	323.15	333.15	343.15
	ρ/g·cm^{-3}							
0.0000	1.2251	1.2218	1.2188	1.2174	1.2162	1.2154	1.2134	1.2119
0.0939	1.2219	1.2179	1.2148	1.2132	1.2119	1.2110	1.2089	1.2071
0.1932	1.2180	1.2140	1.2108	1.2093	1.2079	1.2068	1.2044	1.2026
0.2833	1.2136	1.2097	1.2065	1.2048	1.2032	1.2021	1.1997	1.1978
0.3944	1.2074	1.2037	1.2002	1.1982	1.1968	1.1956	1.1932	1.1912
0.4987	1.1998	1.1960	1.1926	1.1906	1.1890	1.1878	1.1853	1.1831
0.5995	1.1896	1.1861	1.1825	1.1805	1.1789	1.1776	1.1747	1.1723
0.6985	1.1757	1.1717	1.1683	1.1665	1.1650	1.1637	1.1607	1.1579
0.8009	1.1535	1.1499	1.1469	1.1447	1.1431	1.1417	1.1384	1.1343
0.8988	1.1130	1.1098	1.1074	1.1053	1.1033	1.1016	1.0978	1.0942
1.0000	0.9970	0.9957	0.9940	0.9922	0.9902	0.9881	0.9832	0.9778

Apparatus and Procedure. The measurements apparatus and procedure have been described in our previous work.[7,8] The mixtures of IL + H_2O were prepared by mass. A TE2101-L electronic digital balance accurate to within ± 0.1 mg was used. The uncertainty in the mole fraction of the mixtures was estimated to less than ± 0.0001. All molar quantities are based on the IUPAC 2005 relative atomic mass table.[12] The densities of [PDMIM][BF_4] and its mixtures were measured with a

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* Corresponding author. E-mail: geminglan@bipt.edu.cn.

[†] Beijing Institute of Petrochemical Technology.

[‡] Beijing Institute of Technology.

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Table 2. Experimental Viscosities, η, for Binary Mixture of H_2O (1) + [PDMIM][BF_4] (2)

	T/K							
x_1	298.15	303.15	308.15	313.15	318.15	323.15	333.15	343.15
	η/mPa·s							
0.0000	377.28	271.90	201.99	152.20	117.44	92.29	60.45	40.74
0.0939	224.97	167.61	127.89	99.34	78.56	63.30	42.52	29.96
0.1932	134.95	103.29	81.12	64.54	52.07	42.80	34.62	21.84
0.2833	85.25	66.81	53.23	43.20	35.71	29.65	21.37	16.02
0.3944	50.58	40.44	32.95	27.18	22.79	19.32	14.38	11.04
0.4987	31.29	25.50	21.07	17.63	14.97	12.87	9.78	7.66
0.5995	19.71	16.21	13.58	11.52	9.88	8.58	6.65	5.30
0.6985	12.03	10.04	8.53	7.31	6.34	5.55	4.37	3.53
0.8009	6.69	5.67	4.90	4.23	3.71	3.29	2.62	2.15
0.8988	3.23	2.78	2.42	2.14	1.89	1.69	1.39	1.16
1.0000	0.89	0.80	0.72	0.65	0.60	0.55	0.47	0.40

Table 3. Excess Molar Volume, V^E, for Binary Mixture of H_2O (1) + [PDMIM][BF_4] (2)

	T/K							
x_1	298.15	303.15	308.15	313.15	318.15	323.15	333.15	343.15
	V^E/cm^3·mol^{-1}							
0.0939	0.13	0.22	0.24	0.27	0.28	0.29	0.31	0.34
0.1932	0.24	0.33	0.36	0.37	0.40	0.43	0.47	0.50
0.2833	0.33	0.41	0.44	0.48	0.53	0.55	0.59	0.61
0.3944	0.39	0.45	0.50	0.57	0.58	0.61	0.63	0.66
0.4987	0.42	0.49	0.53	0.59	0.61	0.62	0.65	0.68
0.5995	0.45	0.48	0.54	0.58	0.61	0.62	0.66	0.69
0.6985	0.42	0.48	0.52	0.54	0.55	0.57	0.59	0.62
0.8009	0.31	0.36	0.38	0.41	0.41	0.42	0.44	0.50
0.8988	0.19	0.21	0.22	0.23	0.24	0.25	0.26	0.27

Table 4. Viscosity Deviation, $\Delta\eta$, for Binary Mixture of H_2O (1) + [PDMIM][BF_4] (2)

	T/K							
x_1	298.15	303.15	308.15	313.15	318.15	323.15	333.15	343.15
	$\Delta\eta$/mPa·s							
0.0939	−117.0	−78.8	−55.2	−38.6	−27.9	−20.4	−12.3	−7.0
0.1932	−169.6	−116.2	−82.0	−58.4	−42.8	−31.8	−17.2	−11.1
0.2833	−185.4	−128.3	−91.7	−66.1	−48.6	−36.7	−22.1	−13.3
0.3944	−178.3	−124.5	−89.7	−65.2	−48.6	−36.8	−22.4	−13.8
0.4987	−158.3	−111.2	−80.5	−59.0	−44.2	−33.7	−20.8	−13.0
0.5995	−131.9	−93.2	−67.8	−49.8	−37.5	−28.7	−17.8	−11.3
0.6985	−102.3	−72.5	−52.9	−39.0	−29.5	−22.7	−14.2	−9.0
0.8009	−69.1	−49.1	−35.9	−26.6	−20.2	−15.5	−9.8	−6.3
0.8988	−35.8	−25.5	−18.7	−13.8	−10.5	−8.1	−5.1	−3.3

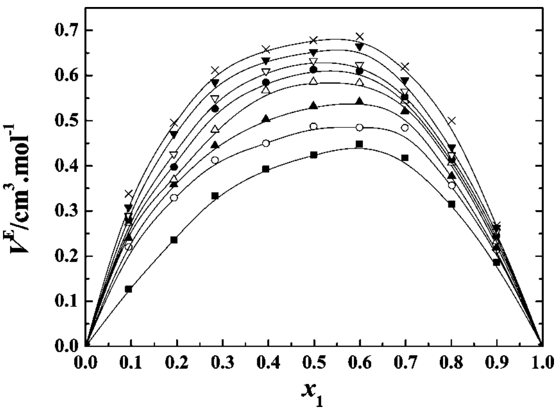

Figure 1. Excess molar volume, V^E, versus molar fraction of water for H_2O (1) + [PDMIM][BF_4] (2). ■, 298.15 K; ○, 303.15 K; ▲, 308.15 K; △, 313.15 K; ●, 318.15 K; ▽, 323.15 K; ▼, 333.15 K; ×, 343.15 K. The symbols represent experimental values; the solid curves are calculated with the Redlich−Kister equation.

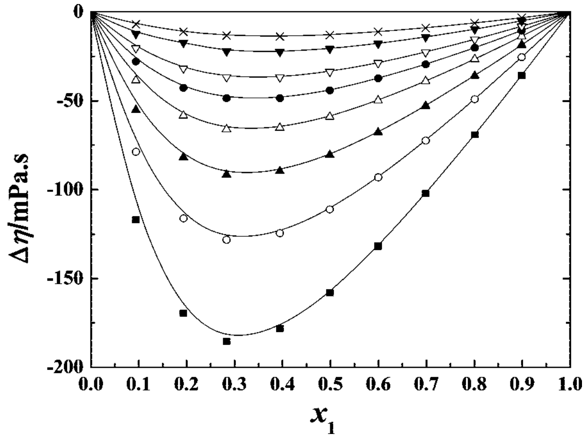

Figure 2. Viscosity deviation, $\Delta\eta$, versus molar fraction of water for H_2O (1) + [PDMIM][BF_4] (2). ■, 298.15 K; ○, 303.15 K; ▲, 308.15 K; △, 313.15 K; ●, 318.15 K; ▽, 323.15 K; ▼, 333.15 K; ×, 343.15K. The symbols represent experimental values; the solid curves are calculated with the Redlich−Kister equation.

Table 5. Coefficients of the Redlich−Kister Equation for V^E and $\Delta\eta$ of the H_2O (1) + [PDMIM][BF_4] (2) System

property	T/K	A_0	A_1	A_2	A_3	σ
V^E/cm^3·mol^{-1}	298.15	1.77	0.53	0.03	−0.36	0.011
	303.15	1.95	0.45	0.84	−0.98	0.011
	308.15	2.14	0.40	0.76	−1.00	0.020
	313.15	2.44	0.28	0.49	−0.75	0.023
	318.15	2.53	0.02	0.45	−0.32	0.028
	323.15	2.55	0.09	0.56	−0.45	0.028
	333.15	2.64	0.16	0.72	−0.73	0.030
	343.15	2.72	0.27	1.16	−1.11	0.025
$\Delta\eta$/mPa·s	298.15	−628.9	462.5	−362.3	210.1	0.99
	303.15	−442.5	315.1	−230.0	123.4	0.54
	308.15	−320.8	221.1	−151.3	75.9	0.43
	313.15	−235.2	156.3	−97.6	42.7	0.26
	318.15	−176.2	112.2	−65.8	27.1	0.14
	323.15	−134.5	83.0	−43.9	13.6	0.10
	333.15	−83.2	40.7	−6.5	0.3	0.48
	343.15	−51.7	25.9	−10.5	2.5	0.07

pycnometer (10 mL), and because its volume varied with temperature, it was calibrated with pure water from (298.15 to 343.15) K. The temperature was controlled by a water bath to within an uncertainty of ± 0.05 K. The capillary was calibrated for kinetic energy and end corrections with double-distilled water over the experimental temperature range

$$\nu = \frac{\eta}{\rho} = k_1 t - k_2/t \tag{1}$$

where t is the flow time, k_1, is the Ubbelhode capillary microviscometer constant, and k_2 is the Hagenbach correction. The kinematic viscosity, ν, for calibration was obtained from literature values of the absolute viscosity and density.[13] An electronic digital stopwatch with a readability of ± 0.01 s was used for flow-time measurement. Experiments were repeated at least four times at each temperature for all mixtures, and the results were averaged. The uncertainty of viscosity measurements depends on equilibrium temperature, flow time, mole fraction, and calibration fluid.

From a propagation of error analysis, the experimental average uncertainties of density and viscosity were estimated to be about ± 1 %. Accordingly, the relative deviations of V^E and $\Delta\eta$ were estimated to be about ± 2 %.

Result and Discussion

The densities and viscosities of the [PDMIM][BF_4] + H_2O mixture, as a function of water content over the temperature range from (298.15 to 343.15) K, are presented in Tables 1 and

2. An increase in water content or temperature causes density or viscosity to decrease.

The excess molar volumes, V^E, and the viscosity deviations, $\Delta\eta$, were calculated from the measurements according to the following equations[14,15]

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \tag{2}$$

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \tag{3}$$

where ρ and η are density and viscosity of mixtures, respectively, x_1 and x_2 are mole fractions, M_1 and M_2 are molar masses, ρ_1 and ρ_2 are densities, and η_1 and η_2 are the viscosities of H_2O (1) and [PDMIM][BF_4] (2), respectively.

All values of V^E and $\Delta\eta$ for the mixtures of H_2O (1) + [PDMIM][BF_4] (2) were fitted to the Redlich−Kister polynomial equation[16,17]

$$Y = x_1(1 - x_1)\sum_{i=0}^{m-1} A_i(2x_1 - 1)^i \tag{4}$$

where $Y = V^E$ or $\Delta\eta$, A_i is adjustable parameter, and x_1 is the mole fraction of water (1). The optimum number of coefficients, A_i, was determined from an examination of variation of standard derivation

$$\sigma(Y) = \left[\sum (Y_{\text{calcd}} - Y_{\text{exptl}})^2/(n - m)\right]^{1/2} \tag{5}$$

where n is the number of experimental data and m is the number of coefficients of the Redlich−Kister equation.

The data of excess molar volume, V^E, and viscosity deviation, $\Delta\eta$, are given in Tables 3 and 4. The V^E and the $\Delta\eta$ versus the mole fraction of water are, respectively, shown in Figures 1 and 2. Table 5 lists the value of the parameters, A_i, together with the standard deviations.

The excess thermodynamic properties, which depend on the composition, temperature, or both, are of great importance in understanding the nature of molecular interaction that exists in the binary mixtures. As shown in Figure 1, the values of V^E were positive for H_2O + [PDMIM][BF_4] mixtures from (298.15 to 343.15) K over the entire range of composition s and increase slightly with the increase in temperature.

The dependence of $\Delta\eta$ on mole fraction, x_1, is presented in Figure 2. The values of viscosity deviations were negative over the whole range of composition, and the minimum existed at $x_1 = 0.3$ within the whole region of experimental temperatures. Simultaneously, viscosity deviations increased slightly from (298.15 to 343.15) K.

Conclusions

The experimental results show that water content has stronger effects on the physical properties and excess thermodynamic properties of ILs for binary system of H_2O + [PDMIM][BF_4]. Furthermore, the present results add useful data on imidazolium-based ILs to the growing database on IL properties, a database that is essential for the many applications of these liquids currently under exploration.

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