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Densities and Viscosities of 1-Butyl-3-methylimidazolium Trifluoromethanesulfonate + H_2O Binary Mixtures at $T = (303.15 \text{ to } 343.15)$ K

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Densities and viscosities for the binary mixtures of H_2O (1) + 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([BMIM][CF_3SO_3]) (2) were measured over the entire mole fraction range from (303.15 to 343.15) K at atmospheric pressure. Excess molar volumes and viscosity deviations as a function of mole fraction average were derived, and the results were fitted to the Redlich−Kister equation using a multiparametric nonlinear regression method. Estimated coefficients of the Redlich−Kister equation and standard error calculated from the Redlich−Kister equation to the experimental data are also presented. The results show that the densities and viscosities are dependent on water content and temperature.

Introduction

Ionic liquids (ILs) are environmentally friendly solvents with no detectable vapor pressure and good solubility for many organic, inorganic, and polymeric substances. Because of this combination of properties, ILs present many possible applications in many fields. Much of the interest has focused on their application to catalytic reaction, separation process, and electrochemistry. Systematic investigations of thermodynamic and thermophysical properties of ILs and in particular of mixtures containing ILs are still few.[1]

Densities and viscosities are needed for the design of new processes involving ILs on an industrial scale. Further experimental data of density and viscosity of a binary mixture are important from a theoretical viewpoint to understand the liquid theory. So, a study on excess thermophysical properties is important to be able to predict the properties of mixtures containing ILs. [2] Furthermore, the presence of water in the ionic liquid phase can dramatically affect the physical properties.[3−5] As noted, the high viscosities of ILs are a hindrance when used in chemical processing.[6]

1-Butyl-3-methylimidazolium trifluoromethanesulfonate ([BMIM][CF_3SO_3], CAS no. 174899-66-2) is one of the air- and water-stable hydrophilic ionic liquids and is also thermally stable. The densities and viscosities of [BMIM][CF_3SO_3] reported in the literature[7−12] are listed in Table 1. In previous works, we have measured activity coefficient γ_i^∞ data of 34 organic solutes in [BMIM][CF_3SO_3] from (303.15 to 363.15) K.[13,14]

In this work, the densities and viscosities of mixtures consisting of [BMIM][CF_3SO_3] and water were measured over the entire range of their compositions from (303.15 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. The effects of water content and temperature on the physical properties have been analyzed, and the interactions and structures were discussed in terms of the behavior of the excess molar volume V^E of the mixture of [BMIM][CF_3SO_3] + water.

Table 1. Comparison of Experimental Densities ρ and Viscosities η of [BMIM][CF_3SO_3] with Literature Values

	ρ/g·cm^{-3}		η/mPa·s	
t/°C	exptl	lit.	exptl	lit.
20	1.3070[a]	1.290[7]	92.092[a]	90[7]
		1.3013 ± 0.0015 (22.6 °C)[8]		99[10]
		1.3055[11b]		109.6409[11b]
		1.3061[12]		
25	1.3028[a]	1.2987[9]	75.282[a]	
		1.3015[11b]		83.6445[11b]
30	1.2984	1.2965 ± 0.0014 (30.8 °C)[8]	63.190	64.2[10]
		1.2975[11b]		65.3992[11b]
		1.2966[12]		
35	1.2949	1.2935[11b]	51.729	52.2381[11b]
40	1.2914	1.2894 ± 0.0012 (40.2 °C)[8]	42.458	44.1[10]
		1.2895[11b]		42.5133[11b]
		1.2876[12]		
45	1.2878	1.2855[11b]	35.174	35.1731[11b]
50	1.2844	1.2790 ± 0.0023 (55.6 °C)[8]	29.553	30.9[10]
		1.2815[11b]		29.5271[11b]
		1.2787[12]		
60	1.2774	1.2705[12]	21.609	22.8[10]
		1.2735[11b]		21.6027[11b]
70	1.2705	1.2700 ± 0.0038 (69.8 °C)[8]	16.376	17.4[10]
		1.2655[11b]		16.4768[11b]
		1.2625[12]		

[a] Extrapolated value from $\rho = b - aT$ and $\eta = \eta_0 \exp[B/(T - T_0)]$; b, a, η_0, and T_0 are fit parameters for the linear fitting. [b] Derived value from correlating equations.

Experimental Section

Materials. In this work, all the aqueous solutions were prepared with deionized water, and the chemicals for preparation of ionic liquid ([BMIM][CF_3SO_3]) were of analytical grade and used without further purification. The ionic liquid [BMIM][CF_3SO_3] was prepared via the traditional two steps. First, 1-butyl-3-methylimidazolium bromide [BMIM][Br] was prepared via the reaction of 1-methylimidazole (0.1 mol) and 1-bromobutane (0.11 mol). Second, [BMIM][CF_3SO_3] was

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Table 2. Experimental Densities ρ for Binary Mixture of H_2O (1) + [BMIM][CF_3SO_3] (2)

	T/K						
x_1	303.15	308.15	313.15	318.15	323.15	333.15	343.15
	ρ/g·cm^{-3}						
0.0000	1.2984	1.2949	1.2914	1.2878	1.2844	1.2774	1.2705
0.1032	1.2945	1.2910	1.2875	1.2838	1.2803	1.2731	1.2660
0.1939	1.2912	1.2877	1.2841	1.2804	1.2768	1.2697	1.2626
0.2987	1.2865	1.2830	1.2794	1.2758	1.2722	1.2650	1.2579
0.3999	1.2808	1.2773	1.2738	1.2702	1.2665	1.2593	1.2522
0.5010	1.2728	1.2693	1.2657	1.2620	1.2583	1.2511	1.2440
0.5923	1.2630	1.2595	1.2559	1.2522	1.2485	1.2413	1.2339
0.7023	1.2462	1.2425	1.2388	1.2349	1.2311	1.2234	1.2156
0.7990	1.2201	1.2166	1.2129	1.2089	1.2052	1.1972	1.1893
0.9010	1.1646	1.1606	1.1567	1.1530	1.1500	1.1426	1.1343
1.0000	0.9957	0.9940	0.9922	0.9902	0.9881	0.9832	0.9778

Table 3. Experimental Viscosities η for Binary Mixture of H_2O (1) + [BMIM][CF_3SO_3] (2)

	T/K						
x_1	303.15	308.15	313.15	318.15	323.15	333.15	343.15
	η/mPa·s						
0	63.190	51.729	42.458	35.174	29.553	21.609	16.376
0.1032	45.696	37.227	30.927	25.041	21.507	16.069	12.443
0.1939	35.415	29.270	24.463	20.791	18.108	13.507	10.545
0.2987	28.969	24.276	20.532	17.549	15.173	11.613	9.1368
0.3999	23.248	19.951	16.880	14.377	12.618	9.8800	7.8156
0.5010	19.187	16.805	13.948	12.001	10.423	8.1008	6.6122
0.5923	15.467	13.202	11.210	9.9072	8.5157	6.7021	5.3842
0.7023	11.556	10.130	8.6049	7.4650	6.5763	5.1369	4.2397
0.7990	8.2063	6.9320	5.9890	5.3393	4.5704	3.6181	2.9364
0.9010	4.5521	3.8692	3.3759	3.1563	3.0054	2.0992	1.7141
1.0000	0.7977	0.7190	0.6532	0.6001	0.5470	0.4665	0.4040

Table 4. Excess Molar Volume V^E for the Binary Mixture of H_2O (1) + [BMIM][CF_3SO_3] (2)

	T/K						
x_1	303.15	308.15	313.15	318.15	323.15	333.15	343.15
	V^E/cm^3·mol^{-1}						
0.1032	0.1693	0.1732	0.1770	0.1965	0.2155	0.2534	0.2908
0.1939	0.1958	0.2026	0.2234	0.2441	0.2783	0.3023	0.3393
0.2987	0.2059	0.2158	0.2380	0.2471	0.2930	0.3189	0.3551
0.3999	0.2253	0.2382	0.2506	0.2624	0.3058	0.3448	0.3801
0.5010	0.2567	0.2729	0.2979	0.3223	0.3634	0.4033	0.4385
0.5923	0.2711	0.2902	0.3165	0.3420	0.3809	0.4213	0.4810
0.7023	0.2167	0.2516	0.2856	0.3251	0.3677	0.4412	0.5217
0.7990	0.2075	0.2327	0.2666	0.3092	0.3429	0.4241	0.4983
0.9010	0.1632	0.2084	0.2491	0.2785	0.2863	0.3348	0.4090

synthesized by metathesis reactions from [BMIM][Br] and $NaCF_3SO_3$ in water. 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 [BMIM][CF_3SO_3] 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 (parts per million, D_2O) appear as follows: δ 8.626 [s, 1H, H(2)], 7.408 [s, 1H, H(4)], 7.360 [s, 1H, H(5)], 4.147 [t, 2H, NCH_2], 3.826 [s, 3H, NCH_3], 1.805 [m, 2H, NCH_2-CH_2], 1.287 [m, 2H, $NCH_2CH_2-CH_2$], and 0.879 [t, 3H, CH_3]. The ^{13}C NMR spectrum (parts per million, D_2O) contains peaks: 136.07 [C(2)], 123.81 [C(4)], 122.47 [C(5)], 118.67 [F_3-C-SO_3], 49.49 [$N-CH_2$], 35.85 [NCH_3], 31.60 [NCH_2-CH_2], 19.00 [$NCH_2CH_2-CH_2$], and 12.79 [CH_3]. Impurity peaks were not observed in the ^1H NMR and ^{13}C NMR spectra. The purity of the ionic liquid was > 99 %. The change in pH values of this IL between room temperature and 343 K was less than 1 %. This phenomenon showed that this ionic liquid 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. Its densities and viscosities at several temperatures are in good agreement with those reported in the literature (in Table 1).

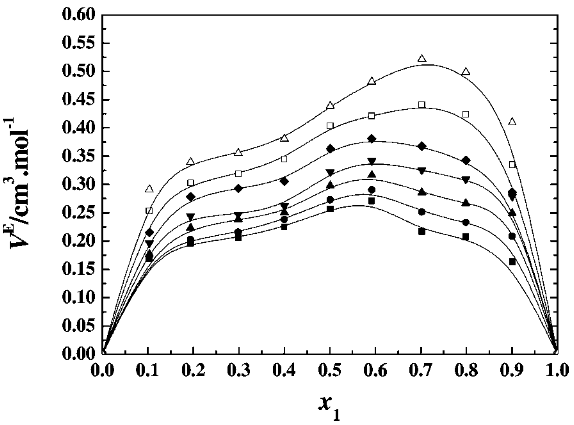

Figure 1. Excess molar volume V^E vs molar fraction of water for H_2O (1) + [BMIM][CF_3SO_3] (2). ■, 303.15 K; ●, 308.15 K; ▲, 313.15 K; ▼, 318.15 K; ◆, 323.15 K; □, 333.15 K; Δ, 343.15 K. The symbols represent experimental values, and the solid curves are calculated with the Redlich−Kister equation.

Apparatus and Procedure. The mixtures of [BMIM]-[CF_3SO_3] and water 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.[15] The densities of the ionic liquid [BMIM][CF_3SO_3] and its mixtures were measured with a pycnometer (10 mL), and since its volume varied with temperature, it was calibrated with pure water from (303.15 to 343.15) K. The temperature was controlled by a water bath to within an uncertainty of ± 0.05 K.

Measurements of the viscosities were carried out in the same water bath using an Ubbelohde capillary viscometer. The capillary was calibrated for kinetic energy correction with double-distilled water at the experimental temperature range

$$\nu = \frac{\eta}{\rho} = k_1 t - k_2/t \qquad (1)$$

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.[16] 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 ± 0.01. Accordingly, the deviations of V^E and $\Delta\eta$ were about ± 0.02.

Result and Discussion

The densities and viscosities of the [BMIM][CF_3SO_3] + H_2O mixture, as a function of water content over the temperature range from (303.15 to 343.15) K, are presented in Tables 2 and

Table 5. Viscosity Deviation $\Delta\eta$ for Binary Mixture of H_2O (1) + [BMIM][CF_3SO_3] (2)

	T/K						
x_1	303.15	308.15	313.15	318.15	323.15	333.15	343.15
				$\Delta\eta$/mPa·s			
0.1032	−11.055	−9.2381	−7.2166	−6.5649	−5.0524	−3.3579	−2.2836
0.1939	−15.678	−12.568	−9.8881	−7.6789	−5.8211	−4.0031	−2.7329
0.2987	−15.584	−12.217	−9.4376	−7.2974	−5.7166	−3.6816	−2.4669
0.3999	−14.993	−11.380	−8.8587	−6.9704	−5.3366	−3.2754	−2.1714
0.5010	−12.746	−9.3686	−7.5642	−5.8513	−4.5989	−2.9175	−1.7596
0.5923	−10.770	−8.3141	−6.4846	−4.7886	−3.8587	−2.3863	−1.5291
0.7023	−7.8175	−5.7750	−4.4912	−3.4277	−2.6078	−1.6262	−0.9162
0.7990	−5.1340	−4.0409	−3.0644	−2.2101	−1.8091	−1.1008	−0.6747
0.9010	−2.4245	−1.9007	−1.4131	−0.8665	−0.4158	−0.4636	−0.2675

3. It can be readily observed that an increase in water content or temperature causes density or viscosity to decrease. Therefore, physical properties of ionic liquids can be adjusted to meet the needs of applications for hydrophilic ionic liquids, e.g., [BMIM][CF_3SO_3], by adding water or changing temperature.

The excess molar volumes V^E and the viscosity deviations $\Delta\eta$ were calculated from the measurements according to the following equations[17,18]

$$V^E = \frac{x_1M_1 + x_2M_2}{\rho} - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2} \tag{2}$$

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

where ρ and η are density and viscosity of mixtures; 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 ionic liquid [BMIM][CF_3SO_3] (2), respectively.

All values of V^E and $\Delta\eta$ for the mixtures of H_2O (1) + [BMIM][CF_3SO_3] (2) were fitted to the Redlich−Kister polynominal equation[19−21]

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

where $Y = V^E$ or $\Delta\eta$; A_i are adjustable parameters; 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

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

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

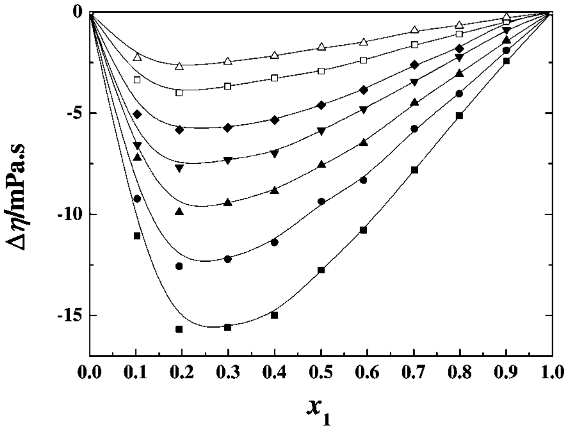

Figure 2. Viscosity deviation $\Delta\eta$ vs molar fraction of water for H_2O (1) + [BMIM][CF_3SO_3] (2). ■, 303.15 K; ●, 308.15 K; ▲, 313.15 K; ▼, 318.15 K; ◆, 323.15 K; □, 333.15 K; △, 343.15 K. The symbols represent experimental values, and the solid curves are calculated with the Redlich−Kister equation.

Table 6. Coefficients of the Redlich−Kister Equation for V^E and $\Delta\eta$ of H_2O (1) + [BMIM][CF_3SO_3] (2) System

property	*T*/K	A_0	A_1	A_2	A_3	σ
V^E/cm^3·mol^{-1}	303.15	0.977	0.128	0.981	−0.250	0.020
	308.15	1.036	0.179	1.218	0.048	0.022
	313.15	1.120	0.205	1.470	0.323	0.024
	318.15	1.196	0.398	1.778	0.129	0.024
	323.15	1.368	0.452	1.819	−0.050	0.021
	333.15	1.528	0.667	2.326	−0.105	0.017
	343.15	1.691	0.908	2.958	−0.124	0.020
$\Delta\eta$/mPa·s	303.15	−51.230	44.038	−36.244	25.340	0.264
	308.15	−38.325	34.162	−35.954	26.153	0.230
	313.15	−30.102	25.782	−26.698	23.424	0.202
	318.15	−22.802	18.493	−25.024	31.519	0.226
	323.15	−18.055	13.509	−16.639	25.881	0.174
	333.15	−11.113	9.352	−13.725	16.246	0.106
	343.15	−6.984	7.190	−10.095	10.243	0.077

The data of excess molar volume and viscosity deviation are given in Tables 4 and 5. The excess molar volumes V^E and the viscosity deviations $\Delta\eta$ versus the mole fraction of water are, respectively, shown in Figures 1 and 2. Table 6 lists the values of the parameters A_i together with the standard deviations.

The 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. As shown in Figure 1, the values of excess molar volume were positive for H_2O + [BMIM][CF_3SO_3] mixtures at all temperatures and over the entire range of compositions. The excess molar volumes V^E increase slightly with the increase of temperature from (303.15 to 343.15) K.

The dependence of the viscosity deviations $\Delta\eta$ on mole fraction x_1 is presented in Figure 2. The values of viscosity deviations were negative over the whole range of compositions, and the minimum existed at $x_1 = 0.2$ within the whole region of experimental temperatures. Simultaneously, viscosity deviations increased slightly from (303.15 to 343.15) K.

Conclusions

The densities and viscosities for the binary mixtures of H_2O + [BMIM][CF_3SO_3] over the whole range of compositions were measured as a function of the temperature at atmospheric pressure. The changes in viscosity and the excess molar volume have been adequately fitted to the Redlich−Kister polynomial equation. Estimated coefficients and standard error values are also presented. The results show that water content has stronger effects on the physical properties and excess thermodynamic properties of ILs for the binary system of H_2O + [BMIM][CF_3SO_3]. The volumetric and transport properties of the hydrophilic ILs can be significantly varied by adding water or changing temperature to meet the needs of industrial requirement. Furthermore, the present results add useful data on imidazolium-based ILs to the growing database on ionic liquid properties, a database which is essential for the many applications of these liquids currently under exploration.

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