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Volumetric Properties of Binary Mixtures Containing Ionic Liquids and Some Aprotic Solvents

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Densities of six binary mixtures containing the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide or 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide mixed with tetrahydrofuran or acetonitrile or dimethyl sulfoxide were determined at atmospheric pressures in the temperature range between 293.15 K and 313.15 K. On the basis of the experimental densities, excess molar volumes were calculated. Comparison of excess molar volumes of six binary systems reveals the slight influence of the IL's cation on these physical properties and the small temperature dependence of V^E for systems containing dimethyl sulfoxide.

Introduction

Ionic liquids (IL) are known to be a new and partly well-established class of liquids used in many fields of application such as chemical separation processes, new catalytic reaction, electrochemistry, heat transfer, solar energy techniques, and many other more special areas.[1–9] The chemical complexity of the cations and anions involved in the liquid structure exhibit also a challenge for theoreticians to understand the thermophysical properties on a molecular basis using molecular dynamics. However, reliable molecular force fields needed for such calculations have to be tested against systematic experimentally determined thermodynamic properties, in the first place caloric properties such as heat capacities and volume properties such as densities and excess volumes in the case of IL + solvent mixtures. In this paper, we present a new series of densities of such binary mixtures providing useful experimental material for testing molecular dynamics calculations and the force field parameters on which these calculations are based.

Experimental Section

Chemicals. The characteristic data of all chemicals used, as well as the water content (determined by means of Coulometric Karl Fischer Titrator, Titroline KF Trace, Schott Instruments GmbH, with standard deviations (3 to 5) ppm), are presented in Table 1. In this table, there are also the literature data[10–33] and experimental densities of the pure substances used in this work.

The ionic liquids 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM NTf_2) and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIM NTf_2) have been dried and degassed under vacuum at elevated temperatures. Tetrahydrofuran (THF), acetonitrile, and dimethyl sulfoxide (DMSO) were used without any other purification after checking the water content and comparing their densities with the literature values. They were also degassed in ultrasonic cleaner before using. During the experiment, the quality of all chemicals was periodically checked by density measurements.

Density Measurements. The densities of all pure chemicals and the corresponding mixtures were measured using a vibrating-tube densimeter (model Anton Paar DMA 602). This measuring set is well-known and has widely been used in the literature. However, in special cases this method implies problems as soon as the viscosities of binary components differ too much from each other. Therefore, one has to decide carefully when viscosity corrections have to be taken into account. Second, the apparatus has to be calibrated at all temperatures using very clean water and air of known humidity. The description of experimental details and procedures has already been reported elsewhere;[34] the estimated experimental error was ± 0.00002 $g\cdot cm^{-3}$ (when the viscosity correction is applied). During our procedure, the correctness of the values obtained was regularly checked by comparison of densities determined for some typical solvents (nonane, cyclohexane, and dichloromethane) where reliable densities are known from the literature.

Since the viscosities of our ionic liquids (EMIM NTf_2 and BMIM NTf_2) are not very high (62.64 $mPa\cdot s$ for BMIM NTf_2, 38.98 $mPa\cdot s$ for EMIM NTf_2 at 293.15 K[10]), it is justified to suppose that the influence of viscosity correction on the V^E data is not very significant. According to an analysis made by Sanmamed and co-workers,[34] it follows that for our binary mixtures density error caused by viscosity can not be higher than 0.0001 $g\cdot cm^{-3}$ (eq 4 and Figure 3 in Sanmamed et al.[35]). This corresponds also to the analysis made by some of us in an earlier paper.[34] On this basis, we calculated the influence of viscosity corrections on the excess molar volumes, V^E, in our present systems. A maximal shift of V^E of about 0.03 $cm^3\cdot mol^{-1}$ was obtained in the worst case (for very concentrated solutions of BMIM NTf_2), which is eventually about a few percent of any V^E value. As a result, neglecting the viscosity correction does not change the data significantly in a quantitative sense.

Results and Discussion

The density measurements, ρ, for six binary mixtures were carried out for the total concentration range at temperatures from (293.15 to 313.15) K (in the case of mixtures containing THF to 308.15 K) in steps of 5 K. The experimental densities are presented in Tables 2 to 7.

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Table 1. Source, Purity, Density ρ, and Amount of Water in Pure Compounds at 298.15 K

compound	source and purity	amount of water	$\rho/(\mathrm{g\cdot cm^{-3}})$ this work	$\rho/(\mathrm{g\cdot cm^{-3}})$ literature	AAD/(%)[a]
tetrahydrofuran	Sigma-Aldrich, puriss. p.a.	107 ppm	0.88198	0.88193[c] 0.88195[d,e] 0.88198[f] 0.881996[g] 0.88201[h] 0.8821[i]	0.004
acetonitrile	HiPerSolv Chromanorm, for HPLC-Isocratic grade	15 ppm	0.77652	0.7762[j] 0.77628[k] 0.7765[l] 0.776533[g] 0.77655[m] 0.776565[h] 0.77662[n] 0.77673[o]	0.016
dimethyl sulfoxide	Fluka Analytical, Puriss p.a. ACS ≥ 99.9 %	148 ppm	1.09530	1.09527[g] 1.09530[h] 1.09534[o] 1.09556[p] 1.0956[q] 1.0959[r]	0.019
EMIM NTf_2	Io-li-tech, 99.9 %	25 ppm	1.51696 (1.51656)[b]	1.51471[s] 1.5187[t] 1.519[u]; 1.5219[v] 1.52[w]; 1.5252[x]	0.24
BMIM NTf_2	Io-li-tech, 99.9 %	39 ppm	1.43683 (1.43634)[b]	1.43573[y]; 1.43601[s] 1.4366[t,z] 1.43664[z] 1.4397[v]	0.063

[a] Absolute Average Deviation $= \sum_{i=1}^{n}|(\rho_{\mathrm{exp}} - \rho_{\mathrm{lit}})/\rho_{\mathrm{exp}}|\cdot(100/n)$. [b] After viscosity correction using viscosity data from ref 10. [c] Ref 11. [d] Ref 12. [e] Ref 13. [f] Ref 14. [g] Ref 15. [h] Ref 16. [i] Ref 17. [j] Ref 18. [k] Ref 19. [l] Ref 20. [m] Ref 21. [n] Ref 22. [o] Ref 23. [p] Ref 24. [q] Ref 25. [r] Ref 26. [s] Ref 27. [t] Ref 28. [u] Ref 29. [v] Ref 10. [w] Ref 30. [x] Ref 31. [y] Ref 32. [z] Ref 33.

Table 2. Densities, ρ, and Excess Molar Volumes, V^E, at Temperatures T for the Binary System EMIM NTf_2 (1) + Tetrahydrofuran (2)

x_1	T/K 293.15	298.15	303.13	308.15
		$\rho/(\mathrm{g\cdot cm^{-3}})$		
0	0.88741	0.88198	0.87647	0.87096
0.1037	1.06502	1.06132	1.05614	1.05120
0.2024	1.17877	1.17360	1.16846	1.16355
0.3255	1.27855	1.27414	1.26966	1.26442
0.3841	1.31559	1.31096	1.30648	1.30180
0.4425	1.34751	1.34257	1.33770	1.33256
0.5469	1.39540	1.39069	1.38578	1.38131
0.6863	1.44480	1.44010	1.43545	1.43062
0.7697	1.46916	1.46451	1.45945	1.45467
0.9177	1.50522	1.50021	1.49517	1.49013
1	1.52208	1.51696	1.51185	1.50680
		$V^E/(\mathrm{cm^3\cdot mol^{-1}})$		
0.1037	−0.707	−0.900	−0.965	−1.054
0.2024	−0.866	−0.930	−1.003	−1.100
0.3255	−0.829	−0.972	−1.115	−1.174
0.3841	−0.791	−0.910	−1.052	−1.170
0.4425	−0.731	−0.811	−0.905	−0.963
0.5469	−0.639	−0.741	−0.823	−0.956
0.6863	−0.395	−0.490	−0.594	−0.668
0.7697	−0.284	−0.380	−0.416	−0.488
0.9177	−0.102	−0.130	−0.152	−0.165

Table 3. Densities, ρ, and Excess Molar Volumes, V^E, at Temperatures T for the Binary System EMIM NTf_2 (1) + Acetonitrile (2)

x_1	T/K 293.15	298.15	303.13	308.15	313.15
			$\rho/(\mathrm{g\cdot cm^{-3}})$		
0	0.78189	0.77652	0.77112	0.76568	0.76020
0.0533	0.94696	0.94154	0.93610	0.93061	0.92526
0.1886	1.18376	1.17850	1.17340	1.16818	1.16268
0.3370	1.31694	1.31168	1.30648	1.30114	1.29639
0.4724	1.39006	1.38482	1.37962	1.37457	1.36951
0.6520	1.45253	1.44740	1.44224	1.43710	1.43202
0.8245	1.49264	1.48758	1.48239	1.47735	1.47228
0.9240	1.51036	1.50526	1.50020	1.49513	1.49011
1	1.52208	1.51696	1.51185	1.50680	1.50174
			$V^E/(\mathrm{cm^3\cdot mol^{-1}})$		
0.0533	−0.337	−0.364	−0.392	−0.421	−0.462
0.1886	−0.605	−0.659	−0.729	−0.792	−0.837
0.3370	−0.648	−0.696	−0.753	−0.796	−0.899
0.4724	−0.583	−0.623	−0.667	−0.726	−0.788
0.6520	−0.409	−0.444	−0.475	−0.504	−0.543
0.8245	−0.206	−0.234	−0.241	−0.264	−0.284
0.9240	−0.083	−0.094	−0.110	−0.117	−0.132

On the basis of the densities, excess molar volumes were calculated according to the equation

$$V^E = V - \sum_{i=1}^{2} x_i V_i \qquad (1)$$

where V is the molar volume; x_i is the mole fraction of component i of the mixture; and V_i is the molar volume of component i of the mixture.

All calculated excess molar volumes are listed in Tables 2 to 7 and are shown in Figures 1 to 6. In Figure 7, a comparison of excess molar volumes of all six mixtures under the test is presented at T = 298.15 K.

For a satisfactory correlation, the change of density with composition was described using the Connors and Wright equation[36]

Table 4. Densities, ρ, and Excess Molar Volumes, V^E, at Temperatures T for the Binary System EMIM NTf_2 (1) + Dimethyl Sulfoxide (2)

	T/K				
x_1	293.15	298.15	303.13	308.15	313.15
	$\rho/(g\cdot cm^{-3})$				
0	1.10031	1.09530	1.09031	1.08527	1.08027
0.0593	1.17370	1.16867	1.16366	1.15866	1.15363
0.1959	1.28973	1.28468	1.27959	1.27453	1.26948
0.3595	1.37556	1.37044	1.36531	1.36026	1.35520
0.5086	1.42776	1.42261	1.41747	1.41242	1.40736
0.6325	1.45988	1.45475	1.44964	1.44459	1.43952
0.7778	1.48912	1.48404	1.47896	1.47389	1.46884
0.9378	1.51361	1.50851	1.50342	1.49838	1.49329
1	1.52208	1.51696	1.51185	1.50680	1.50174
	$V^E/(cm^3\cdot mol^{-1})$				
0.0593	0.344	0.341	0.339	0.334	0.331
0.1959	0.686	0.680	0.679	0.674	0.670
0.3595	0.743	0.741	0.741	0.735	0.731
0.5086	0.635	0.637	0.638	0.633	0.628
0.6325	0.498	0.497	0.496	0.491	0.488
0.7778	0.305	0.298	0.293	0.293	0.288
0.9378	0.141	0.138	0.135	0.133	0.139

Table 5. Densities, ρ, and Excess Molar Volumes, V^E, at Temperatures T for the Binary System BMIM NTf_2 (1) + Tetrahydrofuran (2)

	T/K			
x_1	293.15	298.15	303.13	308.15
	$\rho/(g\cdot cm^{-3})$			
0	0.88741	0.88198	0.87647	0.87096
0.0488	0.97817	0.97369	0.97001	0.96412
0.1139	1.06971	1.06522	1.06065	1.05592
0.1771	1.13661	1.13217	1.12801	1.12234
0.2815	1.21829	1.21374	1.20923	1.20463
0.4048	1.28631	1.28183	1.27724	1.27269
0.4897	1.32141	1.31710	1.31214	1.30742
0.6329	1.36737	1.36288	1.35873	1.35321
0.7468	1.39556	1.39106	1.38629	1.38145
0.9071	1.42674	1.42192	1.41719	1.41245
1	1.44163	1.43683	1.43198	1.42716
	$V^E/(cm^3\cdot mol^{-1})$			
0.0488	−0.442	−0.545	−0.736	−0.718
0.1139	−0.746	−0.860	−0.977	−1.078
0.1771	−0.838	−0.962	−1.124	−1.129
0.2815	−0.847	−0.957	−1.083	−1.199
0.4048	−0.779	−0.892	−1.002	−1.117
0.4897	−0.660	−0.791	−0.843	−0.926
0.6329	−0.472	−0.567	−0.728	−0.668
0.7468	−0.321	−0.406	−0.453	−0.486
0.9071	−0.098	−0.108	−0.141	−0.171

$$\rho = \rho_1 - \left[1 + \frac{bx_1}{(1 - ax_1)}\right](1 - x_1)(\rho_1 - \rho_2) \qquad (2)$$

where ρ_1 and ρ_2 are densities of pure compounds; x_i is the mole fraction of component *i* of the mixture; and the *a* and *b* are fitting constants. Equation 2 was until now generally adopted only for the concentration dependencies of surface tensions,[37] but in our case it also gives a fit better (a low standard deviation from eq 2) than any other simple polynomial.

The coefficients *a* and *b* in eq 2 are presented in Table 8 for all mixtures studied.

The excess volumes were described for each temperature using a Neau equation[38]

$$V^E = x_1(1 - x_1)\sum_{i=0}^{m} A_i\left[x_1 - \frac{1}{(1 + 35x_1)}\right]^i \qquad (3)$$

Table 6. Densities, ρ, and Excess Molar Volumes, V^E, at Temperatures T for the Binary System BMIM NTf_2 (1) + Acetonitrile (2)

	T/K				
x_1	293.15	298.15	303.13	308.15	313.15
	$\rho/(g\cdot cm^{-3})$				
0	0.78189	0.77652	0.77112	0.76568	0.76020
0.0971	1.03465	1.02933	1.02405	1.01947	1.01426
0.2033	1.17545	1.17035	1.16512	1.16025	1.15505
0.2989	1.25206	1.24709	1.24232	1.23721	1.23240
0.4710	1.33515	1.33018	1.32541	1.32049	1.31567
0.6261	1.38043	1.37557	1.37072	1.36588	1.36114
0.7423	1.40479	1.40001	1.39536	1.39045	1.38564
0.8983	1.42903	1.42412	1.41928	1.41454	1.40973
1	1.44163	1.43683	1.43198	1.42716	1.42236
	$V^E/(cm^3\cdot mol^{-1})$				
0.0971	−0.469	−0.503	−0.543	−0.640	−0.692
0.2033	−0.610	−0.659	−0.703	−0.781	−0.831
0.2989	−0.657	−0.712	−0.792	−0.841	−0.921
0.4710	−0.584	−0.621	−0.688	−0.738	−0.801
0.6261	−0.436	−0.471	−0.512	−0.555	−0.611
0.7423	−0.336	−0.369	−0.431	−0.450	−0.480
0.8983	−0.114	−0.107	−0.120	−0.147	−0.159

Table 7. Densities, ρ, and Excess Molar Volumes, V^E, at Temperatures T for the Binary System BMIM NTf_2 (1) + Dimethyl Sulfoxide (2)

	T/K				
x_1	293.15	298.15	303.13	308.15	313.15
	$\rho/(g\cdot cm^{-3})$				
0	1.10031	1.09530	1.09031	1.08527	1.08027
0.1025	1.20234	1.19739	1.19243	1.18749	1.18255
0.1960	1.26315	1.25821	1.25326	1.24831	1.24337
0.2358	1.28338	1.27840	1.27345	1.26849	1.26351
0.3241	1.31945	1.31452	1.30958	1.30464	1.29972
0.4205	1.34972	1.34481	1.33988	1.33499	1.33005
0.4785	1.36467	1.35972	1.35480	1.34987	1.34487
0.5179	1.37361	1.36867	1.36377	1.35886	1.35393
0.5911	1.38828	1.38333	1.37850	1.37359	1.36872
0.6581	1.40007	1.39516	1.39025	1.38542	1.38054
0.8232	1.42306	1.41822	1.41334	1.40848	1.40360
1	1.44163	1.43683	1.43198	1.42716	1.42236
	$V^E/(cm^3\cdot mol^{-1})$				
0.1025	0.525	0.522	0.521	0.515	0.512
0.1960	0.697	0.696	0.695	0.693	0.692
0.2358	0.719	0.722	0.722	0.722	0.726
0.3241	0.757	0.759	0.760	0.761	0.761
0.4205	0.726	0.728	0.729	0.726	0.733
0.4785	0.676	0.686	0.688	0.691	0.708
0.5179	0.650	0.659	0.660	0.662	0.671
0.5911	0.583	0.597	0.589	0.593	0.597
0.6581	0.486	0.495	0.499	0.493	0.500
0.8232	0.276	0.280	0.284	0.287	0.298

where A_i are the fit parameters, and *m* is the degree of polynomial. For all investigated cases, $m \leq 3$.

Values of the coefficients A_i, determined by the least-squares method, are listed in Table 9. Excess molar volumes of the mixtures containing EMIM NTf_2 or BMIM NTf_2 + THF or + acetonitrile, shown in Figures 1, 2, 4, 5, and 7, are negative in the whole concentration range and decrease further with the temperature. For EMIM NTf_2 or BMIM NTf_2 + DMSO, positive V^E values are observed, showing almost no temperature dependence (Figures 3 and 6). The relative magnitude of V^E is in all cases higher than for the IL mixtures containing alcohols.[34,28,39] However, the excess molar volumes obtained in this work are smaller in comparison with the V^E of binary systems IL + water[40] or the same solutes (methanol, THF, acetonitrile, and DMSO) but different ionic liquid (BMIM PF_6).[16] The maxima of the $V^E(x)$ curves are shifted toward smaller concentrations of ionic liquid ($x_{IL} \approx 0.2$ to 0.3). From

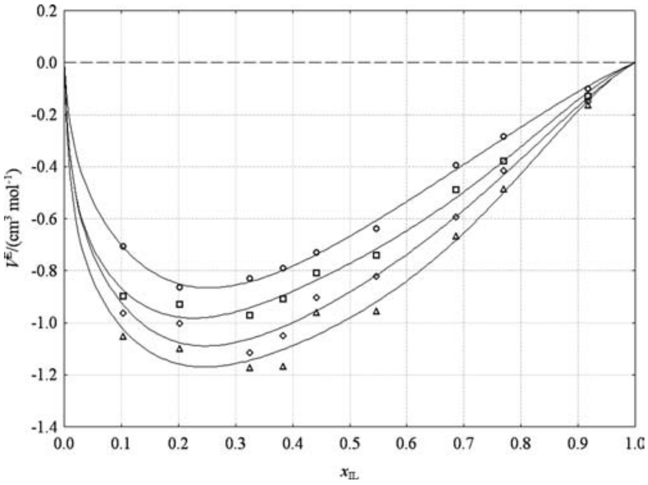

Figure 1. Excess molar volumes of EMIM NTf_2 + tetrahydrofuran at ○, 293.15 K; □, 298.15 K; ◇, 303.15 K; Δ, 308.15 K; points were calculated using eq 1; lines were drawn on the basis of eq 3.

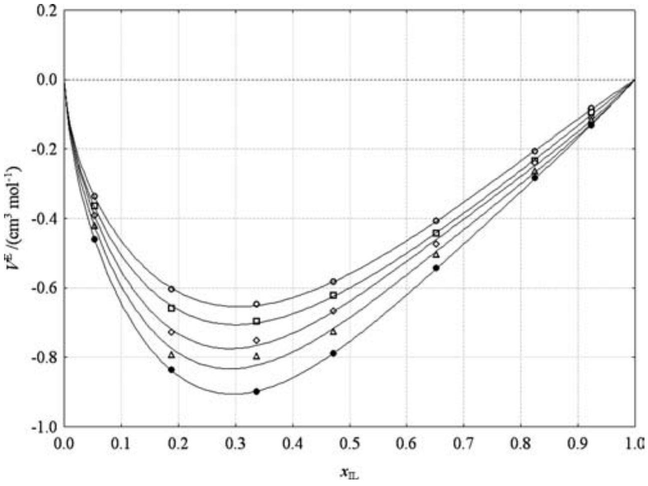

Figure 2. Excess molar volumes of EMIM NTf_2 + acetonitrile at ○, 293.15 K; □, 298.15 K; ◇, 303.15 K, Δ, 308.15 K; ●, 313.15 K; points were calculated using eq 1; lines were drawn on the basis of eq 3.

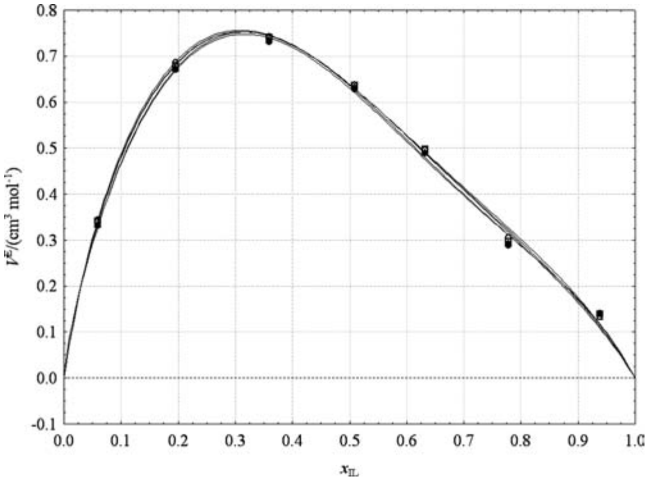

Figure 3. Excess molar volumes of EMIM NTf_2 + dimethyl sulfoxide at ○, 293.15 K; □, 298.15 K; ◇, 303.15 K; Δ, 308.15 K, ●, 313.15 K; points were calculated using eq 1; lines were drawn on the basis of eq 3.

Figure 7, it is also obvious that the excess molar volumes for all mixtures practically do not depend on the kind of IL in the mixture; i.e., the behavior is nearly independent of the cations.

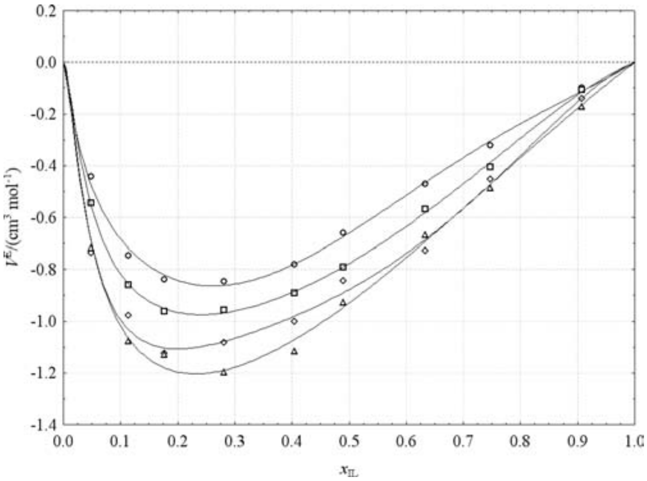

Figure 4. Excess molar volumes of BMIM NTf_2 + tetrahydrofuran at ○, 293.15 K; □, 298.15 K; ◇, 303.15 K; Δ, 308.15 K; points were calculated using eq 1; lines were drawn on the basis of eq 3.

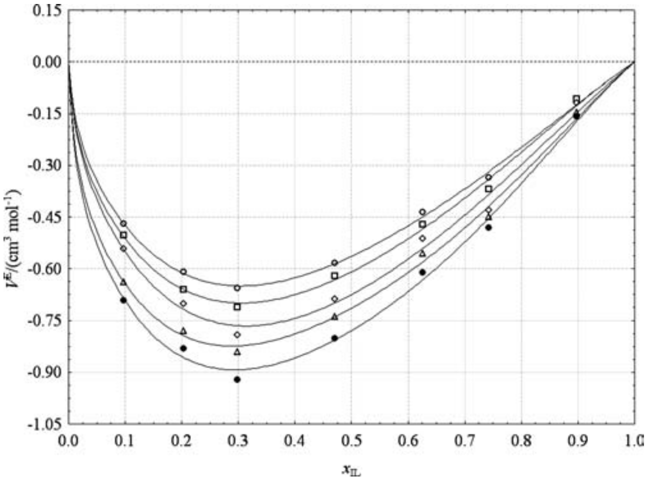

Figure 5. Excess molar volumes of BMIM NTf_2 + acetonitrile at ○, 293.15 K; □, 298.15 K; ◇, 303.15 K; Δ, 308.15 K; ●, 313.15 K; points were calculated using eq 1; lines were drawn on the basis of eq 3.

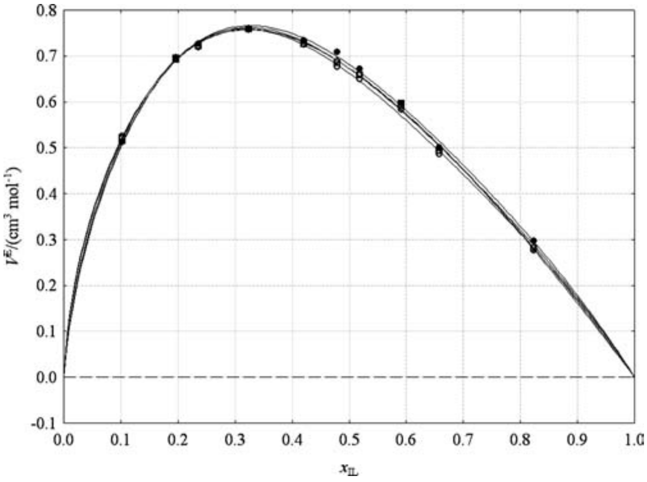

Figure 6. Excess molar volumes of BMIM NTf_2 + dimethyl sulfoxide at ○, 293.15 K; □, 298.15 K; ◇, 303.15 K; Δ, 308.15 K; ●, 313.15 K; points were calculated using eq 1; lines were drawn on the basis of eq 3.

The EMIM NTf_2 + acetonitrile binary system has already been studied in the literature[41] at temperatures different from those in our work. The results fit well into our results; the only significant difference is the perfectly symmetrical shape of the

Table 8. Density Parameters *a* and *b* and Their Standard Deviations and Mean Deviation from Equation 2

	T/K				
	293.15	298.15	303.15	308.15	313.15
	EMIM NTf_2 (1) + Tetrahydrofuran (2)				
a	−2.4070 ± 0.0070	−2.436 ± 0.024	−2.432 ± 0.025	−2.432 ± 0.031	
b	−2.3651 ± 0.0033	−2.387 ± 0.011	−2.392 ± 0.012	−2.397 ± 0.015	
$\delta/(g \cdot cm^{-3})$	0.000087	0.00031	0.00032	0.00042	
	EMIM NTf_2 (1) + Acetonitrile (2)				
a	−4.0704 ± 0.0073	−4.0658 ± 0.0060	−4.0677 ± 0.0082	−4.0634 ± 0.0098	−4.055 ± 0.011
b	−4.0936 ± 0.0043	−4.0903 ± 0.0035	−4.0914 ± 0.0048	−4.0882 ± 0.0058	−4.0947 ± 0.0066
$\delta/(g \cdot cm^{-3})$	0.00010	0.000079	0.00010	0.00012	0.00014
	EMIM NTf_2 (1) + Dimethyl Sulfoxide (2)				
a	−2.3314 ± 0.0099	−2.333 ± 0.010	−2.332 ± 0.010	−2.334 ± 0.010	−2.333 ± 0.011
b	−2.3415 ± 0.0048	−2.3420 ± 0.0049	−2.3405 ± 0.0050	−2.3413 ± 0.0049	−2.3405 ± 0.0054
$\delta/(g \cdot cm^{-3})$	0.000066	0.000074	0.000082	0.000081	0.000086
	BMIM NTf_2 (1) + Tetrahydrofuran (2)				
a	−2.8620 ± 0.0050	−2.888 ± 0.012	−2.946 ± 0.031	−2.945 ± 0.022	
b	−2.8199 ± 0.0025	−2.8435 ± 0.0059	−2.883 ± 0.016	−2.885 ± 0.011	
$\delta/(g \cdot cm^{-3})$	0.000064	0.00016	0.00036	0.00023	
	BMIM NTf_2 (1) + Acetonitrile (2)				
a	−4.733 ± 0.0082	−4.727 ± 0.011	−4.710 ± 0.015	−4.740 ± 0.010	−4.732 ± 0.014
b	−4.7642 ± 0.0050	−4.7589 ± 0.0064	−4.7503 ± 0.0092	−4.7704 ± 0.0060	−4.7667 ± 0.0082
$\delta/(g \cdot cm^{-3})$	0.000084	0.00010	0.00016	0.00011	0.00014
	BMIM NTf_2 (1) + Dimethyl Sulfoxide (2)				
a	−2.7409 ± 0.0063	−2.7479 ± 0.0057	−2.7477 ± 0.0051	−2.7507 ± 0.0048	−2.7568 ± 0.0047
b	−2.7412 ± 0.0032	−2.7427 ± 0.0029	−2.7418 ± 0.0026	−2.7425 ± 0.0024	−2.7434 ± 0.0024
$\delta/(g \cdot cm^{-3})$	0.000048	0.000041	0.000037	0.000035	0.000023

$V^E(x)$ curve presented by Hong and co-workers,[41] whereas our $V^E(x)$ curves have minima shifted toward smaller concentrations of ionic liquid. The analysis of literature data[28,16] for mixtures containing BMIM NTf_2 + alcohols or BMIM PF_6 + acetonitrile

Table 9. Values of the Coefficients A_i, for the Neau Equation (Equation 3), and Standard Deviations δ for Excess Molar Volumes of the Investigated Systems

T/K	A_0[a]	A_1[a]	A_2[a]	A_3[a]	δ[a]
		EMIM NTf_2 (1) + Tetrahydrofuran (2)			
293.15	−6.148 ± 0.088	11.96 ± 0.66	−11.5 ± 2.0	4.9 ± 1.8	0.017
298.15	−7.25 ± 0.16	16.7 ± 1.2	−21.5 ± 3.7	11.3 ± 3.2	0.031
303.15	−7.87 ± 0.23	16.8 ± 1.7	−20.4 ± 5.4	10.4 ± 4.7	0.044
308.15	−8.53 ± 0.27	19.1 ± 2.0	−26.3 ± 6.3	14.9 ± 5.5	0.052
		EMIM NTf_2 (1) + Acetonitrile (2)			
293.15	−4.286 ± 0.015	6.499 ± 0.078	−5.13 ± 0.23	1.89 ± 0.21	0.0027
298.15	−4.653 ± 0.033	7.15 ± 0.17	−5.43 ± 0.50	1.63 ± 0.45	0.0057
303.15	−5.128 ± 0.053	7.65 ± 0.24	−4.21 ± 0.28	0	0.0096
308.15	−5.522 ± 0.082	8.29 ± 0.37	−4.60 ± 0.43	0	0.015
313.15	−5.975 ± 0.012	8.931 ± 0.064	−5.50 ± 0.19	0.76 ± 0.17	0.0022
		EMIM NTf_2 (1) + Dimethyl Sulfoxide (2)			
293.15	4.751 ± 0.079	−5.54 ± 0.27	0	3.06 ± 0.39	0.014
298.15	4.706 ± 0.088	−5.39 ± 0.29	0	2.82 ± 0.43	0.015
303.15	4.693 ± 0.089	−5.33 ± 0.30	0	2.68 ± 0.44	0.015
308.15	4.648 ± 0.083	−5.26 ± 0.28	0	2.63 ± 0.41	0.014
313.15	4.627 ± 0.097	−5.27 ± 0.33	0	2.69 ± 0.48	0.017
		BMIM NTf_2 (1) + Tetrahydrofuran (2)			
293.15	−6.092 ± 0.089	10.45 ± 0.44	−5.88 ± 0.56	0	0.021
298.15	−6.95 ± 0.11	13.01 ± 0.63	−11.7 ± 2.1	4.4 ± 2.0	0.026
303.15	−8.07 ± 0.15	17.54 ± 0.82	−21.0 ± 2.7	10.3 ± 2.6	0.034
308.15	−8.65 ± 0.13	16.82 ± 0.72	−15.1 ± 2.3	5.0 ± 2.2	0.029
		BMIM NTf_2 (1) + Acetonitrile (2)			
293.15	−4.313 ± 0.058	7.02 ± 0.45	−6.7 ± 1.4	2.9 ± 1.2	0.011
298.15	−4.645 ± 0.094	7.65 ± 0.74	−7.7 ± 2.2	3.7 ± 1.9	0.018
303.15	−5.02 ± 0.16	8.0 ± 1.2	−7.8 ± 3.7	3.6 ± 3.2	0.031
308.15	−5.68 ± 0.11	10.54 ± 0.86	−12.1 ± 2.6	5.9 ± 2.2	0.021
313.15	−6.12 ± 0.12	11.24 ± 0.97	−13.1 ± 2.9	6.7 ± 2.5	0.024
		BMIM NTf_2 (1) + Dimethyl Sulfoxide (2)			
293.15	4.826 ± 0.036	−6.46 ± 0.18	3.53 ± 0.24	0	0.0078
298.15	4.824 ± 0.032	−6.82 ± 0.28	5.36 ± 0.85	−1.76 ± 0.75	0.0068
303.15	4.820 ± 0.021	−6.72 ± 0.18	4.96 ± 0.57	−1.35 ± 0.49	0.0045
308.15	4.784 ± 0.032	−6.18 ± 0.17	3.33 ± 0.21	0	0.0070
313.15	4.778 ± 0.032	−6.06 ± 0.17	3.27 ± 0.21	0	0.0070

[a] Units: $cm^3 \cdot mol^{-1}$.

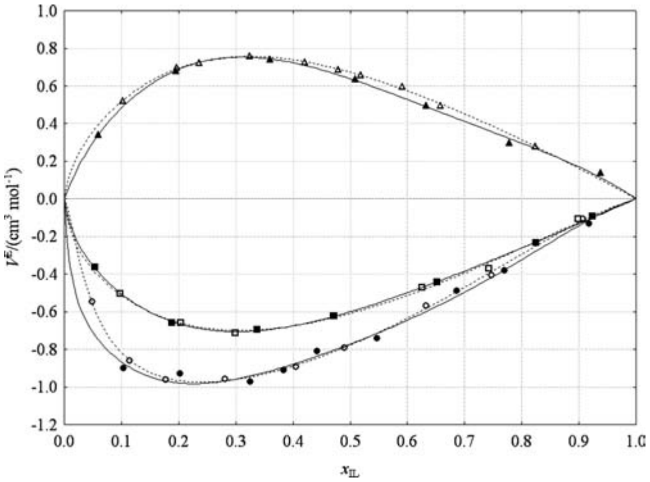

Figure 7. Excess molar volumes of six binary mixtures at 298.15 K: ●, EMIM NTf_2 + tetrahydrofuran; ■, EMIM NTf_2 + acetonitrile; ▲, EMIM NTf_2 + dimethyl sulfoxide; ○, BMIM NTf_2 + tetrahydrofuran; □, BMIM NTf_2 + acetonitrile; Δ, BMIM NTf_2 + dimethyl sulfoxide; points were calculated using eq 1; lines were drawn on the basis of eq 3. Solid lines are for mixtures with EMIM NTf_2, and dotted lines are for mixtures with BMIM NTf_2.

allows us to conclude that the nonsymmetrical $V^E(x)$ shapes are more common than the symmetrical ones.

Zafarani-Moattar and co-workers[16] studied excess molar volumes of binary mixtures of BMIM PF_6 with THF, acetonitrile, and DMSO, i.e., the same solvents as we studied. The order of changes of V^E is the same as in our work, IL + THF < IL + acetonitrile < IL + DMSO, but they are all significantly shifted to more negative values. These authors have observed results from very large and negative V^E for the BMIM PF_6 + THF system to small but still negative V^E for the BMIM PF_6 + DMSO mixture. This indicates a distinct anion influence (PF_6^- and NTf_2^-) on the IL behavior in these solvents.

We resisted the temptation to present a more detailed analysis of the molecular reasons for the behavior observed. This attempt would have a pure speculative character.

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