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Refractive Indices and Deviations in Refractive Indices of Trifluoromethanesulfonate-Based Ionic Liquids in Water

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ABSTRACT: Refractive indices were determined for four different ionic liquid + water binary systems, from (288.15 to 338.15) K, and covering the entire composition range. The four ionic liquids used were 1-ethyl-3-methylimidazolium trifluoromethanesulfonate, 3-butyl-1-ethylimidazolium trifluoromethanesulfonate, 3-butyl-1-methylimidazolium trifluoromethanesulfonate, and 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate, all of them being completely miscible in water. From the experimental data, deviations in refractive indices, defined on a volume fraction basis, have been calculated and fitted to an extended version of the Redlich−Kister equation. The behavior of the deviations in refractive indices with composition, temperature, and size of the anion of ionic liquid has been analyzed and compared with that presented by the excess molar volume of the same systems.

INTRODUCTION

Ionic liquids (ILs) are organic salts with a high degree of asymmetry that inhibits crystallization, consequently having melting points below 100 °C. The cation can be any of a variety of species: imidazolium (the most popular), pyridinium, quaternary ammonium, tetraalkylphosphonium, and pyrrolidinium. The anion can be halide, nitrate, acetate, trifluoroacetate, tetrafluoroborate, trifluoromethanesulfonate, alkylsulfate, and others. These cations, substituents, and anions can be modified to change their chemical and physical properties.[1] ILs exhibit unique properties as alternatives to traditional solvents: they are liquid in a wide range of temperatures, and they have a high thermal stability, a low flammability, and very low vapor pressure.[2] The use of ILs in separation processes is one of multiple alternatives.[3]

To better understand the nature of ILs and expand their applications as well as to design any technological processes, detailed knowledge on the physical, thermodynamic, and transport properties of ILs is required.[4] In the present work, we report refractive indices of binary mixtures of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate, 3-butyl-1-ethylimidazolium trifluoromethanesulfonate, 3-butyl-1-methylimidazolium trifluoromethanesulfonate, and 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate with water over the whole range of compositions, at temperatures from (288.15 to 338.15) K. Volumetric and ultrasonic properties of [emim][triflate] with water have been studied in an earlier work.[5] The values of the deviations in refractive indices were then calculated from the measured refractive index data and fitted to polynomial equations.

Currently, only a few investigations about refractive indices of IL + water systems have been accomplished, mostly at 298.15 K. As far as we know, only Shekaari et al. have reported the refractive indices of some IL + water mixtures at different temperatures, the ILs being 1-pentyl-3-methylimidazolium chloride,[6] 1-butyl-3-methylimidazolium chloride,[7] 1-butyl-3-methylimidazolium iodide,[7] and 1-propyl-3-methylimidazolium methylsulfate.[8] We have not found in the literature experimental refractive index measurements for the binary mixtures studied in this work.

EXPERIMENTAL SECTION

The ILs used were 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][triflate], CAS No. 145022-44-2), 3-butyl-1-ethylimidazolium trifluoromethanesulfonate ([beim][triflate], CAS No. 145022-48-6), 3-butyl-1-methylimidazolium trifluoromethanesulfonate ([bmim][triflate], CAS No. 174899-66-2), and 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate ([bmpyr][triflate], CAS No. 367522-96-1). Because of their hygroscopic character, they were vacuum-dried prior to use. The water mass fraction in the ILs determined by Karl Fischer titration was $x_w < 0.0005$. The water used in binary systems was purchased from Merck, chromatography grade (residue on evaporating $< 5\ \mathrm{g \cdot m^{-3}}$), and it was used without further purification. The chemical specifications of the materials used are reported in Table 1. As shown in Table 2, refractive indices, densities, and speed of sound of all of the chemicals gave a good agreement with the corresponding literature values.[5,9−15]

Samples of (4 to 7) g were prepared by filling glass vials with the liquids and weighing them on a Mettler XP205 Delta Range analytical balance, which was measured with a precision of 0.00001 g. Vials were closed with screw caps to ensure a secure seal and prevent evaporation. The uncertainty in mole fractions was estimated to be less than 0.00001.

Measurements of the refractive index n_D of pure components and binary mixtures were carried out using an automatic refractometer (ABBEMAT-HP, Dr. Kernchen) with a proportional temperature controller that kept the samples at working temperature with an accuracy of 0.01 K. The apparatus was calibrated by measuring the refractive index of Millipore quality water and tetrachloroethylene. The calibration was checked every day with Millipore quality water. Standard uncertainties of measurements were estimated to be less than $5 \cdot 10^{-5}$.

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Table 1. Specifications of Chemical Samples

chemical name	source	mass fraction purity	purification method	final water mass fraction	analysis method
water	Merck	[e]	none		
[emim][triflate][a]	Solvent Innovation	> 0.98	vacuum desiccation	< 0.0005	KF[f]
[beim][triflate][b]	Solvent Innovation	> 0.98	vacuum desiccation	< 0.0005	KF[f]
[bmim][triflate][c]	Solvent Innovation	> 0.98	vacuum desiccation	< 0.0005	KF[f]
[bmpyr][triflate][d]	IoLiTec	> 0.99	vacuum desiccation	< 0.0005	KF[f]

[a] [emim][triflate] = 1-ethyl-3-methylimidazolium trifluoromethanesulfonate. [b] [beim][triflate] = 3-butyl-1-ethylimidazolium trifluoromethanesulfonate. [c] [bmim][triflate] = 3-butyl-1-methylimidazolium trifluoromethanesulfonate. [d] [bmpyr][triflate] = 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate. [e] Conductivity at 298.15 K: $\sigma \leq 1\ \mu\text{S}\cdot\text{cm}^{-1}$. [f] KF = Karl Fischer titration.

Table 2. Comparison of Experimental Density, ρ, Refractive Index, n_D, and Speed of Sound, u, of ILs at 298.15 K with Literature Data

	$\rho/\text{kg}\cdot\text{m}^{-3}$		n_D		$u/\text{m}\cdot\text{s}^{-1}$	
	exptl	lit.	exptl	lit.	exptl	lit.
[emim][triflate]	1383.58	1383.60[a]	1.43322	1.43338[b]	1435.6	1435.6[c]
[beim][triflate]	1263.13	1270[d]	1.43944		1373.1	
[bmim][triflate]	1297.43	1296.8[e]	1.43729	1.4368[f]	1393.0	1392.1[g]
[bmpyr][triflate]	1252.01	1252.5[h]	1.43267		1461.4	

[a] Reference 9. [b] Reference 10. [c] Reference 5. [d] Reference 11 at 295.15 K. [e] Reference 12. [f] Reference 13. [g] Reference 14. [h] Reference 15.

Measurements of the density and speed of sound of pure components were carried out using a digital vibrating-tube densimeter and sound analyzer Anton Paar DSA 5000. Standard uncertainties of density and speed of sound measurements were estimated to be lower than 0.007 $\text{kg}\cdot\text{m}^{-3}$ and 0.1 $\text{m}\cdot\text{s}^{-1}$, respectively.

RESULTS AND DISCUSSION

Values of experimental refractive indices n_D are summarized in Table 3 for binary mixtures of IL (1) ([emim][triflate], [beim][triflate], [bmim][triflate], or [bmpyr][triflate]) with water (2) as a function of IL mole fraction x_1 at temperatures from (288.15 to 338.15) K. It can be seen that the refractive index of all of the mixtures always increases with IL mole fraction and decreases with temperature.

Deviations in refractive index, Δn_D, like any other deviation of a physical property of a liquid mixture, is defined as the difference between the refractive index of mixture n_D and an "ideal" refractive index of mixture

$$\Delta n_D = n_D - n_D^{\text{id}} \tag{1}$$

The ways of defining the "ideal" refractive index of a liquid mixture from the refractive indices of pure components, applying a mixing rule, have been object of controversy in the literature. Early works defined n_D^{id} on a mole fraction x_i basis,

$$n_D^{\text{id}} = x_1 n_{D,1} + x_2 n_{D,2} \tag{2}$$

where x_i and $n_{D,i}$ are the mole fraction and the refractive index of pure component i, respectively, at the same temperature and pressure conditions. The "ideal" refractive index defined by eq 1 leads to

$$\Delta_x n_D = n_D - (x_1 n_{D,1} + x_2 n_{D,2}) \tag{3}$$

Most papers dealing with refractive indices of IL + solvent mixtures define the deviations from the "ideal" mixture in this way.

Brocos et al.[16] and Iglesias-Otero et al.[17] have stated that deviations in refractive index given by eq 3 have no physical ground and usually give meaningless results. It can be a convenient means of reporting high-quality data but is not physically significant. On the contrary, they suggest defining n_D^{id} on a volume fraction basis, ϕ_i $(= x_i V^{\circ}_i / V_m^{\text{id}})$, V°_i, and V_m^{id} $(= x_1 V^{\circ}_1 + x_2 V^{\circ}_2)$ being the volume fraction, the molar volume of component i, and the ideal-mixture molar volume, respectively.

However, there are different ways of defining the "ideal" refractive index of a liquid mixture on a volume fraction basis. The following equation proposed by Brocos et al.[16]

$$n_D^{\text{id}} = \phi_1 n_{D,1} + \phi_2 n_{D,2} \tag{4}$$

has been used for IL-containing mixtures by Singh and Kumar,[18,19] Singh et al.,[20] and Anouti et al.[21,22]

Iglesias-Otero et al.[17] proposed a more rigorous definition of the "ideal" refractive index of a liquid mixture in the way

$$n_D^{\text{id}} = \left[\frac{(n_{D,1})^2 (n_{D,2})^2 + 2\phi_1 (n_{D,1})^2 + 2\phi_2 (n_{D,2})^2}{2 + \phi_1 (n_{D,2})^2 + \phi_2 (n_{D,1})^2}\right]^{1/2} \tag{5}$$

which has been used by Vercher et al.[23] Equation 5 can be substantially simplified to eq 4 under the assumption that the difference between the refractive indices of the two components is small.[17]

Recently, Reis et al.[24] have proposed the following expression for the "ideal" refractive index

$$n_D^{\text{id}} = [\phi_1 (n_{D,1})^2 + \phi_2 (n_{D,2})^2]^{1/2} \tag{6}$$

In any case, it seems evident[16,17,24] that any definition of deviation of refractive index of a liquid mixture must be founded on an "ideal" refractive index of liquid mixture on a volume fraction basis.

Taking into account the great difference between the refractive indices of ILs and water, we have taken for "ideal" refractive index the definition proposed by Iglesias-Otero et al.[17] (eq 5), and hence the deviations in refractive index are given by

$$\Delta_\phi n_D = n_D - \left[\frac{(n_{D,1})^2 (n_{D,2})^2 + 2\phi_1 (n_{D,1})^2 + 2\phi_2 (n_{D,2})^2}{2 + \phi_1 (n_{D,2})^2 + \phi_2 (n_{D,1})^2}\right]^{1/2} \tag{7}$$

The values of $\Delta_\phi n_D$ calculated from eq 7 were correlated with the IL volume fraction, ϕ_1, by means of the Redlich–Kister[25]

Table 3. Values of the Refractive Index n_D of IL (1) + Water (2) Mixtures at T = (288.15 to 338.15) K as a Function of the IL Mole Fraction x_1[a]

	T/K					
x_1	288.15	298.15	308.15	318.15	328.15	338.15
			[emim][triflate] + Water			
0	1.33351	1.33250	1.33123	1.32965	1.32784	1.32581
0.04954	1.37143	1.36929	1.36693	1.36455	1.36203	1.35943
0.09990	1.39058	1.38737	1.38545	1.38286	1.38018	1.37739
0.14834	1.40106	1.39803	1.39582	1.39377	1.39109	1.38829
0.19940	1.40835	1.40554	1.40276	1.39987	1.39710	1.39415
0.30511	1.41770	1.41490	1.41210	1.40921	1.40629	1.40338
0.39515	1.42298	1.42008	1.41711	1.41448	1.41212	1.40853
0.49028	1.42752	1.42456	1.42150	1.41900	1.41627	1.41302
0.60800	1.42996	1.42722	1.42441	1.42164	1.41891	1.41621
0.69535	1.43186	1.42930	1.42634	1.42360	1.42084	1.41807
0.79941	1.43369	1.43086	1.42814	1.42537	1.42264	1.41989
0.84121	1.43434	1.43152	1.42896	1.42620	1.42347	1.42083
0.88772	1.43497	1.43210	1.42942	1.42669	1.42394	1.42121
0.93994	1.43567	1.43277	1.43011	1.42732	1.42452	1.42181
1	1.43599	1.43320	1.43040	1.42767	1.42494	1.42222
			[beim][triflate] + Water			
0	1.33352	1.33250	1.33123	1.32966	1.32784	1.32581
0.05002	1.37880	1.37638	1.37400	1.37145	1.36886	1.36608
0.09989	1.39889	1.39615	1.39343	1.39061	1.38813	1.38556
0.15004	1.41026	1.40736	1.40440	1.40141	1.39882	1.39592
0.19938	1.41759	1.41444	1.41153	1.40850	1.40541	1.40227
0.30226	1.42638	1.42339	1.42038	1.41740	1.41445	1.41150
0.39626	1.43092	1.42795	1.42495	1.42193	1.41894	1.41593
0.49335	1.43425	1.43128	1.42834	1.42535	1.42239	1.41941
0.59563	1.43696	1.43402	1.43111	1.42816	1.42524	1.42231
0.69869	1.43871	1.43579	1.43291	1.42999	1.42710	1.42420
0.78909	1.44000	1.43710	1.43424	1.43134	1.42846	1.42562
0.84434	1.44063	1.43775	1.43482	1.43191	1.42901	1.42616
0.89149	1.44130	1.43833	1.43553	1.43265	1.42980	1.42697
0.95002	1.44182	1.43890	1.43597	1.43313	1.43029	1.42744
1	1.44235	1.43944	1.43650	1.43358	1.43073	1.42788
			[bmim][triflate] + Water			
0	1.33352	1.33250	1.33123	1.32966	1.32784	1.32581
0.04988	1.37738	1.37473	1.37195	1.36953	1.36693	1.36426
0.09969	1.39576	1.39312	1.39045	1.38765	1.38478	1.38184
0.15004	1.40745	1.40435	1.40153	1.39865	1.39571	1.39278
0.19975	1.41452	1.41154	1.40873	1.40574	1.40278	1.39978
0.30110	1.42293	1.42006	1.41705	1.41432	1.41142	1.40852
0.40511	1.42902	1.42610	1.42317	1.42028	1.41736	1.41441
0.49681	1.43220	1.42930	1.42640	1.42362	1.42074	1.41783
0.59400	1.43473	1.43187	1.42904	1.42620	1.42334	1.42046
0.70373	1.43670	1.43385	1.43104	1.42820	1.42539	1.42257
0.80103	1.43813	1.43530	1.43243	1.42962	1.42683	1.42402
0.85700	1.43884	1.43599	1.43319	1.43039	1.42758	1.42480
0.89528	1.43902	1.43618	1.43337	1.43055	1.42775	1.42496
0.94012	1.43949	1.43665	1.43383	1.43103	1.42823	1.42548
1	1.44011	1.43729	1.43448	1.43167	1.42889	1.42614
			[bmpyr][triflate] + Water			
0	1.33352	1.33250	1.33123	1.32966	1.32784	1.32581
0.05008	1.37531	1.37325	1.37130	1.36947	1.36697	1.36399
0.09882	1.39427	1.39160	1.38977	1.38733	1.38434	1.38181
0.15104	1.40522	1.40248	1.40032	1.39829	1.39574	1.39318
0.19932	1.41191	1.40911	1.40659	1.40414	1.40150	1.39896
0.29969	1.41984	1.41694	1.41405	1.41124	1.40899	1.40651
0.39694	1.42477	1.42195	1.41913	1.41627	1.41343	1.41077
0.49924	1.42806	1.42528	1.42248	1.41967	1.41693	1.41416
0.58961	1.43020	1.42744	1.42465	1.42185	1.41911	1.41636
0.69426	1.43190	1.42912	1.42641	1.42365	1.42083	1.41807
0.79984	1.43342	1.43070	1.42795	1.42518	1.42243	1.41972
0.84561	1.43394	1.43117	1.42850	1.42579	1.42305	1.42035
0.89984	1.43446	1.43173	1.42900	1.42624	1.42349	1.42079
0.94047	1.43469	1.43196	1.42926	1.42653	1.42383	1.42114
1	1.43539	1.43267	1.43001	1.42735	1.42468	1.42202

[a] Standard uncertainties u are: $u(T)$ = 0.01 K, $u(n_D) = 5 \cdot 10^{-5}$ and the combined expanded uncertainty U_c is $U_c(x_1)$ = 0.00001 (0.95 level of confidence).

equation

$$\Delta_\phi n_D = \phi_1(1 - \phi_1) \sum_{i=0}^{n} A_i(2\phi_1 - 1)^i \tag{8}$$

Taking into account the influence of temperature on the deviations in refractive index, all of the coefficients A_i for each system have been expressed as a second-order polynomial on T

$$A_i = A_{i_0} + A_{i_1}(T/\mathrm{K} - 273.15) + A_{i_2}(T/\mathrm{K} - 273.15)^2 \tag{9}$$

In this way, the number of coefficients is reduced because the total number of parameters for each binary system will not be $(t \cdot k)$ but $(3k)$, where $k = n + 1$ is the total number of adjustable coefficients in each polynomial term, and t is the number of different temperatures tested for each system. Therefore, using eqs 8 and 9, we will simultaneously correlate the deviations in refractive index with the temperature T and the IL volume fraction ϕ_1. The fitting parameters were estimated by the least-squares method, and the values obtained are given in Table 4, together with the standard deviations calculated by applying the expression

$$\sigma = \left[\frac{\sum_{i=1}^{p} (\Delta_\phi n_{D_{\mathrm{exptl},i}} - \Delta_\phi n_{D_{\mathrm{calcd},i}})^2}{p - 3(n + 1)}\right]^{1/2} \tag{10}$$

in which p is the number of experimental data points. The choice of n value for the polynomial degree in eq 8 was ascertained from an examination of the variation in the standard deviation σ. Figure 1 shows, for each binary system, the experimental values of $\Delta_\phi n_D$ versus the IL volume fraction ϕ_1 at all of the temperatures tested, besides the curves obtained using eqs 8 and 9 with the fitting parameters reported in Table 4.

In Figure 1, it can be seen that, at low temperatures, $\Delta_\phi n_D$ values are positive for all of the systems over the whole range of compositions. When the temperature increases, $\Delta_\phi n_D$ values decrease, and they become negative at high IL concentrations for [emim][triflate], [beim][triflate], and [bmim][triflate], whereas they do not have negative values for [bmpyr][triflate] at least at the tested temperatures. This behavior is opposed to that reported previously for mixtures of [emim][triflate] with acetone, methyl acetate and ethyl acetate,[23] and alkanols,[26] in which $\Delta_\phi n_D$ increases with temperature.

Table 4. Coefficients of the Fitting Equation (Equations 8 and 9) for Deviations in the Refractive Index ($\Delta_\phi n_D$) and the Standard Deviations (σ) of the IL (1) + Water (2) Mixtures

	$10^4 A_{i,0}$	$10^6 A_{i,1}$	$10^8 A_{i,2}$	$10^3 \sigma$
		[emim][triflate] + Water		
$i = 0$	155.681	−336.313	185.247	0.093
$i = 1$	−79.182	83.015	−124.549	
$i = 2$	−0.43273	3.7222	−1.4338	
		[beim][triflate] + Water		
$i = 0$	131.036	−419.031	268.907	0.021
$i = 1$	10.982	−96.696	8.7645	
$i = 2$	−0.074737	0.51656	1.5451	
		[bmim][triflate] + Water		
$i = 0$	166.950	−483.204	274.429	0.023
$i = 1$	−102.389	221.758	−278.396	
$i = 2$	−0.40791	3.3098	−0.96262	
		[bmpyr][triflate] + Water		
$i = 0$	96.454	−138.503	48.277	0.029
$i = 1$	54.225	−405.509	455.277	
$i = 2$	−0.55917	4.5838	−4.9450	

Brocos et al.[16] and Iglesias-Otero et al.[17] have shown a strong negative correlation between the deviations in refractive index on a volume basis $\Delta_\phi n_D$ and the excess molar volume on a molar basis V^E, for liquid binary mixtures at a constant temperature and pressure. We have compared our $\Delta_\phi n_D$ data with those reported in the literature for the molar volume V^E of [emim][triflate] + water[5,9,27] and [bmim][triflate] + water.[27] In both cases the correlation is very satisfactory. Negative values of $\Delta_\phi n_D$ corresponded to positive V^E values and vice versa. The positive-to-negative change of sign of $\Delta_\phi n_D$ matches with the negative-to-positive change of sign of V^E, and the temperature effect on $\Delta_\phi n_D$ and V^E is similar in intensity, but opposite in sign. Iglesias-Otero et al.[17] explain this behavior claiming that a positive V^E value means more free volume in the solution, a higher light velocity in the medium, and a refractive index lower than in an ideal solution. This comparison have not could be done for [beim][triflate] + water and [bmpyr][triflate] + water because there are not reported V^E data for these binary systems.

Figure 2 shows deviations in the refractive index for the four IL + water systems at 318.15 K. As it can be seen, there are minor

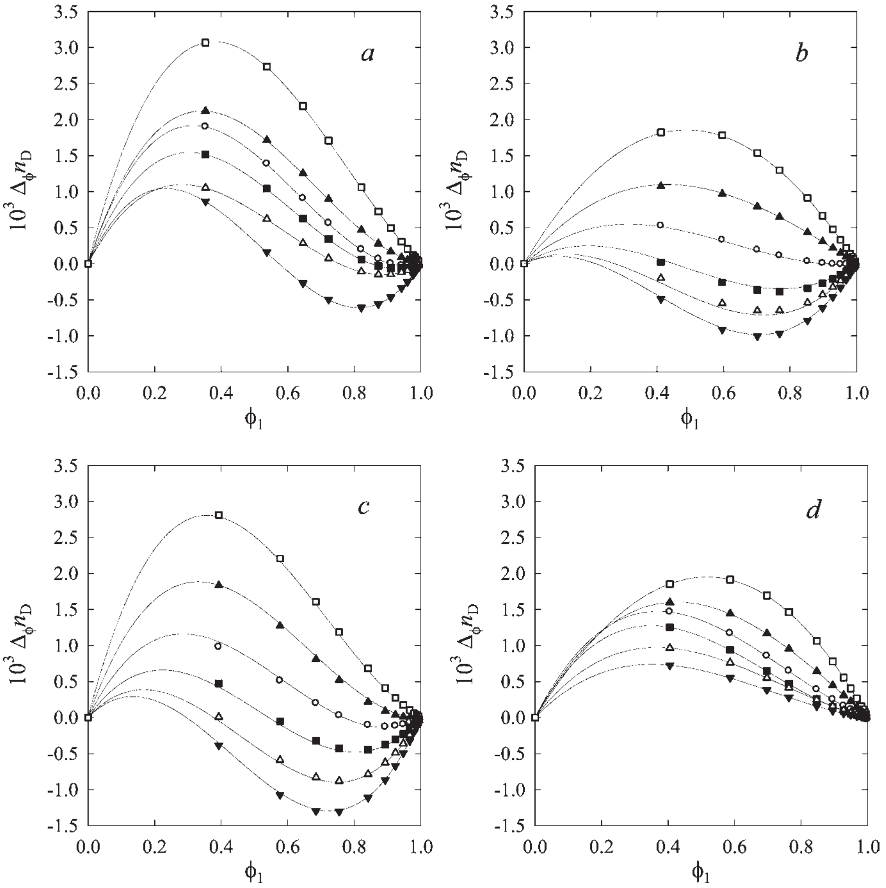

Figure 1. Deviations in the refractive index $\Delta_\phi n_D$ for the IL (1) + water (2) binary systems at different temperatures: □, T = 288.15 K; ▲, T = 298.15 K; ○, T = 308.15 K; ■, T = 318.15 K; △, T = 328.15 K; ▼, T = 338.15 K. The solid lines represent the corresponding correlation by an extended version of the Redlich−Kister equation. IL: (a) [emim][triflate]; (b) [beim][triflate]; (c) [bmim][triflate]; (d) [bmpyr][triflate].

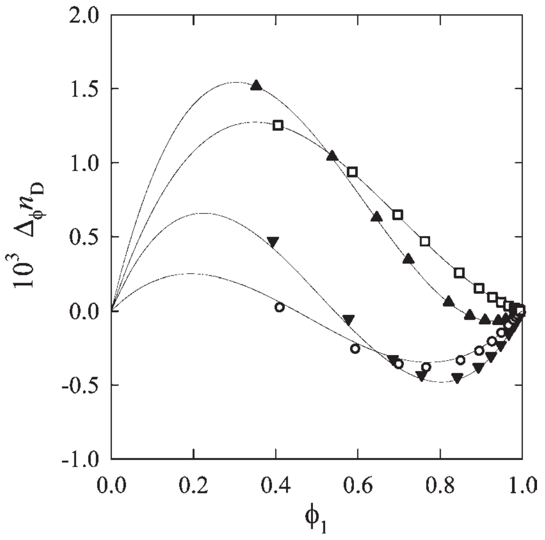

Figure 2. Deviations in the refractive index $\Delta_\phi n_D$ for the IL (1) + water (2) binary systems at T = 318.15 K: ▲, [emim][triflate]; ○, [beim][triflate]; ▼, [bmim][triflate]; □, [bmpyr][triflate]. The solid lines represent the corresponding correlation by using an extended version of the Redlich−Kister equation.

differences between the behavior of the aqueous solutions of the three alkylimidazolium ILs. Given that deviations in the refractive index follow the sequence [emim] > [bmim] > [beim], it seems that $\Delta_\phi n_D$ decreases when the size of alkyl chains of imidazolium ILs increases, which can be due to the expansion of the volume of the substituents.

■ CONCLUSIONS

Deviations in refractive index of mixtures of [emim][triflate], [beim][triflate], [bmim][triflate], and [bmpyr][triflate] with water have been calculated from measured refractive index data at T = (288.15 to 338.15) K in the whole range of concentrations. For each system, the deviations in refractive index on a volume basis were fitted by an extended version of the Redlich−Kister equation, which takes into account simultaneously their dependence on composition and temperature. Deviations in refractive index are positive at lower temperatures, decrease when temperature increases, and can become negative. This behavior is opposed to that reported previously for mixtures of [emim][triflate] with organic solvents, in which $\Delta_\phi n_D$ increases with temperature. A strong correlation between the deviations in refractive index on a volume basis and the excess molar volume for the IL + water system has been found at all tested temperatures. The behavior of both variables is symmetrical and opposite.

As far as the effect of the length of imidazolium alkyl chains is concerned, $\Delta_\phi n_D$ decreases when the length of alkyl chains of imidazolium ILs increases, which can be due to the volume expansion of the substituents.

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