Refractive Indices and Deviations in Refractive Indices for Binary Mixtures of 1-Ethyl-3-methylimidazolium Trifluoromethanesulfonate with Methanol, Ethanol, 1-Propanol, and 2-Propanol at Several Temperatures

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Refractive indices of the binary mixtures of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][triflate]) with methanol, ethanol, 1-propanol, and 2-propanol were experimentally measured over the whole range of compositions at $T = (288.15$ to $338.15)$ K and atmospheric pressure. From the experimental data, deviations in refractive indices have been calculated and fitted to an extended version of the Redlich−Kister equation, which takes into account the dependence on composition and temperature simultaneously. This dependence has been discussed. The deviations are always positive, and their extent follows the sequence methanol > ethanol > 2-propanol > 1-propanol, increasing when temperature increases.

Introduction

Ionic liquids (ILs), salts made up of an organic, greatly asymmetric substituted cation and an inorganic weak anion, exhibit unique properties as alternatives to traditional solvents:[1] very low melting points, a liquidus range of 300 °C, a high thermal stability, a low flammability, and very low vapor pressure.[2] The use of ILs in separation processes is one of the 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 thermodynamic behavior of ILs is required.[4] In the present work, we report refractive indices of binary mixtures of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([emim][triflate]) with methanol, ethanol, 1-propanol, and 2-propanol over the whole range of compositions, at temperatures from (288.15 to 338.15) K. Volumetric and ultrasonic properties of these mixtures 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 temperature and chain dependence of refractive indices of IL + alkanol systems have been accomplished. As far as we know, only [omim][BF_4] + alkanol,[6] [emim][$EtSO_4$] + alkanol,[7,8] and [omim][Cl] + alkanol[9] systems have been reported. We have not found experimental refractive index measurements for binary mixtures of [emim][triflate] with any organic solvent in the literature.

Experimental Section

The IL used was 1-ethyl-3-methylimidazolium trifluoromethanesulfonate supplied by Solvent Innovation (purum, minimum mass fraction 98 %). Because of its hygroscopic character, it was desiccated at 0.2 Pa overnight prior to use. The water mass fraction in the IL determined by Karl Fischer titration was $x_w < 0.05$ %. The solvents used were dried methanol (Riedel-de Haën, analytical reagent, minimum mass fraction 99.8 %), absolute ethanol (Merck, GR grade, minimum mass fraction 99.9 %), 1-propanol (Merck, GR grade, minimum mass fraction 99.5 %), and 2-propanol (Merck, GR grade, minimum mass fraction 99.8 %). These solvents were degassed ultrasonically and dried over molecular sieves of type 3 Å supplied by Grace, and they were used without further purification, their purity being ascertained by gas chromatography. Refractive indices of all of the chemicals at (288.15 and 298.15) K and densities at 298.15 K gave a good agreement with the corresponding literature values,[10−13] as shown in Table 1.

Table 1. Comparison of Experimental Density, ρ, and Refractive Index, n_D, of Pure Liquids with Literature Data

	T	ρ/kg·m^{-3}		n_D	
component	K	exptl	lit.	exptl	lit.
[emim][triflate]	298.15	1383.58	1383.60[a]	1.43322	1.43338[b]
metanol	298.15	786.49	786.49[c]	1.32653	1.3265[d]
	288.15			1.33071	1.3303[d]
ethanol	298.15	785.10	785.07[c]	1.35930	1.3594[d]
	288.15			1.36358	1.3633[d]
1-propanol	298.15	799.56	799.51[d]	1.38318	1.3837[d]
	288.15			1.38732	1.3873[d]
2-propanol	298.15	780.89	780.86[c]	1.37492	1.3752[d]
	288.15			1.37924	1.3792[d]

[a] Ref 10. [b] Ref 11. [c] Ref 12. [d] Ref 13.

Samples of (3 to 5) g were prepared by filling glass vials with the liquids and weighing them on a Mettler XP205 Delta Range analytical balance, which measured with a precision of 0.00001 g. Vials were closed with screw caps to ensure a secure seal and to 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 $2 \cdot 10^{-5}$.

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

	T/K					
x_1	288.15	298.15	308.15	318.15	328.15	338.15
			[emim][triflate] + Methanol			
0	1.33071	1.32653	1.32237	1.31820		
0.04981	1.35401	1.35019	1.34673	1.34425		
0.10059	1.37019	1.36654	1.36360	1.36131		
0.15030	1.38187	1.37846	1.37522	1.37261		
0.20020	1.39131	1.38786	1.38479	1.38175		
0.25165	1.39849	1.39527	1.39212	1.38903		
0.30177	1.40415	1.40103	1.39830	1.39535		
0.39768	1.41297	1.40987	1.40694	1.40394		
0.49902	1.41931	1.41630	1.41325	1.41035		
0.59106	1.42382	1.42086	1.41783	1.41502		
0.70591	1.42818	1.42529	1.42236	1.41954		
0.80539	1.43127	1.42843	1.42553	1.42265		
0.84944	1.43236	1.42952	1.42665	1.42387		
0.90126	1.43359	1.43080	1.42799	1.42515		
1	1.43599	1.43322	1.43040	1.42767		
			[emim][triflate] + Ethanol			
0	1.36358	1.35930	1.35503	1.35073	1.34630	
0.05087	1.37603	1.37224	1.36847	1.36470	1.36088	
0.10037	1.38531	1.38169	1.37828	1.37496	1.37123	
0.15044	1.39279	1.38937	1.38635	1.38336	1.37950	
0.20097	1.39891	1.39566	1.39241	1.38923	1.38584	
0.29906	1.40822	1.40549	1.40179	1.39872	1.39607	
0.39764	1.41506	1.41187	1.40885	1.40581	1.40267	
0.49762	1.42051	1.41741	1.41441	1.41137	1.40841	
0.59345	1.42470	1.42164	1.41857	1.41564	1.41275	
0.69813	1.42832	1.42536	1.42243	1.41956	1.41673	
0.79935	1.43116	1.42826	1.42543	1.42262	1.41981	
0.84070	1.43220	1.42937	1.42653	1.42372	1.42093	
0.89198	1.43344	1.43061	1.42781	1.42501	1.42222	
0.94437	1.43452	1.43172	1.42894	1.42619	1.42346	
1	1.43599	1.43322	1.43040	1.42767	1.42494	
			[emim][triflate] + 1-Propanol			
0	1.38732	1.38318	1.37897	1.37471	1.37036	1.36587
0.05007	1.39381	1.38991	1.38613	1.38243	1.37892	1.37545
0.10135	1.39933	1.39557	1.39221	1.38877	1.38613	1.38306
0.15027	1.40371	1.40010	1.39680	1.39380	1.39112	1.38856
0.20005	1.40743	1.40400	1.40090	1.39795	1.39522	1.39266
0.24971	1.41088	1.40747	1.40434	1.40127	1.39872	1.39631
0.30078	1.41391	1.41061	1.40747	1.40445	1.40173	1.39926
0.39964	1.41854	1.41537	1.41218	1.40923	1.40634	1.40392
0.49649	1.42297	1.41986	1.41681	1.41376	1.41082	1.40780
0.60201	1.42671	1.42372	1.42062	1.41752	1.41447	1.41163
0.70429	1.42943	1.42647	1.42347	1.42076	1.41793	1.41508
0.79450	1.43174	1.42886	1.42604	1.42323	1.42040	1.41758
0.84213	1.43250	1.42963	1.42680	1.42398	1.42115	1.41838
0.89876	1.43378	1.43096	1.42815	1.42533	1.42258	1.41984
1	1.43599	1.43322	1.43040	1.42767	1.42494	1.42222
			[emim][triflate] + 2-Propanol			
0	1.37924	1.37492	1.37048	1.36586	1.36103	1.35599
0.04997	1.38697	1.38304	1.37919	1.37530	1.37148	1.36735
0.09937	1.39302	1.38935	1.38578	1.38236	1.37896	1.37487
0.15041	1.39853	1.39494	1.39186	1.38861	1.38506	1.38103
0.19951	1.40326	1.39957	1.39662	1.39356	1.39032	1.38662
0.25077	1.40739	1.40382	1.40089	1.39817	1.39474	1.39160
0.29966	1.41100	1.40740	1.40439	1.40147	1.39830	1.39544
0.39876	1.41689	1.41365	1.41071	1.40758	1.40457	1.40189
0.50136	1.42209	1.41872	1.41564	1.41261	1.40972	1.40680
0.60119	1.42562	1.42259	1.41956	1.41667	1.41379	1.41098
0.69720	1.42868	1.42574	1.42285	1.41998	1.41714	1.41431
0.79781	1.43159	1.42861	1.42579	1.42298	1.42017	1.41738
0.83423	1.43251	1.42965	1.42678	1.42395	1.42115	1.41837
0.89049	1.43379	1.43098	1.42818	1.42541	1.42264	1.41986
1	1.43599	1.43322	1.43040	1.42767	1.42494	1.42222

Measurements of the density ρ of pure components were carried out using a digital vibrating-tube densimeter Anton Paar DSA 5000. Standard uncertainties of density measurements were estimated to be lower than 0.007 kg·m^{-3}.

Table 3. Coefficients of the Fitting Equation (Equation 2) for Deviations in the Refractive Index (Δn_D) and the Standard Deviations (σ) of the [emim][triflate] (1) + Alkanols (2) Mixtures

	$10^2\ Z_{l,0}$	$10^4\ Z_{l,1}$	$10^6\ Z_{l,2}$	$10^3\ \sigma$
	[emim][triflate] + Methanol			
$Z = A, l = 0$	14.177	1.5666	0.83491	0.136
$Z = A, l = 1$	1.4445	−13.074	28.073	
$Z = A, l = 2$	−1.4961	9.6638	−20.825	
$Z = A, l = 3$				
$Z = B, l = 1$	78.223	−78.285	174.59	
$Z = B, l = 2$				
	[emim][triflate] + Ethanol			
$Z = A, l = 0$	8.1774	0.95991	1.5277	0.136
$Z = A, l = 1$	0.40262	−8.5267	12.247	
$Z = A, l = 2$	−1.0705	10.591	−13.791	
$Z = A, l = 3$	0.0058909	−6.7853	9.5254	
$Z = B, l = 1$	61.492	−88.498	143.57	
$Z = B, l = 2$				
	[emim][triflate] + 1-Propanol			
$Z = A, l = 0$	4.4285	0.24652	2.5216	0.217
$Z = A, l = 1$	−0.39465	3.0326	−3.6001	
$Z = A, l = 2$				
$Z = A, l = 3$				
$Z = B, l = 1$	45.843	35.290	2.4404	
$Z = B, l = 2$				
	[emim][triflate] + 2-Propanol			
$Z = A, l = 0$	5.5321	0.32395	3.1411	0.164
$Z = A, l = 1$	−0.70831	4.3715	−3.6312	
$Z = A, l = 2$				
$Z = A, l = 3$				
$Z = B, l = 1$	31.530	102.08	−76.575	
$Z = B, l = 2$				

Results and Discussion

The experimental values of the refractive index n_D of binary mixtures of [emim][triflate] with methanol, ethanol, 1-propanol, and 2-propanol, as a function of mole fraction x_1 of [emim][triflate] at different temperatures, are listed in Table 2. The deviations in the refractive index Δn_D have been calculated using

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

where x is the mole fraction and the subscripts 1 and 2 represent pure components, [emim][triflate] and alkanol, respectively. The values of Δn_D were correlated with the IL mole fraction, x_1, by means of a modified version[14] of the Redlich−Kister[15] equation

$$\Delta n_D = x_1(1 - x_1)\frac{\sum_{i=0}^{m} A_i(2x_1 - 1)^i}{1 + \sum_{j=1}^{n} B_j(2x_1 - 1)^j} \tag{2}$$

using the Padé (m, n) approximant, which is the best approximation of a function by a rational function of a given order.[16] To take into account the influence of temperature on the excess properties, all of the coefficients A_i and B_j for each system have been expressed as a second-order polynomial on T

$$A_i = A_{i_0} + A_{i_1}(T/\mathrm{K} - 273.15) + A_{i_2}(T/\mathrm{K} - 273.15)^2 \tag{3}$$

$$B_j = B_{j_0} + B_{j_1}(T/\mathrm{K} - 273.15) + B_{j_2}(T/\mathrm{K} - 273.15)^2 \tag{4}$$

Therefore, using eqs 2 to 4, we will simultaneously correlate the excess properties with the temperature T and the IL mole fraction x_1. The fitting parameters were estimated by the least-

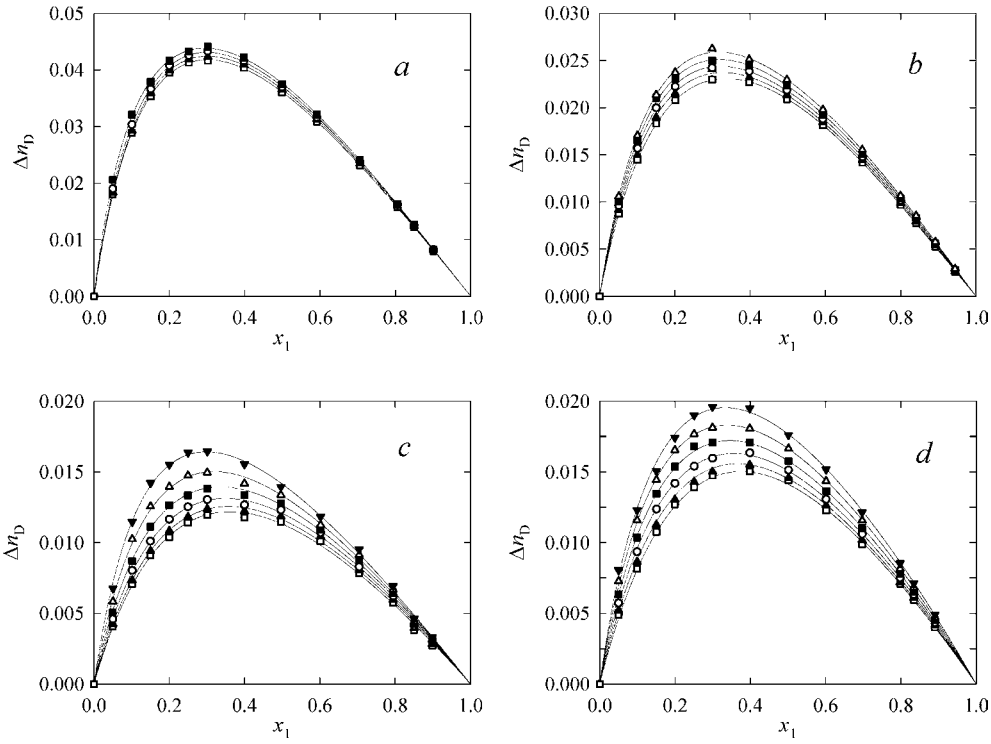

Figure 1. Deviations in the refractive index Δn_D for the [emim][triflate] (1) + alkanol (2) binary systems at different temperatures: □, 288.15 K; ▲, 298.15 K; ○, 308.15 K; ■, 318.15 K; △, 328.15 K; ▼, 338.15 K. The solid lines represent the corresponding correlation by an extended version of the Redlich−Kister equation (eq 2). Alkanol: (a) methanol; (b) ethanol; (c) 1-propanol; (d) 2-propanol.

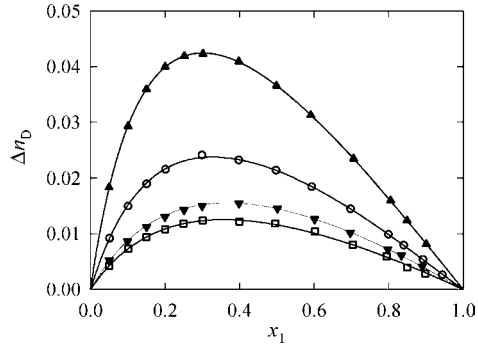

Figure 2. Deviations in the refractive index Δn_D for the [emim][triflate] (1) + alkanol (2) binary systems at 298.15 K: ▲, methanol; ○, ethanol; □, 1-propanol; ▼, 2-propanol. The solid lines represent the corresponding correlation by an extended version of the Redlich−Kister equation (eq 2).

squares method, and the values obtained are given in Table 3, together with the standard deviations calculated by applying the expression

$$\sigma = \left[\frac{\sum_{i=1}^{p} (\Delta n_{D_{exptl,i}} - \Delta n_{D_{calcd,i}})^2}{p - 3(m + n + 1)} \right]^{1/2} \quad (5)$$

in which p is the number of experimental data points. The choice of m and n values for the degrees of polynomics in eq 2 was made using the Akaike's information criterion (AIC).[17] Figure 1 shows the experimental values of Δn_D versus the IL mole fraction x_1 at every temperature tested, together with the curves obtained from eq 2 using the fitting parameters, for every binary system. In Figure 1 it can be seen that Δn_D values are always positive for all of the systems over the entire composition range and at every temperature investigated. The fitting curves are asymmetric, and they present a maximum at values of the IL mole fraction $x_1 \approx 0.35$, which increases and moves to lower values of x_1 when temperature increases, for all of the systems.

Figure 2 shows deviations in the refractive index for the four [emim][triflate] + alkanol systems at 298.15 K. As seen, the extent of deviations in the refractive index from linear dependence on composition follows the sequence methanol > ethanol > 2-propanol > 1-propanol. Thus, for primary alcohols, deviations in the refractive index decrease when the length of the chain of alcohol increases. Moreover, 2-propanol presents refractive index deviations higher than the 1-propanol. Arce et al.[6] and González et al.[8] observed the same behavior for mixtures of ILs with alkanols.

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