Experimental Determination, Correlation, and Prediction of Physical Properties of the Ternary Mixtures Ethanol and 1-Propanol + Water + 1-Ethyl-3-methylpyridinium Ethylsulfate at 298.15 K

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In this work, densities, ρ, refractive indices, n_D, and dynamic viscosities, η, of the ternary mixtures of the alcohols ethanol and 1-propanol + water with 1-ethyl-3-methylpyridinium ethylsulfate [empy][eSO$_4$] have been measured at $T = 298.15$ K and atmospheric pressure. Excess molar volumes, V^E, refractive index deviations, Δn_D, and viscosity deviations, $\Delta\eta$, have been calculated from experimental data and fitted to various correlation equations, obtaining good results. The excess properties have been used to test several prediction models, finding out that symmetric models give lower deviations than asymmetric models.

Introduction

Ionic liquids have been considered as an alternative to volatile organic solvents, but experimental data of physical properties are still limited. There are some literature data of physical properties of pure ionic liquids and of binary mixtures,[1,2] but taking into account the amount of possible ionic liquids, these data are not enough. Experimental data of physical properties of ternary systems are even scarcer in literature. In addition, the correlation and prediction of properties of multicomponent mixtures using models that use information of the properties of their constituent binary mixtures is an area of research in development.

This work is part of a systematic study that is being carried out to determine physical properties of binary and ternary mixtures containing ionic liquids.[3−11] In this paper, density, ρ, refractive index, n_D, and viscosity, η, of the ternary systems ethanol or 1-propanol + water + 1-ethyl-3-methylpyridinium ethylsulfate [empy][eSO$_4$] have been measured. From the physical properties, we can determine the excess molar volumes, V^E, refractive index deviations, Δn_D, and viscosity deviations, $\Delta\eta$. The reason for choosing this ionic liquid and its mixtures is that there is no available literature data of these systems.

Experimental data were correlated using empirical equations[12,13] and predicted using geometrical models that assume that interactions in a ternary mixture depend on the interactions in binary systems.[14−20]

Experimental Section

Chemicals. Ethanol was supplied by Merck with purity higher than 99.8 %, and 1-propanol was purchased by Sigma-Aldrich with purity higher than 99.9 %. They were degassed ultrasonically and dried over molecular sieves type 4 Å, supplied by Aldrich. Water was bidistilled and deionized. The ionic liquid 1-ethyl-3-methylpyridinium ethylsulfate used in this work was synthesized in our laboratory.[11] The ionic liquid was kept in bottles with inert gas. To remove organic solvents and water content to negligible values (mass fraction of water less than $7\cdot10^{-4}$ determined using a 756 Karl Fisher coulometer) vacuum ($2\cdot10^{-1}$ Pa) and moderate temperature (343.15 K) were applied to the IL for several days, always immediately prior to their use. To ensure its purity, a NMR spectrum was performed before and after the measurements, a usual procedure in our laboratory in the work with ionic liquids. No differences in physical properties or NMR spectra were found before and after its using. Table 1 shows a comparison between experimental and literature data of pure components at $T = 298.15$ K. Compared to the literature, the viscosity values for pure [empy][eSO$_4$] are higher than those reported by Crosthwaite et al.[26] The small differences can be due to the water content of ionic liquid (mass fraction of water less than $7\cdot10^{-4}$ for our samples and $2.56\cdot10^{-4}$ for

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Table 1. Comparison of Measured Pure Component Properties Data with Literature Values at $T = 298.15$ K

	ρ (g·cm^{-3})		n_D		$10^3\eta$ (Pa·s)	
	exp	lit.	exp	lit.	exp	lit.
ethanol	0.78546	0.7854[a]	1.35920	1.35941[b]	1.082	1.082[a]
1-propanol	0.79960	0.79960[b]	1.38309	1.38305[c]	2.017	1.951[d]
		0.79952[c]				2.0074[e]
water	0.99705	0.99705[b]	1.33251	1.3325029[b]	0.890	0.89025[b]
[empy][eSO$_4$]	1.22226	na	1.50666	na	161.4	150[f]

[a] From ref 21. [b] From ref 22. [c] From ref 23. [d] From ref 24. [e] From ref 25. [f] From ref 26.

Table 2. Densities, ρ, Refractive Indices, n_D, Dynamic Viscosities, η, Excess Molar Volumes, V^E, Refractive Index Deviations, Δn_D, and Viscosity Deviations, $\Delta\eta$, for the Binary System 1-Propanol (1) + [empy][eSO$_4$] (2) at $T = 298.15$ K

x_1	ρ (g·cm^{-3})	n_D	$10^3\,\eta$ (Pa·s)	V^E (cm^3·mol^{-1})	Δn_D	$10^3\,\Delta\eta$ (Pa·s)
0.0000	1.22220	1.50666	161.4	0.000	0.0000	0.0
0.0863	1.20844	1.50223	126.4	−0.089	0.0062	−21.2
0.1279	1.20122	1.50020	112.4	−0.134	0.0093	−28.7
0.2201	1.18356	1.49524	85.83	−0.215	0.0156	−40.48
0.3243	1.16024	1.48866	62.26	−0.279	0.0219	−47.44
0.4177	1.13568	1.48167	48.86	−0.317	0.0264	−45.96
0.5126	1.10618	1.47321	34.16	−0.338	0.0296	−45.54
0.6093	1.06997	1.46270	24.62	−0.328	0.0310	−39.67
0.7176	1.01990	1.44818	16.27	−0.324	0.0298	−30.75
0.8240	0.95678	1.42970	9.900	−0.304	0.0244	−20.162
0.8834	0.91304	1.41684	7.027	−0.265	0.0188	−13.580
0.9658	0.83778	1.39459	3.411	−0.144	0.0067	−4.053
1.0000	0.79950	1.38370	2.017	0.000	0.0000	0.000

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Table 3. Redlich−Kister Parameters for the Binary System 1-Propanol (1) + [empy][eSO$_4$] (2) and Root-Mean-Square Deviations

property	a_0	a_1	a_2	a_3	a_4	σ
	1-Propanol (1) + [empy][eSO$_4$] (2)					
V^E/(cm^3·mol^{-1})	−1.3379	−0.0790	−0.1266	−1.5087	−1.4877	0.039
Δn_D	0.1168	0.0548	0.0260	0.0179	−0.0006	0.003
10^3 $\Delta\eta$/(Pa·s)	−181.199	76.502	−34.792	13.907	15.460	0.017

Crosthwaite samples), or nonvolatile impurities in their samples or our samples, or different measurement methods.

Apparatus and Procedure. Samples were prepared by syringing known masses of the pure liquids into stoppered bottles. For weight measurements, a Mettler AX-205 Delta Range balance with a uncertainty of $\pm$ 3·10^{-4} g was used. Good mixing was ensured by stirring. All samples were prepared immediately prior to measurements to avoid variations in composition due to evaporation of the components.

Densities were measured using an Anton Paar DSA-5000 digital vibrating-tube densimeter. The uncertainty in experimental measurements has been found to be lower than $\pm$ 2.6·10^{-5} g·cm^{-3} for the density. The DSA-5000 automatically corrects the influence of viscosity on the measured density. The apparatus was calibrated by air and water, according to the manual instruction, and the calibration was checked with pure liquids shown in Table 1.

To measure refractive indices of pure components and their mixtures at T = 298.15 K, an automatic refractometer (Abbemat-HP, Dr. Kernchen) with an uncertainty in the experimental measurements of $\pm$ 4·10^{-5} was used.

Kinematic viscosities were determined using an automatic viscosimeter Lauda PVS1 with four Ubbelhode capillary microviscosimeters of 0.4·10^{-3} m, 0.53·10^{-3} m, 0.70·10^{-3} m diameter (uncertainty in experimental measurement is $\pm$ 0.006 mPa·s) and 1.26·10^{-3} m diameter (uncertainty in experimental measurement is $\pm$ 0.01 mPa·s). The last capillary viscosimeter is used to measure the samples with higher viscosities, such as the pure ionic liquid. Gravity fall is the principle of measurement on which this viscosimeter is based. The capillary is maintained in a D20KP LAUDA thermostat with a resolution of 0.01 K. The capillaries are calibrated and credited by the company. The equipment has a control unit PVS1 (Processor Viscosity System) that is a PC-controlled instrument for the precise measurement of fall time, using standardized glass capillaries, with an uncertainty of 0.01 s.

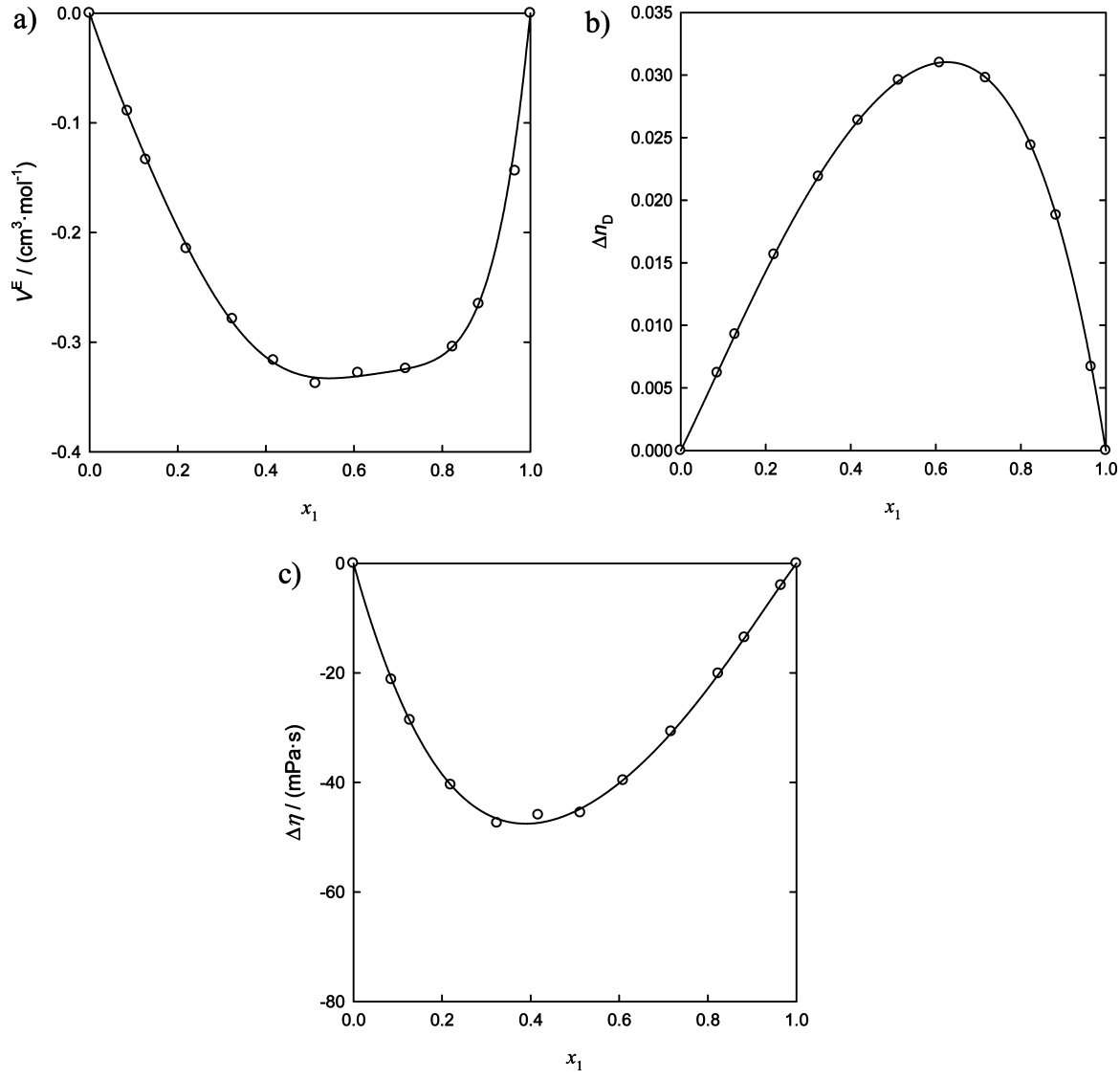

Figure 1. (a) Excess molar volumes, V^E; (b) refractive index deviations, Δn_D; and (c) viscosity deviations, $\Delta\eta$, plotted against mole fraction at T = 298.15 K for the binary mixture 1-propanol (1) + [empy][eSO$_4$] (2), and fitted curves, —, using the Redlich−Kister parameters.

Table 4. Densities, ρ, Refractive Indices, n_D, Dynamic Viscosities, η, Excess Molar Volumes, V^E, Refractive Index Deviations, Δn_D, and Viscosity Deviations, $\Delta\eta$, for the Ternary Systems Alcohol (1) + Water (2) + [empy][eSO$_4$] (3) at $T = 298.15$ K

x_1	x_2	ρ / (g·cm^{-3})	n_D	$10^3\,\eta$ / (Pa·s)	V^E / (cm^3·mol^{-1})	Δn_D	$10^3\,\Delta\eta$ / (Pa·s)
			Ethanol (1) + Water (2) + [empy][eSO$_4$] (3)				
0.0559	0.9196	1.02817	1.37677	2.202	−0.335	0.0384	−2.643
0.1155	0.8615	1.00618	1.37705	2.554	−0.624	0.0373	−2.053
0.1918	0.7872	0.97826	1.37779	2.780	−0.879	0.0363	−1.524
0.2634	0.7175	0.95224	1.37721	2.695	−0.994	0.0341	−1.323
0.3432	0.6397	0.92623	1.37591	2.635	−1.068	0.0309	−1.065
0.4352	0.5501	0.89992	1.37405	2.348	−1.107	0.0269	−0.985
0.6720	0.3194	0.84395	1.36843	1.748	−0.910	0.0158	−0.641
0.8189	0.1764	0.81607	1.36465	1.445	−0.619	0.0086	−0.359
0.0658	0.8853	1.06050	1.39835	3.138	−0.445	0.0555	−5.615
0.1401	0.8149	1.03049	1.39675	3.276	−0.734	0.0525	−4.867
0.2180	0.7411	0.99941	1.39389	3.206	−0.919	0.0482	−4.298
0.3049	0.6587	0.96677	1.39002	3.015	−1.033	0.0427	−3.775
0.3952	0.5731	0.93603	1.38603	2.731	−1.093	0.0370	−3.317
0.6019	0.3773	0.87548	1.37677	2.060	−1.011	0.0239	−2.291
0.0466	0.9420	1.00625	1.35735	1.692	−0.257	0.0216	−1.038
0.1018	0.8875	0.98746	1.36233	2.169	−0.546	0.0251	−0.466
0.1611	0.8289	0.96736	1.36564	2.479	−0.780	0.0269	−0.053
0.2316	0.7592	0.94382	1.36750	2.543	−0.954	0.0270	0.133
0.3119	0.6798	0.91842	1.36822	2.444	−1.044	0.0256	0.173
0.0849	0.8322	1.08841	1.42068	4.488	−0.582	0.0714	−9.725
0.1724	0.7526	1.05228	1.41499	4.225	−0.826	0.0646	−8.731
0.2651	0.6684	1.01510	1.40855	3.859	−0.980	0.0571	−7.768
0.3611	0.5810	0.97846	1.40186	3.363	−1.059	0.0493	−6.886
0.4610	0.4902	0.94290	1.39472	2.901	−1.077	0.0409	−5.914
0.5592	0.4009	0.91029	1.38805	2.499	−1.037	0.0331	−4.907
0.1191	0.7283	1.12032	1.44645	7.444	−0.724	0.0841	−17.965
0.3471	0.5398	1.03289	1.42552	4.852	−1.017	0.0637	−14.261
0.4518	0.4532	0.99275	1.41551	3.954	−1.053	0.0539	−12.267
0.5506	0.3715	0.95519	1.40581	3.239	−1.038	0.0445	−10.254
0.7437	0.2119	0.88211	1.38668	2.142	−0.816	0.0258	−6.018
0.8324	0.1386	0.84884	1.37740	1.723	−0.623	0.0168	−3.987
0.1016	0.5285	1.17767	1.48102	20.115	−0.612	0.0813	−40.178
0.2030	0.4688	1.15016	1.47277	15.065	−0.739	0.0775	−38.540
0.2995	0.4120	1.12126	1.46413	11.517	−0.827	0.0731	−35.729
0.4061	0.3493	1.08625	1.45364	8.503	−0.917	0.0673	−31.718
0.5036	0.2920	1.05000	1.44286	6.354	−0.922	0.0608	−27.439
0.6035	0.2332	1.00938	1.43053	4.707	−0.934	0.0529	−22.508
0.7012	0.1757	0.96443	1.41626	3.470	−0.868	0.0429	−17.303
0.0978	0.3563	1.19468	1.49186	36.488	−0.480	0.0616	−52.029
0.2306	0.3039	1.16567	1.48282	23.769	−0.631	0.0628	−51.883
0.3014	0.2759	1.14791	1.47724	18.706	−0.697	0.0628	−50.077
0.5002	0.1974	1.08679	1.45796	9.494	−0.801	0.0589	−40.025
0.6000	0.1580	1.04816	1.44605	6.633	−0.823	0.0548	−33.218
0.7009	0.1181	1.00135	1.43060	4.514	−0.794	0.0471	−25.554
0.8828	0.0463	0.88886	1.39397	2.076	−0.541	0.0246	−10.362
0.1956	0.1559	1.18684	1.49268	43.650	−0.415	0.0418	−61.364
0.2915	0.1373	1.16747	1.48642	30.870	−0.532	0.0464	−61.755
0.3985	0.1166	1.14171	1.47807	20.634	−0.636	0.0501	−58.170
0.6000	0.0775	1.07627	1.45671	9.162	−0.762	0.0514	−43.598
0.7572	0.0471	0.99985	1.43149	4.453	−0.712	0.0439	−28.005
0.0443	0.9286	1.03153	1.37971	2.345	−0.303	0.0402	−2.226
0.0944	0.8799	1.00586	1.38277	2.731	−0.483	0.0410	−1.707
0.1526	0.8234	0.97712	1.38432	2.982	−0.567	0.0399	−1.300
0.2264	0.7517	0.94676	1.38536	3.112	−0.638	0.0376	−0.973
0.2957	0.6843	0.92275	1.38586	3.107	−0.664	0.0349	−0.792
0.3868	0.5958	0.89683	1.38617	2.967	−0.676	0.0311	−0.689
0.6264	0.3630	0.84824	1.38580	2.547	−0.607	0.0198	−0.468
0.7860	0.2079	0.82494	1.38501	2.273	−0.441	0.0117	−0.316
0.0557	0.8922	1.06016	1.40241	3.276	−0.394	0.0580	−4.655
0.1121	0.8389	1.02999	1.40185	3.534	−0.537	0.0551	−4.043
0.1795	0.7752	0.99697	1.40024	3.642	−0.616	0.0508	−3.513
0.2543	0.7045	0.96542	1.39840	3.582	−0.666	0.0459	−3.104
0.3400	0.6236	0.93466	1.39625	3.464	−0.687	0.0402	−2.686
0.5436	0.4313	0.87893	1.39189	2.966	−0.659	0.0275	−1.909
0.0391	0.9485	1.00726	1.36168	1.811	−0.247	0.0250	−0.783
0.0837	0.9045	0.98596	1.36754	2.276	−0.434	0.0287	−0.291
0.1346	0.8542	0.96171	1.37150	2.605	−0.529	0.0302	0.069
0.1958	0.7938	0.93717	1.37467	2.809	−0.608	0.0304	0.309
0.2665	0.7241	0.91321	1.37736	2.887	−0.645	0.0297	0.430
0.4603	0.5328	0.86717	1.38144	2.670	−0.678	0.0244	0.329
0.0704	0.8361	1.09166	1.42669	5.026	−0.497	0.0743	−8.462
0.1448	0.7692	1.05342	1.42208	4.867	−0.610	0.0673	−7.702
0.2252	0.6969	1.01625	1.41713	4.617	−0.679	0.0597	−6.960
0.3108	0.6199	0.98074	1.41215	4.345	−0.700	0.0519	−6.177
0.4031	0.5369	0.94709	1.40728	3.976	−0.701	0.0439	−5.407
0.0956	0.7479	1.11747	1.44815	7.846	−0.589	0.0836	−14.113
0.1915	0.6686	1.07334	1.43991	6.960	−0.656	0.0733	−12.884
0.2888	0.5881	1.03180	1.43191	6.104	−0.693	0.0634	−11.595
0.3927	0.5022	0.99060	1.42361	5.119	−0.700	0.0529	−10.288
0.4879	0.4235	0.95562	1.41657	4.547	−0.686	0.0440	−8.762
0.6912	0.2553	0.88815	1.40270	3.282	−0.568	0.0259	−5.544
0.1038	0.1883	1.19589	1.49678	58.404	−0.269	0.0357	−37.418
0.2167	0.1646	1.17083	1.48986	37.020	−0.349	0.0386	−46.979
0.3185	0.1432	1.14482	1.48261	27.653	−0.394	0.0402	−45.696
0.4164	0.1226	1.11618	1.47455	19.856	−0.430	0.0407	−43.241
0.5212	0.1006	1.08039	1.46443	14.398	−0.422	0.0397	−37.729
0.6176	0.0804	1.04203	1.45340	10.192	−0.412	0.0371	−31.845
0.7244	0.0579	0.99168	1.43903	6.781	−0.384	0.0320	−24.081
0.1017	0.5391	1.16720	1.47899	19.195	−0.537	0.0788	−29.921
0.2017	0.4791	1.13385	1.47069	15.215	−0.601	0.0724	−28.656
0.4003	0.3599	1.06217	1.45248	9.400	−0.616	0.0580	−24.060
0.5051	0.2970	1.02173	1.44209	7.403	−0.599	0.0496	−20.564
0.5982	0.2412	0.98413	1.43226	5.986	−0.568	0.0415	−17.100
0.6988	0.1807	0.94177	1.42129	4.672	−0.527	0.0325	−13.135
0.1026	0.3681	1.18516	1.49008	32.143	−0.418	0.0602	−39.754
0.2960	0.2888	1.13083	1.47552	19.578	−0.503	0.0557	−37.257
0.3940	0.2486	1.09910	1.46692	14.858	−0.521	0.0522	−34.350
0.4947	0.2073	1.06299	1.45703	11.087	−0.525	0.0476	−30.280
0.5923	0.1672	1.02383	1.44628	7.939	−0.493	0.0419	−25.824
0.6936	0.1257	0.97879	1.43351	5.848	−0.477	0.0344	−20.026

Results and Discussion

Experimental Results. Experimental data of the binary mixtures 1-propanol (1) + water (2), and ethanol (1) + [empy][eSO_4] (2) were already published in previous works.[10,11] Physical properties and derived properties of the binary mixture 1-propanol (1) + [empy][eSO_4] (2) are reported in Table 2. Excess properties have been fitted using the Redlich−Kister equation,[27] and parameters obtained are reported in Table 3, together with the root-mean-square deviations. Experimental data and fitted curves using the Redlich−Kister parameters are presented in Figure 1. Excess molar volumes and viscosity deviations of this binary mixture are negative over the whole composition range, while the refractive index deviations present a positive deviation from ideality.

The measured densities, ρ, refractive indices, n_D, and dynamic viscosities, η, for the ternary mixtures ethanol or 1-propanol (1) + water (2) + [empy][eSO_4] (3) at $T = 298.15$ K and atmospheric pressure are listed in Table 4.

For the calculation of excess properties we have used the same equations used in previous works.[6] Excess volumes, V^E, refractive index deviations, Δn_D, and viscosity deviations, $\Delta\eta$, for the ternary systems ethanol or 1-propanol (1) + water (2) + [empy][eSO_4] (3) are summarized in Table 4.

Correlation of Physical Properties. The V^E, Δn_D, and $\Delta\eta$ data of ternary systems were correlated using the equations proposed by Cibulka[12] and Singh et al.[13] The following expressions were used

Cibulka equation

$$Q^E_{123} = Q^E_{12} + Q^E_{13} + Q^E_{23} + x_1x_2x_3(A + Bx_1 + Cx_2) \quad (1)$$

Singh et al. equation

$$Q^E_{123} = Q^E_{12} + Q^E_{13} + Q^E_{23} + Ax_1x_2x_3 + Bx_1(x_2 - x_3) + Cx_1^2(x_2 - x_3)^2 \quad (2)$$

where A, B, and C are fitting parameters and Q^E_{ij} is the contribution to the excess property of the constituent binary mixtures evaluated by Redlich−Kister equation[27]

$$Q^E_{ij} = x_ix_j\sum_{p=0}^{M} B_p(x_i - x_j)^p \quad (3)$$

where x_i is the mole fraction of component i and B_p are adjustable parameters. The parameters and the root-mean-square deviations for the excess properties of the binary mixtures ethanol (1) + water (2), 1-propanol (1) + water (2), ethanol (1) + [empy][eSO_4] (2), and water (1) + [empy][eSO_4] (2) are presented in previous papers,[7,10,11] and the parameters and deviations for the binary mixture 1-propanol (1) + [empy][eSO_4] (2) are reported in Table 3.

The fit parameters root-mean-square deviations of the correlation equations for the studied ternary systems are given in Table 5. As can be observed in this table, for the ternary system ethanol (1) + water (2) + [empy][eSO_4] (3) both correlation equations give similar deviations for all the studied properties, while for the mixture 1-propanol (1) + water (2) + [empy]-[eSO_4] (3) the better fitting is given by Cibulka. In Figures 2 and 3, the isolines of the excess properties V^E, Δn_D, and $\Delta\eta$ calculated from Cibulka for both ternary systems at $T = 298.15$ K and atmospheric pressure are shown.

Prediction of Physical Properties. Several empirical methods have been proposed to estimate ternary excess properties from experimental results of the constituent binary systems. These methods are of great interest, since as the number of components in the mixture increases, the determination of its properties becomes more laborious.

Table 5. Fit Parameters and Root-Mean-Square Deviations for Correlation Equations

	V^E / (cm^3·mol^{-1})	Δn_D	$10^3\,\Delta\eta$ / (Pa·s)
Ethanol (1) + Water (2) + [empy][eSO_4] (3)			
Cibulka			
A	6.153	−0.552	231.2
B	−5.472	1.131	−127.5
C	−1.910	1.438	−123.4
σ	0.047	0.039	0.207
Singh et al.			
A	3.582	0.310	146.3
B	0.028	−0.011	0.813
C	−0.064	0.024	−2.910
σ	0.048	0.099	0.476
1-Propanol (1) + Water (2) + [empy][eSO_4] (3)			
Cibulka			
A	4.823	−0.259	413.702
B	−6.427	0.575	−428.133
C	−4.706	0.652	−98.432
σ	0.045	0.028	0.178
Singh et al.			
A	0.978	0.159	220.835
B	0.043	−0.006	0.120
C	−0.133	0.010	−5.764
σ	0.049	0.048	0.381

The predictive methods can be divided into symmetric and asymmetric, depending on whether the assumption of the three binary mixtures contributing equally to the ternary mixture magnitude is accepted or not. Asymmetry is usually understood to be caused by the strongly polar or associative behavior of any of the compounds in the mixture. In these cases, different geometric criteria are applied to match each point of ternary composition with the contributing binary compositions.

To predict the excess properties (V^E, Δn_D, $\Delta\eta$), we have used symmetric[14−17] and asymmetric[18−20] geometrical solution models. These models are available in a previous paper.[9]

Table 6 lists the root-mean-square deviations of fit for each dependent variable and equation.

The root-mean-square deviations, σ, presented in Tables 3, 5, and 6 were calculated as

$$\sigma = \left\{\sum_i^{n_{dat}}\left(\frac{z_{exp} - z_{cal}}{z_{exp}}\right)^2/n_{dat}\right\}^{1/2} \quad (4)$$

where z_{exp}, z_{calc}, and $n_{dat,}$ are the values of the experimental and calculated property and the number of experimental data, respectively.

Deviations obtained with the empirical equations to predict the excess properties are rather high. This fact can be due to the importance of the ternary contribution term to the studied magnitude. Of the geometrical solution models used to predict the excess properties, the one of Radojkovic gives reasonably good results for all properties for the two studied systems. In general, symmetric equations give better predictive results, especially the ones of Radojkovic, Jacob and Fitzner, and Kohler. The predictions of the asymmetric equations of Tsao and Smith and Scatchard disagree significantly with experimental data. This behavior of the predictive models agrees with previous works.[7]

Conclusions

Densities, refractive indices and viscosities for the ternary mixtures ethanol and 1- propanol + water + [empy][eSO_4] were

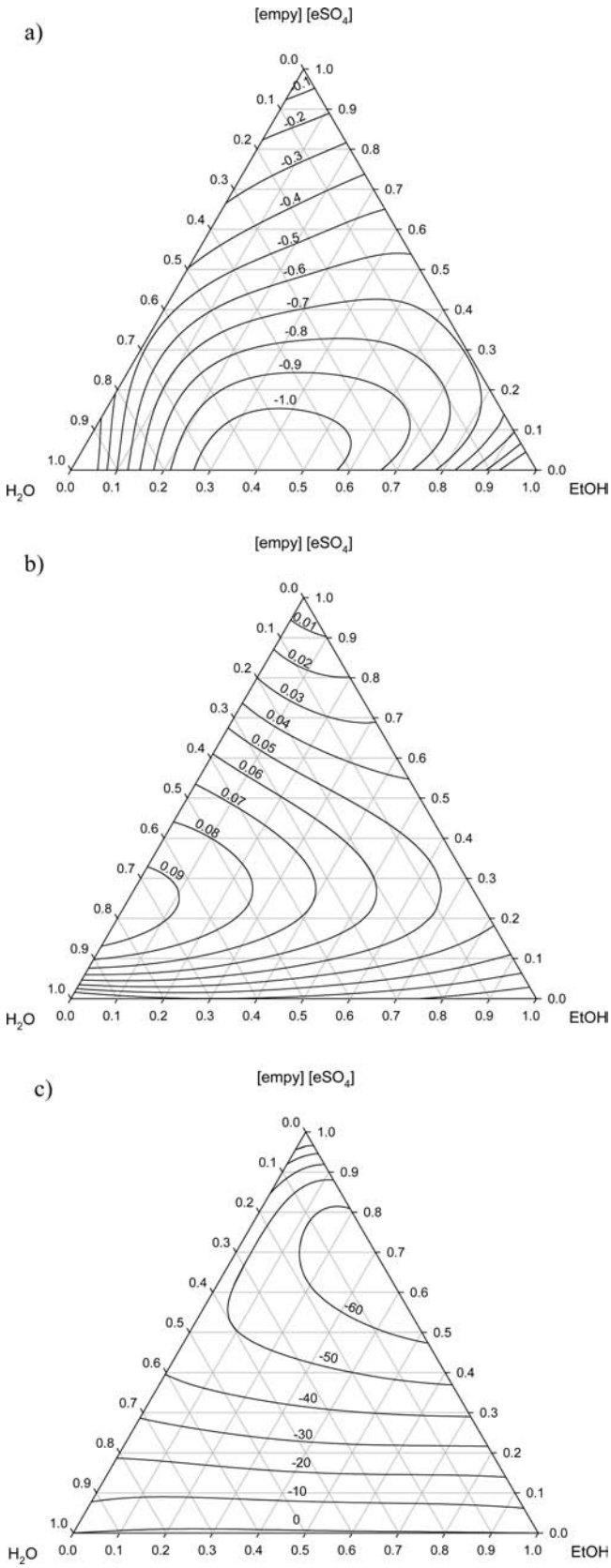

Figure 2. Isolines for (a) excess molar volumes, V^{E}_{123}; (b) refractive index deviations, Δn_{D123}; and (c) viscosity deviations, $\Delta\eta_{123}$ from Cibulka equation for the ternary system ethanol (1) + water (2) + [empy][eSO_4] (3) at T = 298.15 K.

measured at T = 298.15 K and atmospheric pressure over the whole range of compositions. From these physical properties the derived and excess properties were calculated.

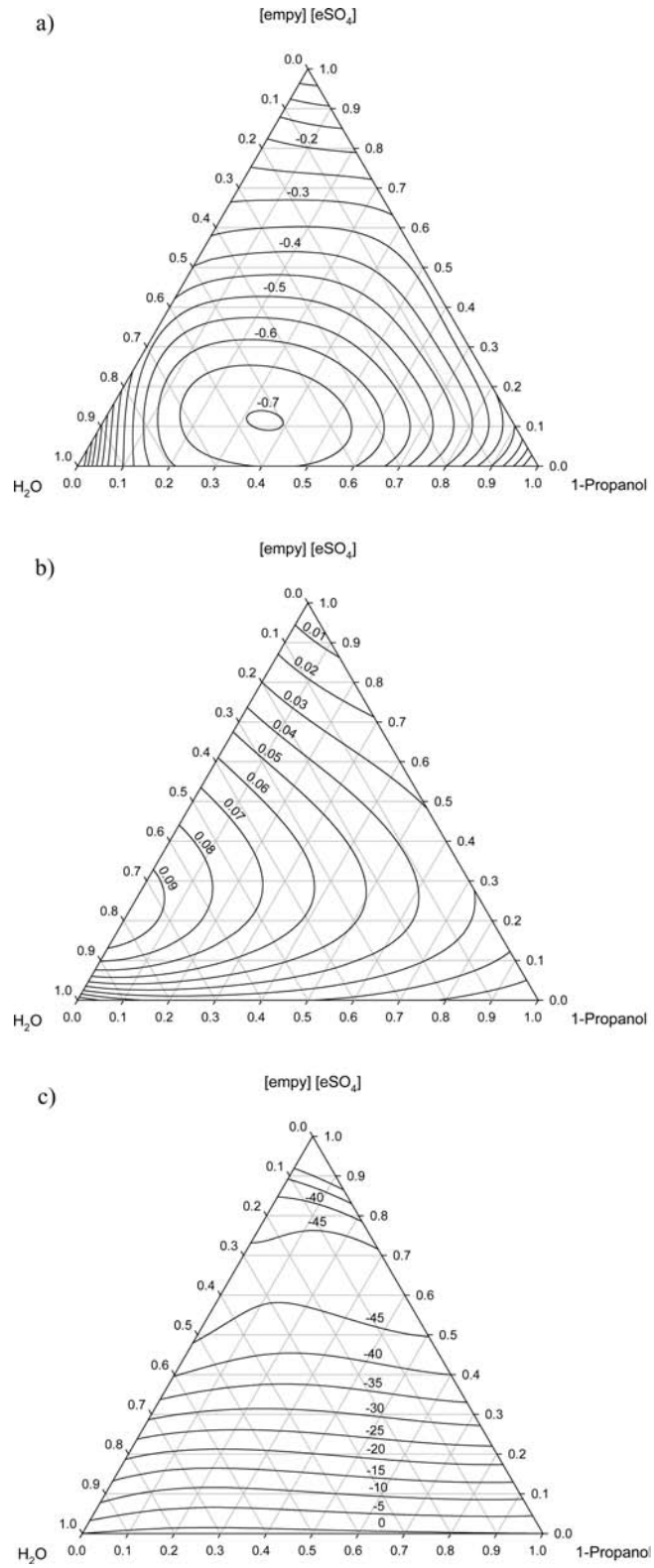

Figure 3. Isolines for (a) excess molar volumes, V^{E}_{123}; (b) refractive index deviations, Δn_{D123}; and (c) viscosity deviations, $\Delta\eta_{123}$ from Cibulka equation for the ternary system 1-propanol (1) + water (2) + [empy][eSO_4] (3) at T = 298.15 K.

Excess molar volumes show negative deviations from ideal behavior over the whole range of compositions for both systems studied. It is noticeable that the trend is similar for both ternary mixtures, although in case of ethanol, the values of the excess molar volume are slightly lower.

Table 6. Root-Mean-Square Deviations of Predictions of Excess Molar Volumes, Refractive Index Deviations, and Viscosity Deviations for Alcohol (1) + Water (2) + [empy][eSO$_4$] (3) at T = 298.15 K

prediction models	σ (V^E_{123})	σ (Δn_D)	σ ($\Delta\eta$)
Ethanol (1) + Water (2) + [empy][eSO$_4$] (3)			
Radojkovic	0.091	0.140	0.265
Rastogi	0.340	0.323	1.377
Jacob and Fitzner	0.099	0.276	1.560
Kohler	0.111	0.093	0.476
Toop[a]	0.218	0.154	0.444
Toop[b]	0.214	0.275	1.076
Toop[c]	0.186	0.380	1.872
Tsao and Smith[a]	0.249	0.259	0.613
Tsao and Smith[b]	0.266	0.203	0.739
Tsao and Smith[c]	0.323	0.388	1.861
Scatchard[a]	0.328	0.950	2.308
Scatchard[b]	0.662	0.323	9.265
Scatchard[c]	0.649	0.398	2.672
1-Propanol (1) + Water (2) + [empy][eSO$_4$] (3)			
Radojkovic	0.052	0.078	0.933
Rastogi	0.355	0.315	0.944
Jacob and Fitzner	0.096	0.211	0.988
Kohler	0.072	0.118	0.572
Toop[a]	0.180	0.146	0.624
Toop[b]	0.211	0.249	0.774
Toop[c]	0.140	0.362	2.065
Tsao and Smith[a]	0.217	0.320	0.924
Tsao and Smith[b]	0.231	0.215	0.860
Tsao and Smith[c]	0.258	0.374	2.049
Scatchard[a]	0.357	1.007	2.661
Scatchard[b]	0.386	0.208	9.682
Scatchard[c]	0.577	0.398	2.032

[a] Alcohol is the asymmetric component. [b] Water is the asymmetric component. [c] [empy][eSO$_4$] is the asymmetric component.

Refractive index deviations are positive over the whole range of compositions for the two studied ternary systems, and they present a very similar trend, as in case of excess molar volume.

For the dynamic viscosity deviations, negative deviations are obtained except in the alcohol + water rich region, where there is low ionic liquid concentration, where the deviations of dynamic viscosity present positive values.

Of the considered correlation equations, the Cibulka equation gives the smaller deviations for all the studied excess properties and for both systems, although both correlation equations used are capable of representing the experimental data.

The geometrical solution model, Radojkovic give reasonably good predictive results for all properties for the two studied systems. In general, the symmetric equations give better predictive results than the asymmetric methods.

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