Experimental Determination, Correlation, and Prediction of Physical Properties of the Ternary Mixtures Ethanol + Water with 1-Octyl-3-methylimidazolium Chloride and 1-Ethyl-3-methylimidazolium Ethylsulfate

Noelia Calvar, Elena Gómez, Begoña González, and Ángeles Domínguez*

Chemical Engineering Department, Vigo University, 36310 Vigo, Spain

In this work, densities, ρ, refractive indices, n_D, speeds of sound, u, and dynamic viscosities, η, of the ternary mixtures ethanol + water with 1-octyl-3-methylimidazolium chloride ([C$_8$mim][Cl]) and 1-ethyl-3-methylimidazolium ethylsulfate (EMISE) have been measured at 298.15 K and atmospheric pressure. Excess molar volumes, V_m^E, refractive index deviations, Δn_D, isentropic compressibilities, κ_S, molar isentropic compressibilities, $K_{S,m}$, isentropic compressibility deviations, $\Delta\kappa_S$, excess molar isentropic compressibilities, $K_{S,m}^E$, viscosity deviations, $\Delta\eta$, and excess free energies of activation of viscous flow, ΔG^{*E}, have been calculated from experimental data and fitted to Cibulka and Singh et al. equations. The excess properties have been used to test several prediction models.

1. Introduction

Ionic liquids are taking a great importance as alternatives to the organic solvents, but experimental data of physical properties are still very 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 more scarce in the literature. In addition, the correlation and prediction of properties of multicomponent mixtures using models which use information of the properties of their constituent binary mixtures is an area of research in development.

In this work, density, speed of sound, refractive index, and viscosity of the ternary systems ethanol + water with 1-octyl-3-methylimidazolium chloride ([C$_8$mim][Cl]) and 1-ethyl-3-methylimidazolium ethylsulfate (EMISE) have been measured. From the physical properties, we can determine the excess molar volumes, V_m^E, deviations of refractive index, Δn_D, isentropic compressibilities, κ_S, molar isentropic compressibilities, $K_{S,m}$, deviations of isentropic compressibility, $\Delta\kappa_S$, excess molar isentropic compressibility, $K_{S,m}^E$, viscosity deviations, $\Delta\eta$, and excess free energies of activation of viscous flow, ΔG^{*E}.

Experimental data were correlated using empirical equations[3,4] and predicted using geometrical models that assume that interactions in a ternary mixture depend on the interactions in binary systems.[5−11]

2. Experimental

2.1. Chemicals. Ethanol was supplied by Merck with a purity higher than 99.8 %. It was degassed ultrasonically and dried over molecular sieves type 4 Å, supplied by Aldrich. Water was bidistilled and deionized. The ionic liquids used in this work were synthesized in our laboratory.[12,13] Table 1 shows a comparison between experimental and literature data of pure components at 298.15 K.

* To whom correspondence should be addressed. E-mail: admguez@uvigo.es. Fax: +34986812380. Tel: +34986812422.

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

	ρ/g·cm^{-3}		$10^3\eta$/Pa·s	
component	exptl	lit.	exptl	lit.
ethanol	0.78546	0.78546[a]	1.082	1.082[a]
water	0.99705	0.99705[b]	0.890	0.890[b]
[C$_8$mim][Cl]	1.00882	1.0104[c]	20868	
EMISE	1.23763	1.23915[d] 1.2296[e]	97.580	100.77[d]

[a] From ref 14. [b] From ref 15. [c] From ref 16. [d] From ref 17. [e] From ref 18.

Table 2. Refractive Indices, n_D, Speeds of Sound, u, Isentropic Compressibilities, κ_S, Refractive Index Deviation, Δn_D, and Isentropic Compressibility Deviations, $\Delta\kappa_S$ for the Binary Mixture Water (1) + [C$_8$mim][Cl] (2) at 298.15 K

x_1	n_D	u / m·s^{-1}	κ_S / TPa^{-1}	Δn_D	$\Delta\kappa_S$ / TPa^{-1}
0.0000	1.51051	1721.0	334.7	0.0000	0.0
0.1484	1.50760	1666.7	356.6	0.0235	20.4
0.2030	1.50625	1655.1	361.4	0.0319	24.5
0.4076	1.49957	1633.8	370.3	0.0616	29.8
0.5334	1.49329	1632.2	370.6	0.0777	26.6
0.6807	1.48143	1639.3	367.6	0.0921	16.6
0.8185	1.45934	1650.7	363.7	0.0945	−0.6
0.8803	1.44036	1651.4	364.3	0.0865	−11.9
0.9307	1.41432	1639.6	370.6	0.0695	−22.1
0.9635	1.38658	1611.3	384.8	0.0476	−26.2
1.0000	1.33251	1497.0	447.6	0.0000	0.0

2.2. Apparatus and Procedure. Densities, speeds of sound, refractive indices, and viscosities of pure liquids and mixtures were measured with the apparatus presented in a previous work.[19] In the mentioned work, the following procedure is also explained.

3. Results and Discussion

3.1. Experimental Results. Physical properties of binary mixtures of ethanol and water with [C$_8$mim][Cl] and with

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Table 3. Densities, Speeds of Sound, Refractive Indices, Isentropic Compressibilities, Molar Isentropic Compressibilities and Dynamic Viscosities for the Ternary Systems Ethanol (1) + Water (2) + [C$_8$mim][Cl] (3) and Ethanol (1) + Water (2) + EMISE (3) at 298.15 K

Ethanol (1) + Water (2) + [C$_8$mim][Cl] (3)							Ethanol (1) + Water (2) + EMISE (3)						
x_1	x_2	ρ / g·cm^{-3}	u / m·s^{-1}	n_D	κ_S / TPa^{-1}	$10^3\eta$ / Pa·s	x_1	x_2	ρ / g·cm^{-3}	u / m·s^{-1}	n_D	$K_{S,m}$ / m^3·TPa^{-1}·mol^{-1}	$10^3\eta$ / Pa·s
0.0467	0.9348	0.9837	1590.1	1.36831	402.1	2.514	0.0898	0.1724	1.21812	1668.3	1.47286	0.04397	43.71
0.0962	0.8862	0.9688	1587.6	1.37031	409.6	2.748	0.3528	0.1226	1.16262	1576.8	1.45898	0.04238	18.65
0.2254	0.7596	0.9315	1514.6	1.37306	468.0	2.603	0.4657	0.1012	1.13017	1526.6	1.45066	0.04220	12.87
0.3057	0.6808	0.9103	1458.9	1.37294	516.1	2.662	0.6548	0.0654	1.05615	1421.4	1.43155	0.04324	6.067
0.5377	0.4533	0.8588	1329.3	1.36990	659.0	1.472	0.8545	0.0276	0.93319	1277.3	1.39925	0.04767	2.451
0.0826	0.9100	0.9706	1600.1	1.35765	402.4	2.007	0.0906	0.3653	1.20700	1679.5	1.46675	0.03390	26.40
0.1329	0.8601	0.9555	1587.3	1.36124	415.4	2.881	0.1867	0.3267	1.18516	1640.8	1.46136	0.03424	19.71
0.2008	0.7927	0.9353	1540.2	1.36427	450.7	2.822	0.6042	0.1590	1.04741	1424.7	1.42761	0.03891	5.533
0.2733	0.7208	0.9147	1482.5	1.36592	497.5	2.591	0.9667	0.0134	0.81749	1172.7	1.36802	0.05384	1.317
0.3651	0.6297	0.8913	1418.2	1.36663	557.8	2.282	0.2030	0.4762	1.15574	1632.9	1.44988	0.02632	11.23
0.6077	0.3891	0.8421	1293.0	1.36557	710.3	1.864	0.3097	0.4125	1.12171	1570.5	1.44198	0.02814	8.578
0.0558	0.9143	0.9824	1593.2	1.38190	401.0	3.908	0.4044	0.3559	1.08842	1514.0	1.43426	0.03008	6.856
0.1867	0.7875	0.9455	1535.3	1.38199	448.7	3.207	0.6484	0.2101	0.98706	1364.7	1.41004	0.03697	3.500
0.2604	0.7162	0.9259	1488.1	1.38087	487.8	3.164	0.2130	0.6721	1.07337	1608.2	1.41571	0.01647	4.695
0.3386	0.6405	0.9063	1439.5	1.37926	532.5	2.729	0.3172	0.5831	1.03243	1522.0	1.40876	0.01971	4.026
0.4437	0.5387	0.8822	1380.4	1.37657	594.9	2.553	0.7178	0.2410	0.88202	1275.2	1.38045	0.03727	2.045
0.0679	0.8854	0.9816	1594.6	1.39833	400.7	7.008	0.9072	0.0792	0.81704	1187.9	1.36663	0.04929	1.343
0.2958	0.6690	0.9221	1466.3	1.39021	504.4	3.560	0.0829	0.8208	1.10117	1722.3	1.41144	0.01150	4.237
0.3954	0.5743	0.8986	1410.6	1.38593	559.3	2.873	0.1776	0.7360	1.06192	1631.9	1.40690	0.01394	3.981
0.5841	0.3951	0.8588	1319.1	1.37780	669.2	2.156	0.3540	0.5781	0.99203	1479.1	1.39703	0.01986	3.217
0.7005	0.2845	0.8370	1269.7	1.37290	741.1	1.923	0.4582	0.4849	0.95275	1404.8	1.39078	0.02417	2.967
0.8470	0.1454	0.8108	1208.9	1.36639	843.9	1.508	0.5636	0.3905	0.91567	1342.2	1.38464	0.02903	2.443
0.0766	0.8576	0.9823	1594.2	1.41129	400.6	10.50	0.6675	0.2976	0.88130	1288.8	1.37857	0.03438	2.007
0.3335	0.6189	0.9191	1449.6	1.39734	517.8	3.791	0.7723	0.2038	0.85023	1242.6	1.37282	0.04022	1.728
0.4166	0.5418	0.9001	1406.3	1.39250	561.7	3.353	0.0723	0.8613	1.07912	1719.8	1.39785	0.01003	3.311
0.5440	0.4234	0.8728	1344.9	1.38532	633.4	2.522	0.1532	0.7862	1.04425	1646.3	1.39590	0.01203	3.265
0.1218	0.7443	0.9818	1572.8	1.44104	411.8	18.90	0.2354	0.7098	1.01132	1565.2	1.39287	0.01460	3.148
0.2235	0.6582	0.9604	1520.2	1.43225	450.6	10.37	0.3235	0.6281	0.97697	1487.2	1.38917	0.01784	3.109
0.3218	0.5748	0.9396	1473.1	1.42378	490.4	7.072	0.4195	0.5389	0.94271	1416.8	1.38499	0.02179	2.799
0.4363	0.4778	0.9150	1419.7	1.41372	542.2	4.956	0.5210	0.4447	0.90982	1355.4	1.38047	0.02638	2.385
0.5320	0.3966	0.8942	1375.7	1.40523	590.9	3.823	0.6339	0.3399	0.87660	1297.9	1.37558	0.03207	1.976
0.6374	0.3073	0.8711	1327.4	1.39554	651.5	2.912	0.8653	0.1250	0.81680	1199.3	1.36553	0.04628	1.406
0.0929	0.8165	0.9822	1586.9	1.42562	404.3	13.64	0.0603	0.8923	1.05992	1706.3	1.38604	0.00919	2.787
0.1807	0.7375	0.9615	1537.1	1.41834	440.2	7.695	0.1307	0.8254	1.03207	1658.6	1.38628	0.01067	2.848
0.3069	0.6239	0.9325	1469.9	1.40940	496.3	5.009	0.2036	0.7562	1.00216	1584.5	1.38518	0.01289	3.061
0.3714	0.5658	0.9179	1437.3	1.40940	527.4	4.285	0.2884	0.6757	0.97039	1506.7	1.38307	0.01588	2.836
0.4443	0.5002	0.9019	1401.7	1.39964	564.4	3.630	0.3804	0.5884	0.93821	1434.4	1.38030	0.01960	2.550
0.6743	0.2932	0.8527	1295.5	1.38333	698.8	2.278	0.4793	0.4944	0.90735	1371.3	1.37712	0.02403	2.444
0.2624	0.3089	0.9837	1544.6	1.48118	426.1	119.1	0.7086	0.2767	0.84706	1260.1	1.36966	0.03608	1.737
0.3599	0.2680	0.9709	1514.0	1.47289	449.3	58.73	0.0540	0.9172	1.03613	1677.3	1.37164	0.00855	2.239
0.4432	0.2332	0.9586	1487.6	1.46531	471.4	33.75	0.1162	0.8569	1.01270	1652.9	1.37430	0.00969	2.603
0.5558	0.1860	0.9386	1446.8	1.45230	509.0	16.16	0.1798	0.7952	0.98790	1593.2	1.37537	0.01151	2.666
0.1594	0.6721	0.9791	1554.6	1.44928	422.6	21.90	0.2581	0.7192	0.95950	1518.5	1.37524	0.01423	2.751
0.3263	0.5386	0.9463	1478.2	1.43391	483.6	9.470	0.3439	0.6361	0.93060	1446.8	1.37423	0.01767	2.653
0.3660	0.5069	0.9385	1460.8	1.43040	499.3	8.153	0.4403	0.5426	0.90210	1382.8	1.37261	0.02191	2.299
0.4617	0.4303	0.9185	1418.9	1.42100	540.8	5.846	0.5486	0.4376	0.87400	1323.7	1.37050	0.02721	2.109
0.5878	0.3295	0.8908	1361.8	1.40841	605.3	3.918	0.0462	0.9365	1.01820	1638.4	1.36004	0.00830	1.767
0.7599	0.1919	0.8502	1278.6	1.38964	719.4	2.375	0.1018	0.8819	0.99850	1647.0	1.36450	0.00903	2.162
0.2008	0.4721	0.9852	1553.2	1.47378	420.8	68.12	0.1618	0.8230	0.97720	1605.4	1.36735	0.01051	2.558
0.2777	0.4267	0.9741	1525.8	1.46709	441.0	41.41	0.2358	0.7503	0.95100	1531.1	1.36892	0.01305	2.537
0.3806	0.3659	0.9577	1489.5	1.45750	470.7	24.18	0.3196	0.6680	0.92390	1458.3	1.36932	0.01635	2.391
0.5079	0.2907	0.9345	1442.0	1.44384	514.6	11.59	0.4138	0.5756	0.89710	1392.7	1.36892	0.02046	2.347
0.6004	0.2361	0.9149	1402.5	1.43252	555.7	7.378	0.6523	0.3414	0.84330	1273.3	1.36615	0.03269	1.735
0.6991	0.1777	0.8913	1355.3	1.41902	610.8	4.710	0.0425	0.9493	1.00020	1602.0	1.34953	0.00818	1.473
0.7997	0.1184	0.8623	1296.9	1.40247	689.5	2.964	0.0885	0.9037	0.98520	1631.8	1.35476	0.00859	2.015
0.0984	0.1869	1.0029	1617.4	1.50191	381.2	2330	0.1473	0.8454	0.96600	1607.7	1.35959	0.00984	2.302
0.1968	0.1665	0.9943	1583.3	1.49589	401.2	855.1	0.2156	0.7777	0.94350	1543.4	1.36274	0.01204	2.443
0.2833	0.1486	0.9860	1556.1	1.49005	418.8	402.0	0.2972	0.6968	0.91790	1469.5	1.36457	0.01520	2.342
0.6985	0.0625	0.9199	1408.2	1.44546	548.2	11.08	0.3862	0.6086	0.89380	1404.8	1.36534	0.01902	2.334
0.7937	0.0428	0.8922	1351.9	1.42733	613.3	5.553	0.4911	0.5046	0.86910	1343.9	1.36541	0.02399	2.027

EMISE were previously published.[12,13,20] For the binary system water + [C$_8$mim][Cl], the refractive index and speed of sound data were not published. These experimental data together with isentropic compressibility, refractive index deviations, and isentropic compressibility deviations are presented in Table 2.

The measured densities, ρ, speeds of sound, u, refractive indices, n_D, and dynamic viscosities, η, together with the isentropic compressibilities, κ_S (determined by means of the Laplace equation), for the ternary mixture ethanol + water + [C$_8$mim][Cl], and together with the molar isentropic compressibilities, $K_{S,m}$, for the ternary mixture ethanol + water +

Table 4. Excess Molar Volumes, Deviations of Refractive Index, Deviations of Isentropic Compressibility, Excess Molar Isentropic Compressibility, Viscosity Deviations, and Excess Free Energies of Activation of Viscous Flow for the Ternary Systems Ethanol (1) + Water (2) + [C$_8$mim][Cl] (3) and Ethanol (1) + Water (2) + EMISE (3) at 298.15 K

Ethanol (1) + Water (2) + [C$_8$mim][Cl] (3)							Ethanol (1) + Water (2) + EMISE (3)						
		V^E		$\Delta\kappa_S$	$10^3\Delta\eta$	ΔG^{*E}			V^E		$K^E_{S,m}$	$10^3\Delta\eta$	ΔG^{*E}
x_1	x_2	cm^3·mol^{-1}	Δn_D	TPa^{-1}	Pa·s	J·mol^{-1}	x_1	x_2	cm^3·mol^{-1}	Δn_D	m^3·TPa^{-1}·mol^{-1}	Pa·s	J·mol^{-1}
0.0467	0.9348	−0.215	0.03122	−67.8	−384.481	2502.8	0.0898	0.1724	−0.179	0.02948	−0.00291	−28.54	1674.2
0.0962	0.8862	−0.435	0.03201	−86.3	−364.204	2745.7	0.3528	0.1226	−0.566	0.03963	−0.00737	−33.04	1909.1
0.2254	0.7596	−0.821	0.03163	−95.4	−312.075	2643.1	0.4657	0.1012	−0.684	0.04162	−0.00879	−29.99	1964.8
0.3057	0.6808	−0.953	0.02956	−89.4	−279.476	2698.3	0.6548	0.0654	−0.731	0.03979	−0.00981	−22.005	1677.4
0.5377	0.4533	−1.016	0.02088	−67.9	−186.760	1153.9	0.8545	0.0276	−0.553	0.02573	−0.00757	−10.008	987.35
0.0826	0.9100	−0.408	0.02152	−87.4	−154.916	2053.8	0.0906	0.3653	−0.370	0.05181	−0.00398	−27.12	3175.2
0.1329	0.8601	−0.621	0.02379	−100.7	−145.496	2975.2	0.1867	0.3267	−0.518	0.05220	−0.00564	−28.27	2992.8
0.2008	0.7927	−0.824	0.02503	−100.9	−134.013	2946.1	0.6042	0.1590	−0.792	0.04357	−0.00967	−18.369	2102.5
0.2733	0.7208	−0.953	0.02478	−92.0	−121.936	2744.1	0.9667	0.0134	−0.212	0.00579	−0.00230	−1.687	329.00
0.3651	0.6297	−1.037	0.02308	−79.5	−106.653	2417.5	0.2030	0.4762	−0.658	0.06463	−0.00663	−20.71	3704.9
0.6077	0.3891	−0.959	0.01564	−53.8	−65.859	1781.5	0.3097	0.4125	−0.792	0.06008	−0.00799	−19.233	3323.7
0.0558	0.9143	−0.225	0.04252	−72.3	−620.966	3482.8	0.4044	0.3559	−0.869	0.05533	−0.00890	−17.287	3021.3
0.1867	0.7875	−0.683	0.03972	−93.3	−535.170	3025.0	0.6484	0.2101	−0.871	0.03877	−0.00932	−11.197	1996.4
0.2604	0.7162	−0.843	0.03697	−93.0	−486.519	2997.5	0.2130	0.6721	−0.857	0.06042	−0.00736	−7.347	3687.4
0.3386	0.6405	−0.947	0.03363	−89.3	−435.305	2628.1	0.3172	0.5831	−1.028	0.05281	−0.00848	−6.565	3293.9
0.4437	0.5387	−1.008	0.02863	−82.1	−366.041	2443.6	0.7178	0.2410	−0.869	0.02199	−0.00773	−2.967	1587.2
0.0679	0.8854	−0.248	0.05562	−77.1	−967.999	4714.5	0.9072	0.0792	−0.410	0.00698	−0.00365	−1.031	536.01
0.2958	0.6690	−0.829	0.04322	−93.4	−733.371	3081.4	0.0829	0.8208	−0.519	0.06249	−0.00512	−5.980	3713.6
0.3954	0.5743	−0.934	0.03707	−91.0	−629.936	2554.9	0.1776	0.7360	−0.797	0.05678	−0.00684	−5.292	3530.3
0.5841	0.3951	−0.944	0.02539	−80.6	−433.511	1828.5	0.3540	0.5781	−1.066	0.04475	−0.00864	−4.299	2947.5
0.7005	0.2845	−0.842	0.01830	−70.0	−312.133	1520.4	0.4582	0.4849	−1.064	0.03721	−0.00891	−3.511	2715.3
0.8470	0.1454	−0.521	0.00904	−44.4	−159.494	877.9	0.5636	0.3905	−0.998	0.02978	−0.00867	−2.985	2197.7
0.0766	0.8576	−0.260	0.06493	−79.5	−1364.76	5422.1	0.6675	0.2976	−0.856	0.02243	−0.00787	−2.387	1672.1
0.3335	0.6189	−0.834	0.04712	−98.4	−989.078	2989.5	0.7723	0.2038	−0.734	0.01539	−0.00662	−1.623	1255.8
0.4166	0.5418	−0.908	0.04103	−98.4	−865.916	2708.8	0.0723	0.8613	−0.475	0.05358	−0.00468	−4.016	3265.0
0.5440	0.4234	−0.944	0.03194	−94.2	−677.089	2033.2	0.1532	0.7862	−0.725	0.05023	−0.00636	−3.518	3208.8
0.1218	0.7443	−0.377	0.08132	−84.2	−2775.19	5540.8	0.2354	0.7098	−0.925	0.04579	−0.00752	−3.082	3090.9
0.2235	0.6582	−0.568	0.07248	−100.2	−2460.42	4224.0	0.3235	0.6281	−1.018	0.04058	−0.00828	−2.527	3029.7
0.3218	0.5748	−0.719	0.06395	−113.3	−2150.885	3441.4	0.4195	0.5389	−1.061	0.03474	−0.00869	−2.191	2728.7
0.4363	0.4778	−0.834	0.05382	−123.2	−1788.809	2756.2	0.5210	0.4447	−1.046	0.02848	−0.00870	−1.922	2281.4
0.5320	0.3966	−0.879	0.04528	−126.0	−1485.570	2278.7	0.6339	0.3399	−0.961	0.02165	−0.00813	−1.571	1749.1
0.6374	0.3073	−0.873	0.03552	−122.2	−1151.402	1788.6	0.8653	0.1250	−0.500	0.00762	−0.00444	−0.583	749.40
0.0929	0.8165	−0.307	0.07441	−81.5	−1877.36	5626.5	0.0603	0.8923	−0.355	0.04489	−0.00405	−2.698	2911.4
0.1807	0.7375	−0.526	0.06626	−92.4	−1700.466	4272.1	0.1307	0.8254	−0.670	0.04371	−0.00584	−2.308	2950.0
0.3069	0.6239	−0.762	0.05606	−103.5	−1440.107	3300.5	0.2036	0.7562	−0.850	0.04112	−0.00700	−1.753	3115.0
0.3714	0.5658	−0.839	0.05542	−106.8	−1306.479	2960.8	0.2884	0.6757	−1.000	0.03729	−0.00794	−1.581	2899.2
0.4443	0.5002	−0.906	0.04494	−108.6	−1155.242	2601.7	0.3804	0.5884	−1.061	0.03265	−0.00848	−1.436	2599.7
0.6743	0.2932	−0.860	0.02634	−96.7	−677.409	1611.4	0.4793	0.4944	−1.068	0.02746	−0.00865	−1.078	2443.5
0.2624	0.3089	−0.519	0.06508	−109.9	−8828.4	2515.0	0.7086	0.2767	−0.842	0.01535	−0.00723	−0.711	1437.1
0.3599	0.2680	−0.574	0.06417	−143.9	−7706.57	2025.8	0.0540	0.9172	−0.321	0.03339	−0.00352	−1.449	2395.0
0.4432	0.2332	−0.648	0.06290	−170.7	−6721.29	1722.0	0.1162	0.8569	−0.626	0.03461	−0.00532	−0.913	2771.4
0.5558	0.1860	−0.690	0.05842	−199.2	−5372.67	1326.1	0.1798	0.7952	−0.822	0.03420	−0.00651	−0.675	2830.0
0.1594	0.6721	−0.455	0.08234	−89.1	−3496.78	5088.1	0.2581	0.7192	−0.987	0.03226	−0.00750	−0.375	2897.0
0.3263	0.5386	−0.690	0.06830	−118.9	−2810.485	3466.6	0.3439	0.6361	−1.066	0.02925	−0.00811	−0.236	2783.5
0.3660	0.5069	−0.749	0.06511	−124.7	−2646.029	3203.6	0.4403	0.5426	−1.096	0.02539	−0.00843	−0.324	2384.0
0.4617	0.4303	−0.829	0.05648	−135.4	−2247.645	2643.4	0.5486	0.4376	−1.054	0.02077	−0.00826	−0.217	2100.0
0.5878	0.3295	−0.861	0.04489	−139.4	−1721.958	2002.3	0.0462	0.9365	−0.258	0.02370	−0.00285	−0.807	1802.1
0.7599	0.1919	−0.740	0.02750	−119.0	−1003.192	1246.8	0.1018	0.8819	−0.551	0.02677	−0.00478	−0.325	2318.4
0.2008	0.4721	−0.495	0.07748	−94.6	−6758.10	3955.4	0.1618	0.8230	−0.785	0.02812	−0.00617	0.166	2746.9
0.2777	0.4267	−0.560	0.07426	−118.0	−6127.85	3348.0	0.2358	0.7503	−0.952	0.02784	−0.00718	0.260	2730.1
0.3806	0.3659	−0.646	0.06932	−146.8	−5266.05	2846.7	0.3196	0.6680	−1.053	0.02613	−0.00789	0.245	2570.5
0.5079	0.2907	−0.735	0.06141	−175.1	−4191.82	2042.4	0.4138	0.5756	−1.090	0.02338	−0.00829	0.349	2490.5
0.6004	0.2361	−0.758	0.05425	−186.5	−3406.476	1655.7	0.6523	0.3414	−0.936	0.01463	−0.00749	0.110	1569.2
0.6991	0.1777	−0.774	0.04521	−187.4	−2565.692	1318.2	0.0425	0.9493	−0.219	0.01464	−0.00236	−0.215	1332.6
0.7997	0.1184	−0.658	0.03319	−165.7	−1709.028	953.2	0.0885	0.9037	−0.475	0.01865	−0.00418	0.356	2134.8
0.0984	0.1869	−0.306	0.03946	−37.1	−12584	2438.9	0.1473	0.8454	−0.733	0.02192	−0.00576	0.679	2487.7
0.1968	0.1665	−0.291	0.04459	−77.1	−12432.0	1870.5	0.2156	0.7777	−0.922	0.02327	−0.00687	0.864	2651.2
0.2833	0.1486	−0.346	0.04856	−112.3	−11454.4	1670.3	0.2972	0.6968	−1.030	0.02294	−0.00765	0.814	2548.4
0.6985	0.0625	−0.609	0.05105	−236.6	−4976.53	552.5	0.3862	0.6086	−1.091	0.02136	−0.00813	0.864	2517.8
0.7937	0.0428	−0.589	0.04371	−229.7	−3407.771	542.8	0.4911	0.5046	−1.078	0.01865	−0.00823	0.622	2113.1

EMISE at 298.15 K and atmospheric pressure are listed in Table 3. The molar isentropic compressibilities, $K_{S,m}$, were calculated instead of the isentropic compressibilities, κ_S, as suggested by Douhéret et al.,[21,22] for the ternary system containing EMISE, but the calculations for the system containing [C$_8$mim][Cl] were not possible because there are no available heat capacity data in the literature for this ionic liquid. $K^{id}_{S,m}$ is defined by the approach developed by Benson and Kiyohara.[23]

For the calculation of excess properties, we have used the same equations used elsewhere.[19]

Table 5. Redlich−Kister Parameters for the Binary Systems and Root-Mean-Square Deviations

property	a_0	a_1	a_2	a_3	a_4	σ
			Ethanol + $[C_8mim][Cl]$			
$V^E/cm^3 \cdot mol^{-1}$	−1.9483	−1.3894	−0.3691	−2.7090	−2.4461	0.004
Δn_D	0.1782	0.1027	0.0599	0.0683	0.0430	$2 \cdot 10^{-4}$
$\Delta \kappa_S/TPa^{-1}$	−41.59	−248.92	−227.88	−489.73	−395.68	1.02
$10^3\ \Delta\eta/Pa \cdot s$	−41672	34253	−22919	51212	−48575	153.5
$\Delta G^{*E}/J \cdot mol^{-1}$	1756.6	−810.2	1455.9	5124.3	−2560.5	21.54
			Water + $[C_8mim][Cl]$			
$V^E/cm^3 \cdot mol^{-1}$	−2.2426	−0.3201	2.3025	1.2131	−0.7369	0.002
Δn_D	0.3008	0.2338	0.0170	0.3057	0.6535	0.002
$\Delta \kappa_S/TPa^{-1}$	100.27	−54.54	308.47	−204.80	−908.71	3.39
$10^3\ \Delta\eta/Pa \cdot s$	−37779	33579	−33320	36507	−21929	51.1
$\Delta G^{*E}/J \cdot mol^{-1}$	25981	34408	17275	33971	39862	105.1
			Ethanol + Water			
$V^E/cm^3 \cdot mol^{-1}$	−4.2143	1.2235	−2.2301	−0.5044	1.8678	0.011
Δn_D	0.0679	−0.0468	0.0455	−0.0137	−0.0155	$1.5 \cdot 10^{-4}$
$\Delta \kappa_S/TPa^{-1}$	−785.59	478.50	−613.71	724.94	−394.26	2.21
$K^E_{S,m}/m^3 \cdot TPa^{-1} \cdot mol^{-1}$	−0.0328	0.0027	−0.0144	0.0085	0.0002	$6.52 \cdot 10^{-5}$
$10^3\ \Delta\eta/Pa \cdot s$	3.611	−4.913	6.077	−0.372	−3.219	0.019
$\Delta G^{*E}/J \cdot mol^{-1}$	7724.5	−6706.8	7506.6	−5084.8	1646.1	18.54
			Ethanol + EMISE			
$V^E/cm^3 \cdot mol^{-1}$	−2.2696	−1.8707	0.0953	−1.1140	−1.8363	0.008
Δn_D	0.1348	0.0756	0.0467	0.0252	0.0013	$1.5 \cdot 10^{-4}$
$K^E_{S,m}/m^3 \cdot TPa^{-1} \cdot mol^{-1}$	−0.0555	−0.0343	−0.0158	−0.0358	−0.0461	$1.65 \cdot 10^{-4}$
$10^3\ \Delta\eta/Pa \cdot s$	−133.096	57.328	−18.008	14.396	−8.954	0.059
$\Delta G^{*E}/J \cdot mol^{-1}$	6099.3	1694.8	−1250.9	2211.8	4158.4	47.64
			Water + EMISE			
$V^E/cm^3 \cdot mol^{-1}$	−1.1585	−1.3068	−1.1589	0.8021	1.6604	0.013
Δn_D	0.2491	0.1774	0.1139	0.2931	0.2864	$8.8 \cdot 10^{-4}$
$K^E_{S,m}/m^3 \cdot TPa^{-1} \cdot mol^{-1}$	−0.0114	−0.0072	−0.0036	−0.0112	−0.0197	$2.35 \cdot 10^{-5}$
$10^3\ \Delta\eta/Pa \cdot s$	−97.494	31.556	7.923	7.091	−17.981	0.203
$\Delta G^{*E}/J \cdot mol^{-1}$	15 502	9261.5	7279.1	16 244	13 738	44.62

Excess volumes, V^E_m, deviations of refractive index, Δn_D, viscosity deviations, $\Delta\eta$, excess free energies of activation of viscous flow, ΔG^{*E}, and deviations of isentropic compressibility, $\Delta\kappa_S$, for the system ethanol + water + $[C_8mim][Cl]$ or excess molar isentropic compressibility, $K^E_{S,m}$, for the system ethanol + water + EMISE, are summarized in Table 4.

3.2. Correlation of Physical Properties. The V^E_m, Δn_D, $\Delta\kappa_S$, $K^E_{S,m}$, $\Delta\eta$, and ΔG^{*E} data were correlated using the equations proposed by Cibulka[3] and Singh et al.[4]

For the two equations, the contribution to the excess property of the constituent binary mixtures was evaluated by the Redlich−Kister equation.[24]

The parameters and the root-mean-square deviations for the excess properties of the four binary mixtures containing ionic liquids involved in the ternary system are presented in previous papers,[12,13,19] and they are listed in Table 5.

The fit parameters of the correlation equations and root-mean-square deviations are given in Table 6. As can be observed in this table, for all the studied properties the better fitting is given by Cibulka, where the correlated values are in good agreement with the experimental data. In Figures 1 to 4, the isolines of the excess properties V^E_m, Δn_D, $\Delta\eta$, and ΔG^{*E} calculated from Cibulka for both ternary systems are shown.

3.3. 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 because as the number of components in the mixture increases the determination of its properties becomes more laborious.

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. Asymmetry is usually understood to be caused by the strongly polar or associative behavior of any of

Table 6. Fit Parameters and Root-Mean-Square Deviations for Empirical Equations

	V^E		$\Delta\kappa_S$	$10^3\Delta\eta$	ΔG^{*E}
	$cm^3 \cdot mol^{-1}$	Δn_D	TPa^{-1}	$Pa \cdot s$	$J \cdot mol^{-1}$
			Ethanol (1) + Water (2) + $[C_8mim][Cl]$ (3)		
			Cibulka		
A	2.190	−0.5607	−1945.7	182491	36781
B	−1.318	1.1472	1211.2	−185258	10121
C	26.155	1.4702	11071.4	−173977	−235417
σ	$2.9 \cdot 10^{-2}$	$2.0 \cdot 10^{-3}$	14.6	251	330
			Singh et al.		
A	10.728	0.3523	2286.7	52421	−43475
B	−0.509	0.0139	98.8	−1354	5989
C	−1.504	0.0196	−8.8	1976	24666
σ	$5.1 \cdot 10^{-2}$	$2.5 \cdot 10^{-3}$	22.4	405	500

	V^E		$K^E_{S,m}$	$10^3\Delta\eta$	ΔG^{*E}
	$cm^3 \cdot mol^{-1}$	Δn_D	$m^3 \cdot TPa^{-1} \cdot mol^{-1}$	$Pa \cdot s$	$J \cdot mol^{-1}$
			Ethanol (1) + Water (2) + EMISE (3)		
			Cibulka		
A	2.338	−0.4377	0.1142	−48.49	−11963
B	−2.038	0.8508	0.1963	130.5	41002
C	3.016	1.0757	−0.1965	108.1	−26962
σ	$1.8 \cdot 10^{-2}$	$9.0 \cdot 10^{-4}$	$6.33 \cdot 10^{-4}$	$4.2 \cdot 10^{-1}$	123
			Singh et al.		
A	2.921	0.2275	0.1079	37.27	−8828.3
B	0.006	0.0070	−0.0022	1.422	−95.377
C	−0.170	0.0092	0.0077	−5.546	1104.50
σ	$1.9 \cdot 10^{-2}$	$1.5 \cdot 10^{-3}$	$8.02 \cdot 10^{-4}$	$4.3 \cdot 10^{-1}$	153

Table 7. Root-Mean-Square Deviations of Predictions of Excess Molar Volumes, Deviations of Refractive Index, Deviations of Isentropic Compressibility, Viscosity Deviations, and Excess Free Energies of Activation of Viscous Flow for Ethanol + Water + [C$_8$mim][Cl] and Ethanol + Water + EMISE at 298.15 K

Ethanol (1) + Water (2) + [C$_8$mim][Cl] (3)						Ethanol (1) + Water + EMISE (3)					
	V^E		$\Delta\kappa_S$	$10^3\Delta\eta$	ΔG^{*E}		V^E		$10^3K^E_{S,m}$	$10^3\Delta\eta$	ΔG^{*E}
	$cm^3 \cdot mol^{-1}$	Δn_D	TPa^{-1}	Pa·s	$J \cdot mol^{-1}$		$cm^3 \cdot mol^{-1}$	Δn_D	$m^3 \cdot TPa^{-1} \cdot mol^{-1}$	Pa·s	$J \cdot mol^{-1}$
Radojkovic	0.197	0.008	45	952	1306	Radojkovic	0.041	0.004	1.66	0.655	216
Rastogi	0.230	0.015	53	365	726	Rastogi	0.333	0.012	1.67	3.524	733
Jacob and Fitzner	0.158	0.011	55	963	946	Jacob and Fitzner	0.057	0.008	1.37	1.652	254
Kohler	0.208	0.005	71	1410	1835	Kohler	0.055	0.004	1.87	0.573	508
Toop[a]	0.227	0.007	54	1813	1895	Toop[a]	0.103	0.010	2.25	1.721	597
Toop[b]	0.212	0.013	75	1876	870	Toop[b]	0.089	0.013	3.65	1.553	413
Toop[c]	0.286	0.017	67	1326	2862	Toop[c]	0.122	0.003	2.18	2.873	961
Tsao and Smith[a]	0.262	0.013	73	2606	3131	Tsao and Smith[a]	0.115	0.031	2.76	2.795	975
Tsao and Smith[b]	0.294	0.008	87	2650	913	Tsao and Smith[b]	0.118	0.010	9.71	3.328	383
Tsao and Smith[c]	0.372	0.018	118	1326	2995	Tsao and Smith[c]	0.186	0.014	4.88	2.854	1065
Scatchard[a]	0.339	0.041	71	4771	5871	Scatchard[a]	0.144	0.010	2.13	7.249	2078
Scatchard[b]	0.512	0.015	63	5037	982	Scatchard[b]	0.341	0.007	3.61	12.533	574
Scatchard[c]	0.523	0.019	91	1326	3173	Scatchard[c]	0.326	0.013	4.08	2.894	1264

[a] Ethanol is the asymmetric component. [b] Water is the asymmetric component. [c] Ionic liquid is the asymmetric component.

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_m, Δn_D, $\Delta\kappa_S$, $K^E_{S,m}$, $\Delta\eta$, and ΔG^{*E}), we have used symmetric[5−8] and asymmetric[9−11] geometrical solution models.

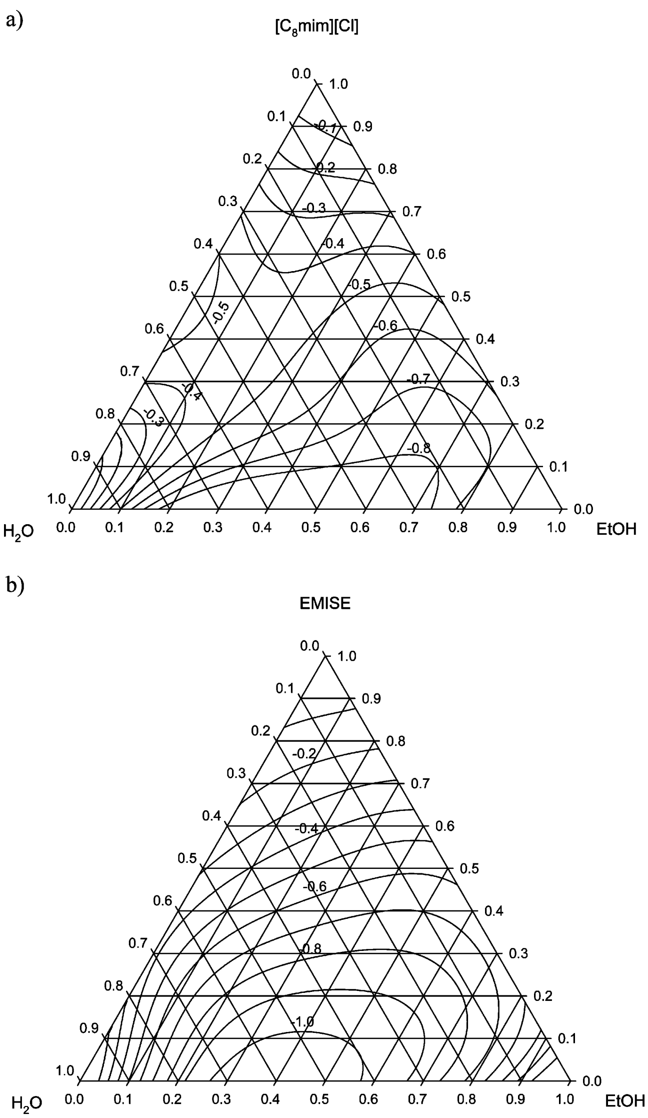

Figure 1. Isolines for excess molar volumes, V^E_{123} in $cm^3 \cdot mol^{-1}$, from the Cibulka equation for the ternary systems (a) ethanol (1) + water (2) + [C$_8$mim][Cl] (3) and (b) ethanol (1) + water (2) + EMISE (3).

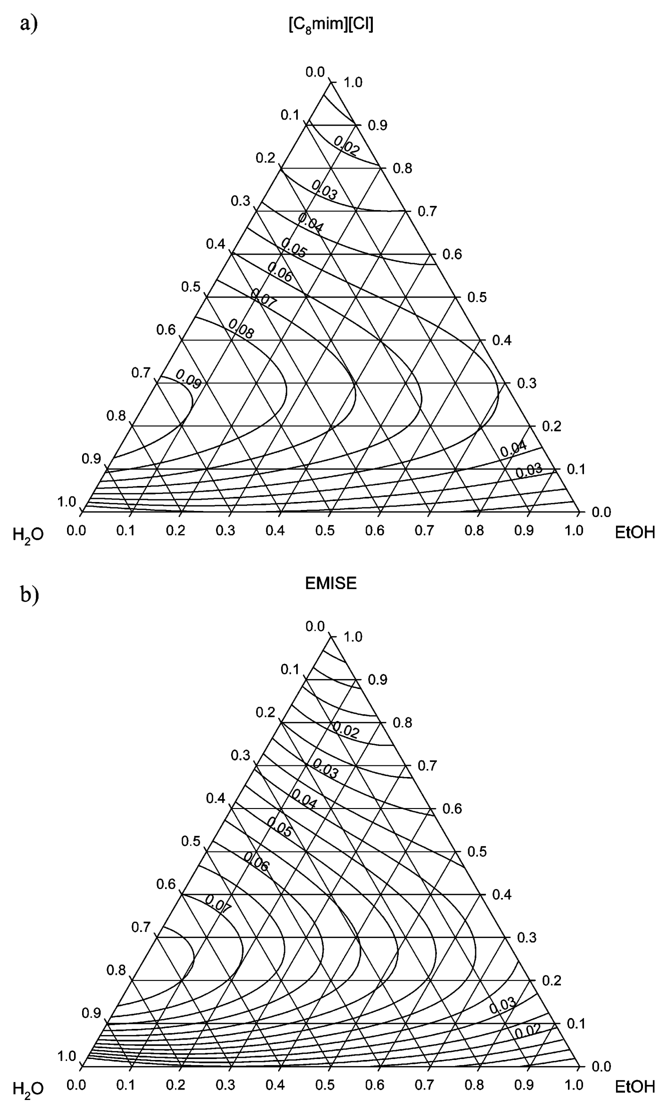

Figure 2. Isolines for the changes of refractive index, Δn_{D123}, from the Cibulka equation for the ternary systems (a) ethanol (1) + water (2) + [C$_8$mim][Cl] (3) and (b) ethanol (1) + water (2) + EMISE (3).

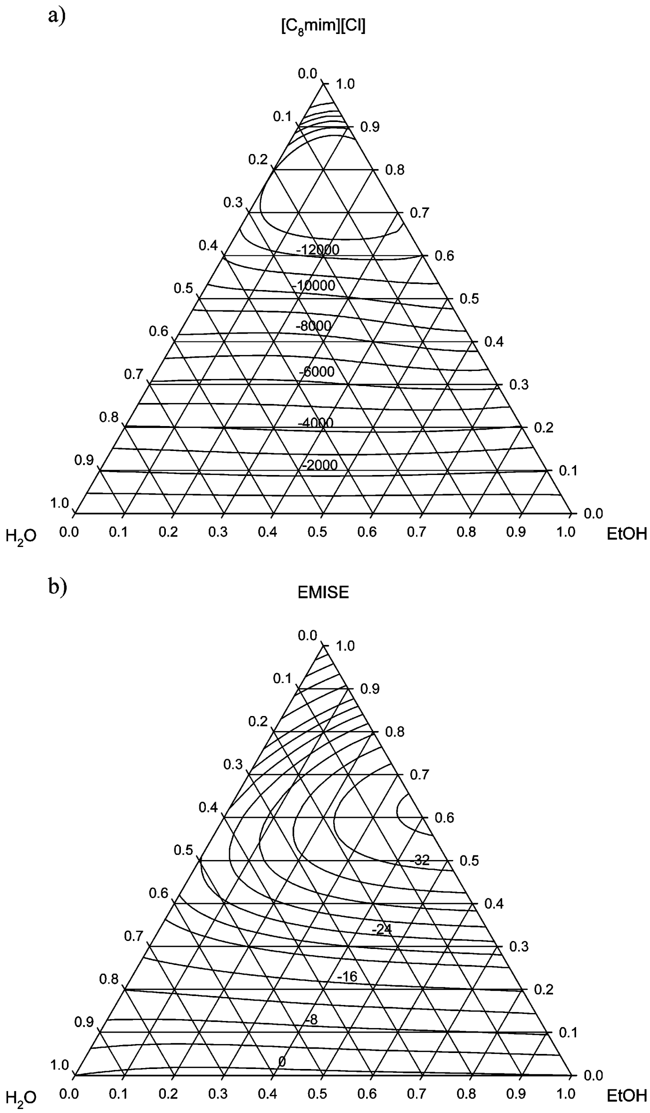

Figure 3. Isolines for the deviation of dynamic viscosity, $\Delta\eta_{123}$ in mPa·s, from the Cibulka equation for the ternary systems (a) ethanol (1) + water (2) + [C$_8$mim][Cl] (3) and (b) ethanol (1) + water (2) + EMISE (3).

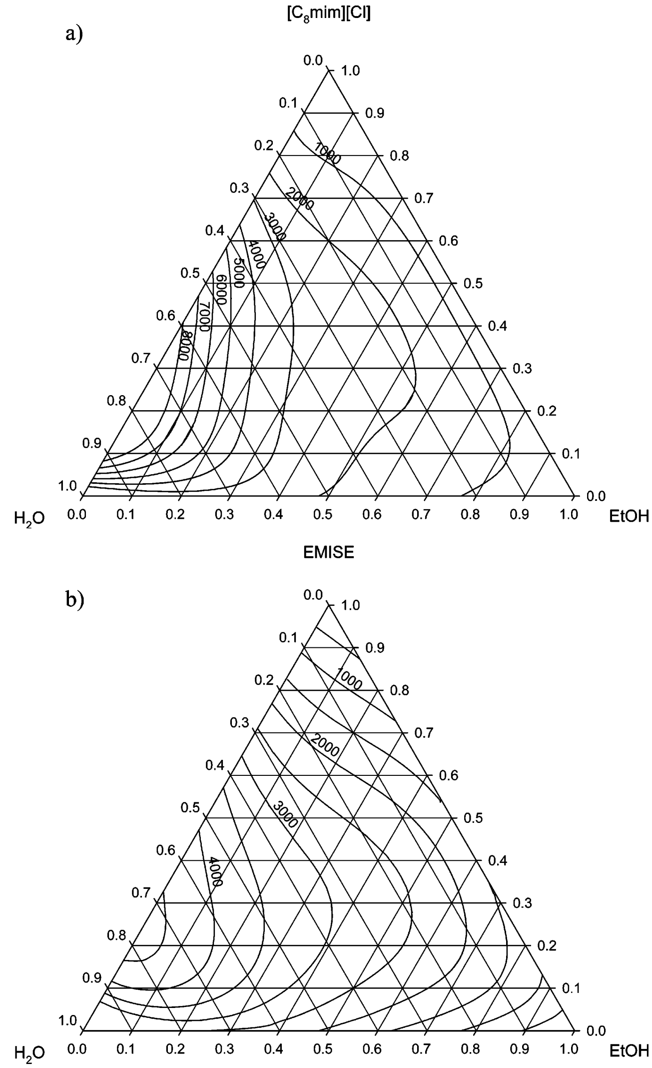

Figure 4. Isolines for the excess free energy of activation of viscous flow, ΔG^{*E}_{123} in J·mol^{-1}, from the Cibulka equation for the ternary systems (a) ethanol (1) + water (2) + [C$_8$mim][Cl] (3) and (b) ethanol (1) + water (2) + EMISE (3).

Table 7 lists the root-mean-square deviations of fit for each dependent variable and equation.

The root-mean-square deviations, σ, presented in Tables 5 to 7 were calculated as

$$\sigma = \{\sum_{i}^{n_{\text{dat}}} (z_{\text{exptl}} - z_{\text{calcd}})^2/n_{\text{dat}}\}^{1/2} \qquad (1)$$

where z_{exptl}, z_{calcd}, and n_{dat} are the values of the experimental and calculated properties and the number of experimental data, respectively.

4. Conclusions

Densities, speeds of sound, refractive indices, and viscosities for the ternary mixtures ethanol + water + [C$_8$mim][Cl] and ethanol + water + EMISE were measured at 298.15 K and atmospheric pressure over the whole range of compositions. From these physical properties, the excess properties were calculated.

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

Refractive index deviations and excess free energies of activation of viscous flow are both positive over the whole range of compositions.

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.

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. The high viscosity deviations and excess free energies of activation of viscous flow for the system containing the ionic liquid [C$_8$-mim][Cl] are due to the high viscosity of the pure ionic liquid. In general, the 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. It is noteworthy that in all asymmetric models the best results for the ΔG^{*E} are obtained when water is the asymmetric component.

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