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Vapor Pressures and Activity Coefficients of *n*-Alcohols and Benzene in Binary Mixtures with 1-Methyl-3-butylimidazolium Octyl Sulfate and 1-Methyl-3-octylimidazolium Tetrafluoroborate

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Vapor−liquid equilibria (VLE) of binary mixtures containing methanol, ethanol, propanol-1, and benzene in the ionic liquid [BMIM][OctS] or [OMIM][BF$_4$] were studied by using a static method. VLE measurements were carried out over the whole concentration range at four different temperatures in the range from 298.15 K to 313.15 K. Activity coefficients γ_i of these solvents in the ionic liquids and osmotic coefficients ϕ_i of the ionic liquids have been determined from the VLE data and are described formally by using the NRTL equation.

Introduction

Room temperature ionic liquids (IL) are salts that are liquids at ambient temperatures. They are excellent solvents for a broad range of polar organic compounds, and they show partial miscibility with aromatic hydrocarbons. Typical ILs have a stable liquid range of over 300 K and have a very low vapor pressure at room temperature. These unique properties have suggested that ILs might be useful as environmentally benign solvents that could replace volatile organic compounds. By varying the length and branching of the alkane chains of the cationic core and the anionic precursor, the solvent properties of ILs can be tailored to meet the requirements of specific applications to create an almost infinite set of “designer solvents”. In this context thermodynamic properties of liquid mixtures containing ILs are of large interest, in particular a systematic study of mixture properties such as VLE data and activity coefficients is required. We have contributed to such a systematic collection of thermophysical data in the past by determining activity coefficients of different classes of solutes in ILs.[1−11] In continuation of our recent work,[5] we present new data of activity coefficients covering the whole range of concentrations in binary mixtures containing ionic liquids.

Vapor pressure measurements of four solutes in the ionic liquid 1-methyl-3-butylimidazolium octyl sulfate [BMIM][OctS] or 1-methyl-3-octylimidazolium tetrafluoroborate [OMIM][BF$_4$] have been performed. In contrast to previous work where VLE data of low volatile solutes in ILs were measured using the transpiration method,[10,11] in the present work a series of binary mixtures of alcohols or benzene with the ionic liquids have been studied using a static vapor pressure method.[5] From the pressure data, activity coefficients γ_i at different temperatures have been obtained.

Experimental Section

Materials. The alcohols and benzene were of commercial origin. The purities of these substances were 99.9 % according to specification. The water content of the purchased solutes was less then 0.01 %, also according specification. All chemicals were used without further purification but were carefully degassed. The [BMIM][OctS] and [OMIM][BF$_4$] have been synthesized by the research group of Prof. Wasserscheid in Erlangen. Before using, the IL was subjected to vacuum evaporation at 333 K over 24 h to remove possible traces of solvents and moisture. The water concentration (< 100 ppm) was checked by Karl Fischer titration.

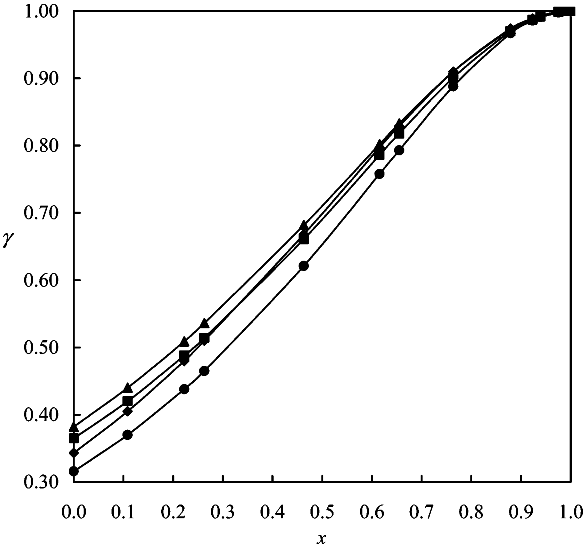

Figure 1. Plot of activity coefficient γ of methanol in CH_3OH + [BMIM]-[OctS] mixture vs mole fraction x of CH_3OH: ◆, 298.15 K; ▲, 303.15 K; ■, 308.15 K; ●, 313.15 K. Points and solid lines: eq 3.

Experimental Procedure. The VLE measurements of binary solutions of ILs with (CH_3OH, C_2H_5OH, C_3H_7OH, or C_6H_6) have been performed by using a static method.[5] The experimental setup consisted of a bolted-top glass cell surrounded by a water bath that was kept at constant temperature (± 0.02 K). The measuring cell is equipped with an injection port containing a septum. A special construction of the injection port allows evacuation of the injection port before and after injecting a liquid sample and prevents pressure fluctuation in the measuring cell

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Table 1. Experimental Vapor Pressure Values of Investigated Solutions

	298.15 K		303.15 K		308.15 K		313.15 K			298.15 K		303.15 K		308.15 K		313.15 K	
x_1	p/Pa	γ_1	p/Pa	γ_1	p/Pa	γ_1	p/Pa	γ_1	x_1	p/Pa	γ_1	p/Pa	γ_1	p/Pa	γ_1	p/Pa	γ_1
$x\mathrm{CH_3OH} + (1 - x)[\mathrm{BMIM}][\mathrm{OctS}]$																	
0.0000	0	0.343	0	0.382	0	0.365	0	0.316	0.7638	10155	0.910	12880	0.910	16058	0.901	19880	0.888
0.1083	1142	0.405	1417	0.440	1739	0.420	2101	0.37	0.8792	13903	0.974	17732	0.973	22429	0.970	28172	0.967
0.2222	1708	0.48	2102	0.509	2544	0.488	3101	0.438	0.9235	15713	0.989	19952	0.989	24961	0.987	31222	0.986
0.2629	2066	0.51	2570	0.536	3130	0.514	3813	0.465	0.9392	16150	0.993	20583	0.993	25914	0.992	32289	0.991
0.4629	3612	0.668	4482	0.682	5507	0.661	6673	0.621	0.9754	16621	0.999	21348	0.999	27136	0.999	34240	0.998
0.6156	6101	0.797	7603	0.802	9404	0.786	11402	0.758	0.9874	16682	1	21485	1	27405	1	34710	1
0.6549	7046	0.829	8769	0.833	10796	0.818	13260	0.793	1.0000	16958	1	21880	1	27960	1	35450	1
$x\mathrm{C_2H_5OH} + (1 - x)[\mathrm{BMIM}][\mathrm{OctS}]$																	
0.0000	0	0.455	0	0.413	0	0.389	0	0.392	0.6364	5550	1.012	6659	0.912	7730	0.855	9007	0.822
0.0617	304	0.493	369	0.444	428	0.416	495	0.417	0.6992	6405	1.071	7862	0.975	9454	0.922	11168	0.887
0.1429	571	0.548	707	0.489	863	0.456	1058	0.453	0.7299	6789	1.096	8477	1.004	10306	0.954	12313	0.918
0.1794	752	0.575	921	0.512	1124	0.476	1360	0.471	0.7831	7359	1.13	9398	1.046	11688	1.005	14342	0.97
0.2873	1330	0.663	1683	0.586	2082	0.543	2567	0.531	0.8343	7668	1.146	10004	1.072	12722	1.043	16002	1.01
0.3544	1864	0.724	2346	0.639	2940	0.591	3610	0.575	0.87474	7824	1.141	10275	1.078	13240	1.061	16842	1.031
0.3861	2142	0.754	2723	0.666	3357	0.616	4062	0.598	0.95435	7851	1.065	10406	1.036	13625	1.037	17669	1.023
0.4892	3326	0.858	3976	0.761	4818	0.706	5817	0.68	1	7876	1	10468	1	13768	1	17928	1
0.5515	4164	0.924	4949	0.824	5892	0.766	6900	0.737									
$x\mathrm{C_3H_7OH} + (1 - x)[\mathrm{BMIM}][\mathrm{OctS}]$																	
0.0000	0	0.325	0	0.281	0	0.251	0	0.250	0.59067	1400	0.851	1861	0.823	2430	0.799	3130	0.776
0.1218	146	0.395	177	0.353	218	0.326	277	0.317	0.72583	1982	1.024	2608	0.982	3402	0.944	4386	0.943
0.1464	171	0.411	210	0.369	260	0.343	322	0.332	0.79989	2491	1.096	3225	1.039	4070	0.995	5220	1.008
0.1724	197	0.429	248	0.388	304	0.362	372	0.350	0.85309	2730	1.121	3560	1.054	4600	1.013	5944	1.032
0.31478	454	0.539	596	0.503	778	0.482	987	0.459	0.90911	2754	1.106	3674	1.042	4875	1.014	6422	1.030
0.38852	680	0.611	902	0.577	1175	0.558	1508	0.531	1.00000	2786	1.000	3826	1.000	5199	1.000	6986	1.000
0.56081	1290	0.812	1705	0.784	2240	0.762	2865	0.736									
$x\mathrm{C_6H_6} + (1 - x)[\mathrm{BMIM}][\mathrm{OctS}]$																	
0.0000	0	1.660	0	1.492	0	1.444	0	1.436	0.6988	12101	1.334	14847	1.312	17951	1.288	21735	1.266
0.0624	1335	1.635	1480	1.487	1736	1.439	2109	1.425	0.7843	12529	1.262	15541	1.247	19012	1.232	23260	1.217
0.1498	2958	1.600	3463	1.479	4114	1.430	4904	1.410	0.8183	12620	1.227	15706	1.214	19264	1.204	23655	1.193
0.2467	4760	1.562	5700	1.465	6805	1.418	8205	1.393	0.87018	12635	1.166	15845	1.157	19500	1.152	24050	1.147
0.3758	6963	1.509	8320	1.440	9948	1.396	12032	1.366	0.91993	12651	1.096	15861	1.091	19581	1.091	24200	1.091
0.4165	7725	1.491	9274	1.430	11082	1.387	13340	1.357	0.959	12679	1.038	15872	1.036	19586	1.037	24224	1.039
0.5480	10143	1.428	12191	1.388	14479	1.352	17484	1.322	0.97415	12692	1.019	15877	1.017	19594	1.018	24239	1.02
0.6275	11365	1.382	13780	1.353	16496	1.322	19824	1.296	1	12704	1	15919	1	19659	1	24331	1
$x\mathrm{CH_3OH} + (1 - x)[\mathrm{OMIM}][\mathrm{BF_4}]$																	
0.0000	0	0.691	0	0.66	0	0.626	0	0.597	0.4444	8577	1.125	10779	1.103	13434	1.077	16527	1.064
0.0388	515	0.736	626	0.705	745	0.670	875	0.641	0.5473	10465	1.157	13243	1.14	16523	1.121	20554	1.116
0.0657	851	0.767	1054	0.736	1282	0.700	1515	0.671	0.6278	12120	1.155	15300	1.141	19076	1.129	23759	1.128
0.0931	1139	0.799	1408	0.768	1724	0.732	2086	0.703	0.7474	14063	1.113	17912	1.105	22469	1.100	27997	1.103
0.1740	2548	0.891	3128	0.861	3787	0.825	4544	0.797	0.8860	15858	1.036	20185	1.034	25398	1.033	31626	1.035
0.2228	3586	0.944	4406	0.915	5302	0.879	6403	0.853	0.9400	16254	1.012	20770	1.011	26263	1.011	33026	1.012
0.3539	6602	1.067	8239	1.041	10137	1.009	12553	0.99	1	16958	1	21880	1	27960	1	35450	1
0.4243	8160	1.115	10258	1.091	12744	1.064	15682	1.049									
$x\mathrm{C_2H_5OH} + (1 - x)[\mathrm{OMIM}][\mathrm{BF_4}]$																	
0.0000	0	1.763	0	1.552	0	1.380	0	1.225	0.5721	6001	1.331	7705	1.285	9834	1.245	12283	1.196
0.0838	1103	1.676	1336	1.513	1575	1.372	1863	1.252	0.6202	6379	1.303	8189	1.258	10433	1.222	13086	1.172
0.1226	1565	1.64	1876	1.495	2263	1.367	2742	1.261	0.7258	7043	1.235	9043	1.193	11618	1.164	14643	1.113
0.2113	2610	1.565	3237	1.455	4010	1.353	4908	1.274	0.8596	7652	1.128	9921	1.093	12890	1.074	16352	1.04
0.2510	3068	1.535	3813	1.437	4667	1.346	5756	1.276	0.9196	7750	1.067	10150	1.044	13200	1.033	16930	1.015
0.4046	4524	1.431	5801	1.368	7235	1.307	9089	1.258	0.9346	7760	1.051	10180	1.032	13278	1.024	17089	1.01
0.4883	5293	1.38	6801	1.328	8631	1.279	10795	1.232	1.0000	7876	1	10468	1	13768	1	17928	1
$x\mathrm{C_3H_7OH} + (1 - x)[\mathrm{OMIM}][\mathrm{BF_4}]$																	
0.0000	0	2.153	0	1.990	0	1.867	0	1.852	0.7281	2679	1.319	3577	1.282	4717	1.242	6057	1.189
0.1742	954	1.959	1211	1.822	1528	1.706	1955	1.626	0.8026	2739	1.217	3695	1.194	4917	1.169	6384	1.134
0.3484	1730	1.771	2235	1.662	2872	1.562	3591	1.463	0.8407	2753	1.164	3727	1.148	4975	1.130	6526	1.104
0.5068	2286	1.594	2971	1.513	3781	1.435	4759	1.344	0.8656	2758	1.130	3742	1.118	4998	1.104	6602	1.084
0.6075	2510	1.474	3278	1.413	4226	1.351	5361	1.274	0.9228	2765	1.057	3764	1.052	5056	1.047	6753	1.039
0.7041	2654	1.351	3522	1.309	4622	1.265	5929	1.207	1.0000	2786	1.000	3826	1.000	5199	1.000	6986	1.000
$x\mathrm{C_6H_6} + (1 - x)[\mathrm{OMIM}][\mathrm{BF_4}]$																	
0.0000	0	1.342	0	1.356	0	1.383	0	1.411	0.6905	11226	1.288	13881	1.268	16646	1.234	19816	1.190
0.1839	3209	1.350	3981	1.346	4868	1.345	5949	1.344	0.7464	12006	1.263	14830	1.247	17701	1.214	21120	1.168
0.2640	4398	1.350	5458	1.340	6663	1.330	8146	1.319	0.7586	12189	1.257	15036	1.241	17954	1.209	21432	1.163
0.3583	5995	1.347	7427	1.331	9048	1.311	11053	1.290	0.7620	12223	1.255	15083	1.240	18070	1.207	21532	1.162
0.5299	9006	1.329	11072	1.308	13321	1.276	15966	1.241	0.78731	12452	1.24	15476	1.227	18670	1.196	22072	1.15
0.5660	9517	1.322	11702	1.301	14105	1.268	16893	1.231	0.83959	12578	1.201	15700	1.193	19099	1.166	22760	1.122
0.6417	10581	1.304	13050	1.283	15720	1.249	18719	1.207	1	12704	1.000	15919	1	19659	1	24331	1

during the injection procedure. The pressure was measured using a calibrated high accuracy sensor head (type 615A, MKS Baratron) connected to the signal conditioner (type 670A, MKS Baratron) attached to the top of the cell. The sensor head and the connecting line from the cell to the sensor were thermostated at 333.15 ± 0.01 K. This temperature is always kept above the

Table 2. Vapor Pressure of Pure Solvent p^*, Second Virial Coefficient B_s of Vapor Solvent, and Molar Volume V_s^* of Liquid Solvent at Different Temperatures

T/K	p^*/Pa	B_s/(m^3·mol^{-1})	V_s^*/(m^3·mol^{-1})
		CH_3OH	
298.15	16958	$-2172.5 \cdot 10^{-6}$	$4.075 \cdot 10^{-5}$
303.15	21880	$-1942.3 \cdot 10^{-6}$	$4.099 \cdot 10^{-5}$
308.15	27960	$-1746.6 \cdot 10^{-6}$	$4.124 \cdot 10^{-5}$
313.15	35450	$-1579.0 \cdot 10^{-6}$	$4.150 \cdot 10^{-5}$
		C_2H_5OH	
298.15	7878	$-1723.5 \cdot 10^{-6}$	$5.868 \cdot 10^{-5}$
303.15	10467	$-1598.8 \cdot 10^{-6}$	$5.901 \cdot 10^{-5}$
308.15	13765	$-1485.5 \cdot 10^{-6}$	$5.933 \cdot 10^{-5}$
313.15	17906	$-1382.50 \cdot 10^{-6}$	$5.967 \cdot 10^{-5}$
		C_3H_7OH	
298.15	2786	$-4290.0 \cdot 10^{-6}$	$7.514 \cdot 10^{-5}$
303.15	3826	$-4013.9 \cdot 10^{-6}$	$7.553 \cdot 10^{-5}$
308.15	5199	$-3713.3 \cdot 10^{-6}$	$7.592 \cdot 10^{-5}$
313.15	6986	$-3401.1 \cdot 10^{-6}$	$7.631 \cdot 10^{-5}$
		C_6H_6	
298.15	12704	$-1487.2 \cdot 10^{-6}$	$8.972 \cdot 10^{-5}$
303.15	15919	$-1427.5 \cdot 10^{-6}$	$9.032 \cdot 10^{-5}$
308.15	19659	$-1370.3 \cdot 10^{-6}$	$9.092 \cdot 10^{-5}$
313.15	24331	$-1315.5 \cdot 10^{-6}$	$9.153 \cdot 10^{-5}$

Table 3. Parameters of the NRTL Equation

T/K	$g_{12} - g_{22}$/kJ·mol^{-1}	$g_{21} - g_{11}$/kJ·mol^{-1}	α
	[BMIM][OctS] + CH_3OH		
298.15	8.0724	−9.1630	0.066000
303.15	7.4383	−7.7183	0.115305
308.15	7.2666	−7.6077	0.130082
313.15	8.7675	−7.6110	0.190745
	[BMIM][OctS] + C_2H_5OH		
298.15	14.6410	−2.8453	0.473715
303.15	10.4976	−3.1573	0.581989
308.15	10.6081	−3.1498	0.646143
313.15	8.71510	−3.2087	0.724067
	[BMIM][OctS] + C_3H_7OH		
298.15	14.5163	−3.93663	0.433270
303.15	12.4091	−5.71747	0.323728
308.15	13.4425	−7.84145	0.217442
313.15	12.8970	−6.46235	0.304570
	[BMIM][OctS] + C_6H_6		
298.15	10.48160	0.18828	0.540124
303.15	10.16110	−0.05297	0.560224
308.15	10.21300	−0.02100	0.592528
313.15	10.35190	0.08343	0.626204
	[OMIM][BF_4] + CH_3OH		
298.15	17.5946	−10.6776	0.0829920
303.15	18.7938	−11.6934	0.0762082
308.15	18.8500	−11.7274	0.0791801
313.15	18.8500	−11.5082	0.0852811
	[OMIM][BF_4] + C_2H_5OH		
298.15	7.3539	0.5835	0.738565
303.15	5.4044	0.2292	0.847269
308.15	4.6222	−0.1298	0.874348
313.15	6.8620	−3.1375	0.237928
	[OMIM][BF_4] + C_3H_7OH		
298.15	7.81180	0.31896	0.506809
303.15	7.17494	0.34482	0.576685
308.15	6.41188	0.42227	0.677377
313.15	5.19239	0.73850	0.897891
	[OMIM][BF_4] + C_6H_6		
298.15	12.23260	−0.12479	0.539563
303.15	12.73850	−0.00409	0.554543
308.15	11.19300	0.15823	0.643358
313.15	7.22581	0.29446	0.895654

temperatures of the measuring cell in order to avoid any condensation in the pressure head. The experimental uncertainties were ± 0.01 K for the temperature and ± 10 Pa for the pressure.

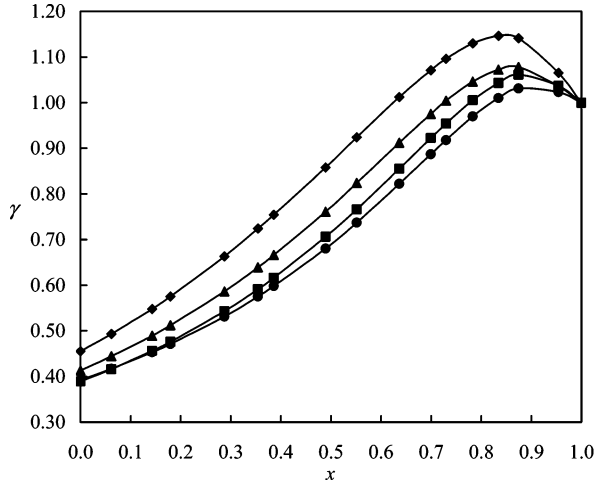

Figure 2. Plot of activity coefficient γ of ethanol in C_2H_5OH + [BMIM]-[OctS] mixture vs mole fraction x of C_2H_5OH: ◆, 298.15 K; ▲, 303.15 K; ■, 308.15 K; ●, 313.15 K. Points and solid lines: eq 3.

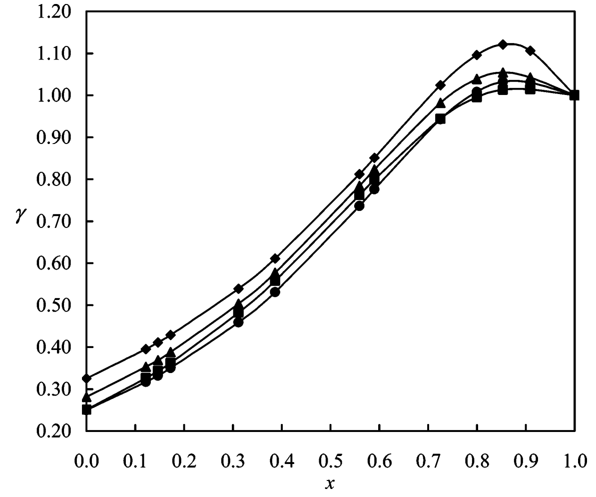

Figure 3. Plot of activity coefficient γ of propanol in C_3H_7OH + [BMIM]-[OctS] mixture vs mole fraction x of C_3H_7OH: ◆, 298.15 K; ▲, 303.15 K; ■, 308.15 K; ●, 313.15 K. Points and solid lines: eq 3.

Table 4. Comparison of Values of γ_i^∞ at 298 K Derived in This Work for ILs with Those Obtained by the GC Method (ref 9 and ref 16)

	[OMIM][BF_4]	γ_i^∞ at 298 K	[BMIM][OctS]	γ_i^∞ at 298 K
solute i	this work	ref 9	this work	ref 16
benzene	1.34	1.19	1.66	1.42
methanol	0.69	1.07	0.34	0.39
ethanol	1.76	1.75		
propanol	2.15	2.18		

To start an experimental series of measurements, a certain amount of degassed IL was placed into the cell using a weighted syringe. The cell loaded with the IL is kept at room temperature under vacuum for ca. 12 h (until the pressure sensor indicates zero point). Exactly known amounts of the degassed solvent were injected stepwise into the thermostated equilibrium cell with the help of special glass injectors. Phase equilibrium was reached in each step by using a magnetic stirrer with a Teflon-coated magnet inside the cell. The vapor phase consists exclusively of the solvent, and equilibration in the cell is a rapid process. A constant pressure is reached within 15 min. Equilibrium pressure readings are registered in 10 min intervals. The method was checked[9] by measuring the vapor pressure of pure methanol[12] as well as the vapor−liquid equilibrium (VLE) of the binary mixture (benzene + tetradecane), where reliable VLE

Table 5. Calculated Activity of Solvent a_s and Osmotic Coefficients ϕ of the Investigated Solutions

	$T = 298.15$ K		$T = 303.15$ K		$T = 308.15$ K		$T = 313.15$ K			$T = 298.15$ K		$T = 303.15$ K		$T = 308.15$ K		$T = 313.15$ K	
x_1	a_s	ϕ	a_s	ϕ	a_s	ϕ	a_s	ϕ	x_1	a_s	ϕ	a_s	ϕ	a_s	ϕ	a_s	ϕ
xCH$_3$OH + (1 − x)[BMIM][OctS]																	
0.9874	0.9840	0.633	0.9823	0.701	0.9805	0.770	0.9796	0.808	0.6549	0.4192	0.839	0.4049	0.872	0.3908	0.907	0.3793	0.936
0.9754	0.9804	0.392	0.9761	0.480	0.9711	0.582	0.9666	0.674	0.6156	0.3633	0.825	0.3514	0.852	0.3407	0.877	0.3265	0.912
0.9392	0.9530	0.373	0.9417	0.466	0.9281	0.579	0.9126	0.710	0.4629	0.2156	0.674	0.2077	0.690	0.2001	0.707	0.1916	0.726
0.9235	0.9276	0.456	0.9133	0.551	0.8946	0.676	0.8831	0.755	0.2629	0.1235	0.383	0.1193	0.389	0.1139	0.398	0.1097	0.405
0.8792	0.8221	0.719	0.8131	0.759	0.8053	0.795	0.7983	0.827	0.2222	0.1021	0.335	0.0976	0.342	0.0926	0.349	0.0893	0.355
0.7638	0.6025	0.831	0.5928	0.857	0.5791	0.896	0.5663	0.933	0.1083	0.0683	0.170	0.0658	0.172	0.0633	0.175	0.0605	0.178
xC$_2$H$_5$OH + (1 − x)[BMIM][OctS]																	
0.95435	0.9966	0.036	0.9942	0.061	0.9899	0.106	0.9869	0.137	0.4892	0.4236	0.414	0.3815	0.464	0.3519	0.503	0.3271	0.538
0.87474	0.9932	0.024	0.9818	0.064	0.9622	0.135	0.9412	0.212	0.3861	0.2730	0.411	0.2615	0.424	0.2454	0.444	0.2286	0.467
0.8343	0.9735	0.068	0.9561	0.113	0.9248	0.197	0.8947	0.281	0.3544	0.2376	0.397	0.2253	0.411	0.2150	0.424	0.2032	0.440
0.7831	0.9345	0.123	0.8985	0.194	0.8502	0.294	0.8026	0.399	0.2873	0.1696	0.360	0.1617	0.369	0.1523	0.382	0.1446	0.392
0.7299	0.8624	0.201	0.8109	0.284	0.7503	0.390	0.6898	0.504	0.1794	0.0959	0.258	0.0885	0.267	0.0823	0.275	0.0767	0.282
0.6992	0.8139	0.241	0.7524	0.333	0.6886	0.436	0.6261	0.547	0.1429	0.0729	0.220	0.0680	0.226	0.0632	0.232	0.0596	0.237
0.6364	0.7057	0.307	0.6378	0.396	0.5636	0.505	0.5055	0.600	0.0617	0.0388	0.108	0.0355	0.111	0.0313	0.115	0.0279	0.119
0.5515	0.5300	0.393	0.4745	0.461	0.4301	0.522	0.3877	0.586									
xC$_3$H$_7$OH + (1 − x)[BMIM][OctS]																	
0.9091	0.9886	0.057	0.9605	0.202	0.9381	0.319	0.9200	0.417	0.3863	0.2450	0.447	0.2369	0.458	0.2274	0.471	0.2174	0.485
0.8530	0.9800	0.059	0.9309	0.208	0.8856	0.353	0.8520	0.465	0.3116	0.1636	0.416	0.1566	0.426	0.1506	0.435	0.1424	0.448
0.7996	0.8946	0.223	0.8437	0.340	0.7842	0.486	0.7490	0.578	0.1724	0.0710	0.284	0.0652	0.293	0.0589	0.304	0.0537	0.314
0.7253	0.7124	0.449	0.6830	0.505	0.6561	0.558	0.6300	0.612	0.1464	0.0617	0.246	0.0552	0.256	0.0504	0.264	0.0465	0.271
0.5896	0.5037	0.495	0.4880	0.518	0.4693	0.546	0.4504	0.576	0.1218	0.0526	0.212	0.0465	0.221	0.0422	0.228	0.0400	0.232
0.5595	0.4643	0.490	0.4472	0.514	0.4327	0.535	0.4124	0.566									
xC$_6$H$_6$ + (1 − x)[BMIM][OctS]																	
0.97415	0.9991	0.019	0.9974	0.053	0.9967	0.066	0.9963	0.075	0.6275	0.8954	0.095	0.8667	0.123	0.8406	0.149	0.8168	0.174
0.9590	0.9980	0.023	0.9971	0.034	0.9963	0.043	0.9957	0.051	0.5480	0.7997	0.139	0.7675	0.164	0.7387	0.188	0.7213	0.203
0.91993	0.9959	0.024	0.9964	0.021	0.9961	0.023	0.9947	0.031	0.4165	0.6100	0.182	0.5849	0.197	0.5665	0.209	0.5515	0.219
0.87018	0.9946	0.018	0.9954	0.016	0.9920	0.027	0.9886	0.039	0.3758	0.5501	0.186	0.5250	0.200	0.5088	0.210	0.4978	0.217
0.8183	0.9934	0.015	0.9867	0.030	0.9801	0.046	0.9726	0.063	0.2467	0.3766	0.166	0.3603	0.174	0.3487	0.179	0.3402	0.184
0.7843	0.9863	0.025	0.9765	0.044	0.9674	0.061	0.9565	0.082	0.1498	0.2343	0.134	0.2192	0.140	0.2111	0.143	0.2037	0.147
0.6988	0.9529	0.057	0.9333	0.081	0.9140	0.106	0.8946	0.131	0.0624	0.1058	0.079	0.0938	0.083	0.0892	0.085	0.0877	0.085
xCH$_3$OH + (1 − x)[OMIM][BF$_4$]																	
0.9400	0.9591	0.327	0.9501	0.401	0.9404	0.481	0.9330	0.543	0.3539	0.3929	0.258	0.3806	0.267	0.3671	0.277	0.3592	0.283
0.8860	0.9361	0.257	0.9238	0.308	0.910	0.367	0.8943	0.435	0.2228	0.2140	0.223	0.2042	0.230	0.1927	0.238	0.1839	0.245
0.7474	0.8314	0.274	0.8212	0.292	0.8067	0.319	0.7934	0.343	0.1740	0.1522	0.200	0.1451	0.205	0.1377	0.211	0.1307	0.216
0.6278	0.7178	0.281	0.7029	0.299	0.6865	0.319	0.6751	0.333	0.0931	0.0681	0.139	0.0654	0.141	0.0628	0.143	0.0601	0.145
0.5473	0.6207	0.290	0.6094	0.301	0.5957	0.315	0.5852	0.326	0.0657	0.0509	0.106	0.0490	0.107	0.0467	0.109	0.0436	0.111
0.4444	0.5096	0.272	0.4970	0.282	0.4854	0.291	0.4717	0.303	0.0388	0.0308	0.071	0.0291	0.072	0.0272	0.074	0.0252	0.075
0.4243	0.4850	0.269	0.4731	0.278	0.4607	0.288	0.4478	0.298									
xC$_2$H$_5$OH + (1 − x)[OMIM][BF$_4$]																	
0.9346	0.9851	0.107	0.9728	0.197	0.9649	0.255	0.9549	0.330	0.4883	0.6731	0.190	0.6513	0.205	0.6290	0.222	0.6053	0.241
0.9196	0.9838	0.093	0.9699	0.175	0.9593	0.238	0.9461	0.317	0.4046	0.5756	0.189	0.5559	0.201	0.5277	0.218	0.5101	0.230
0.8596	0.9715	0.089	0.9482	0.163	0.9369	0.200	0.9141	0.275	0.2510	0.3908	0.159	0.3659	0.170	0.3409	0.182	0.3236	0.190
0.7258	0.8945	0.148	0.8648	0.193	0.8451	0.223	0.8193	0.264	0.2113	0.3326	0.149	0.3107	0.158	0.2930	0.166	0.2761	0.174
0.6202	0.8106	0.172	0.7835	0.200	0.7595	0.225	0.7328	0.255	0.1226	0.1996	0.114	0.1802	0.121	0.1655	0.127	0.1544	0.132
0.5721	0.7628	0.182	0.7375	0.204	0.7161	0.224	0.6881	0.251	0.0838	0.1407	0.091	0.1284	0.095	0.1153	0.100	0.1050	0.104
xC$_3$H$_7$OH + (1 − x)[OMIM][BF$_4$]																	
0.9228	0.9925	0.045	0.9839	0.097	0.9727	0.165	0.9669	0.201	0.7041	0.9528	0.058	0.9210	0.098	0.8898	0.139	0.8499	0.194
0.8656	0.9900	0.032	0.9782	0.071	0.9616	0.126	0.9455	0.180	0.6075	0.9014	0.081	0.8575	0.119	0.8140	0.160	0.7691	0.204
0.8407	0.9882	0.031	0.9743	0.069	0.9572	0.115	0.9347	0.178	0.5068	0.8213	0.102	0.7776	0.130	0.7288	0.163	0.6832	0.196
0.8026	0.9832	0.034	0.9660	0.070	0.9462	0.113	0.9146	0.182	0.3484	0.6221	0.128	0.5857	0.144	0.5543	0.159	0.5164	0.178
0.7281	0.9618	0.052	0.9353	0.090	0.9079	0.130	0.8681	0.190	0.1742	0.3435	0.114	0.3179	0.122	0.2955	0.130	0.2817	0.135
xC$_6$H$_6$ + (1 − x)[OMIM][BF$_4$]																	
0.83959	0.9902	0.026	0.9864	0.036	0.9718	0.075	0.9362	0.173	0.6417	0.8340	0.164	0.8212	0.178	0.8014	0.200	0.7717	0.234
0.78731	0.9803	0.037	0.9724	0.052	0.9502	0.095	0.9083	0.179	0.5660	0.7507	0.189	0.7370	0.201	0.7198	0.217	0.6971	0.238
0.7620	0.9624	0.062	0.9480	0.086	0.9200	0.134	0.8863	0.194	0.5299	0.7106	0.195	0.6976	0.206	0.6801	0.220	0.6592	0.238
0.7586	0.9598	0.065	0.9450	0.089	0.9142	0.142	0.8822	0.198	0.3583	0.4739	0.212	0.4689	0.215	0.4630	0.219	0.4575	0.222
0.7464	0.9455	0.083	0.9322	0.104	0.9014	0.154	0.8695	0.207	0.2640	0.3480	0.193	0.3450	0.195	0.3415	0.196	0.3377	0.198
0.6905	0.8845	0.138	0.8730	0.153	0.8482	0.185	0.8164	0.228	0.1839	0.2541	0.158	0.2519	0.159	0.2497	0.160	0.2469	0.161

data exist in the literature.[13] The experiments were carried out in the temperature range T = (298.15 to 313.15) K. The experimental vapor pressure is assessed to be reliable to within ± 1 % according to the test measurements.

Results and Discussion

Experimental vapor pressures p of binary mixtures of [BMIM][OctS] or [OMIM][BF$_4$] with (CH$_3$OH, C$_2$H$_5$OH, C$_3$H$_7$OH, or C$_6$H$_6$) measured at T = (298.15 to 313.15) K are listed in Table 1.

Binary mixtures of ILs with nonelectrolyte components belong to the class of electrolyte solutions covering the whole range of composition including the pure liquid electrolyte. Since there exists no reliable theoretical models for the Gibbs energy of mixing of this kind of mixtures, we have tried to describe the results of activity coefficients using purely empirical expressions well-known in thermodynamics of nonelectrolyte mixtures. It turned out[5] that the NRTL equation gives the best empirical description of the activity coefficients. Equation 1 has been used to determine activity coefficients γ_1 using the NRTL

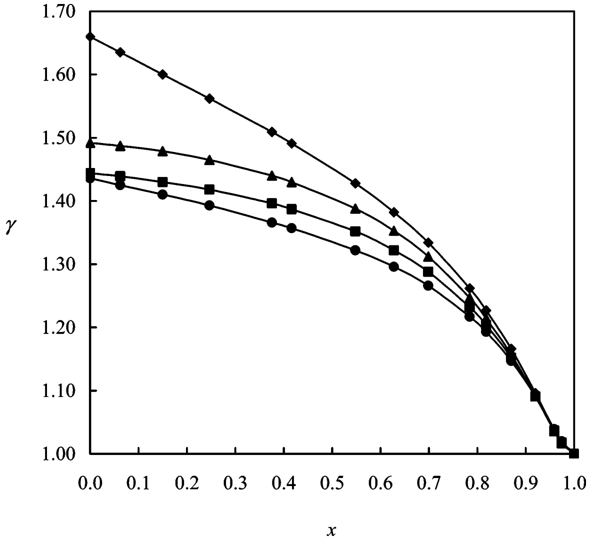

Figure 4. Plot of activity coefficient γ of benzene in C_6H_6 + [BMIM]-[OctS] mixture vs mole fraction x of C_6H_6: ◆, 298.15 K; ▲, 303.15 K; ■, 308.15 K; ●, 313.15 K. Points and solid lines: eq 3.

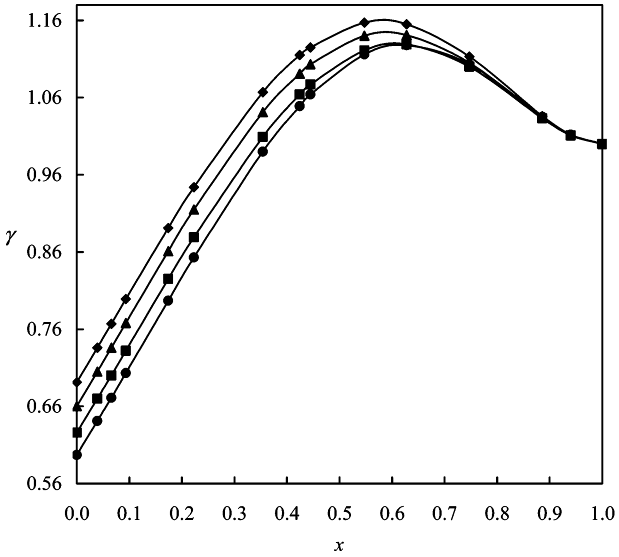

Figure 5. Plot of activity coefficient γ of methanol in CH_3OH + [OMIM]-[BF$_4$] mixture vs mole fraction x of CH_3OH: ◆, 298.15 K; ▲, 303.15 K; ■, 308.15 K; ●, 313.15 K. Points and solid lines: eq 3.

equation from experimental data of partial pressures p_1 including the vapor pressure of the pure solutes p_{10}:

$$p_1\frac{\varphi_1}{\varphi_{10}} = p_{10}x_1\gamma_1^{\mathrm{NRTL}} \tag{1}$$

Corrections due to fugacity coefficients φ_1 and φ_{10} have been accounted for by

$$\frac{\varphi_1}{\varphi_{10}} = \exp[-(V_1 - B_{11})(p_1 - p_{10})/RT] \tag{2}$$

The second virial coefficients B_{11} of the alcohols and benzene have been taken from ref 14; the molar liquid volumes V_1 are from ref 15. These data are presented in Table 2. It turned out that the eq 2 is only a small correction for the values of γ_1, which is within ± 1 %. The expression for ln γ_1 is

$$\ln\gamma_1^{\mathrm{NRTL}} = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2 + x_1G_{12})^2}\right] \tag{3}$$

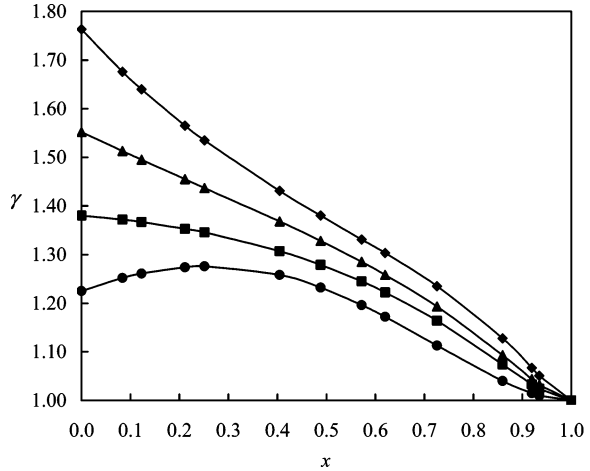

Figure 6. Plot of activity coefficient γ of ethanol in C_2H_5OH + [OMIM]-[BF$_4$] mixture vs mole fraction x of C_2H_5OH: ◆, 298.15 K; ▲, 303.15 K; ■, 308.15 K; ●, 313.15 K. Points and solid lines: eq 3.

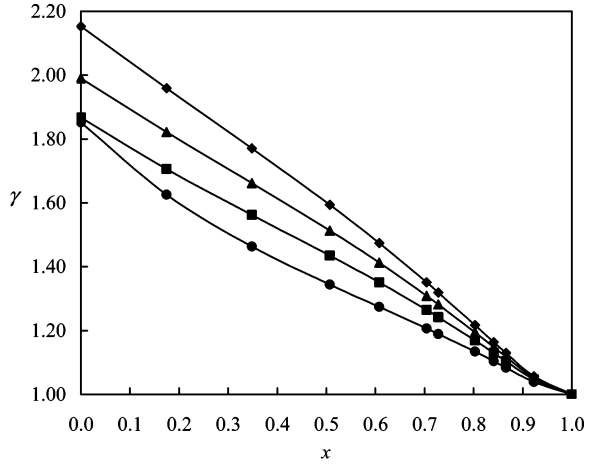

Figure 7. Plot of activity coefficient γ of propanol in C_3H_7OH + [OMIM]-[BF$_4$] mixture vs mole fraction x of C_3H_7OH: ◆, 298.15 K; ▲, 303.15 K; ■, 308.15 K; ●, 313.15 K. Points and solid lines: eq 3).

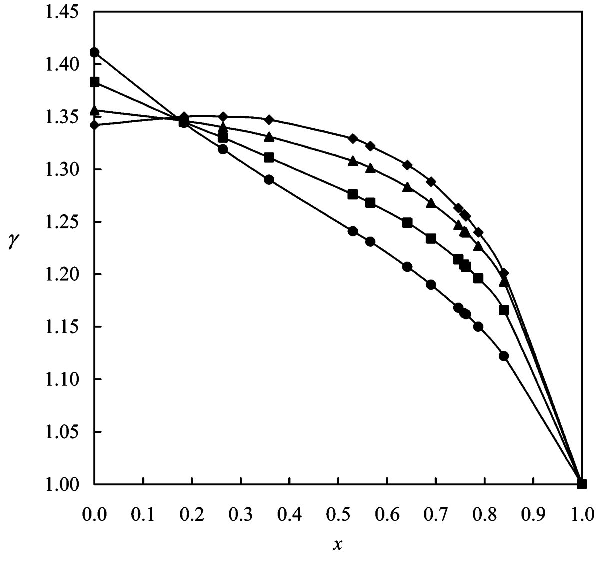

Figure 8. Plot of activity coefficient γ of benzene in C_6H_6 + [OMIM]-[BF$_4$] mixture vs mole fraction x of C_6H_6: ◆, 298.15 K; ▲, 303.15 K; ■, 308.15 K; ●, 313.15 K. Points and solid lines: eq 3.

with $G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$, $\tau_{ij} = (g_{ij} - g_{jj})/RT$ and $\alpha_{ij} = \alpha_{ji} = \alpha$ (i, j = 1, 2; $i \neq j$). Table 3 contains the parameters α_{ij} and ($g_{ij} - g_{jj}$) obtained by fitting γ_1^{NRTL} to the experimental VLE data.

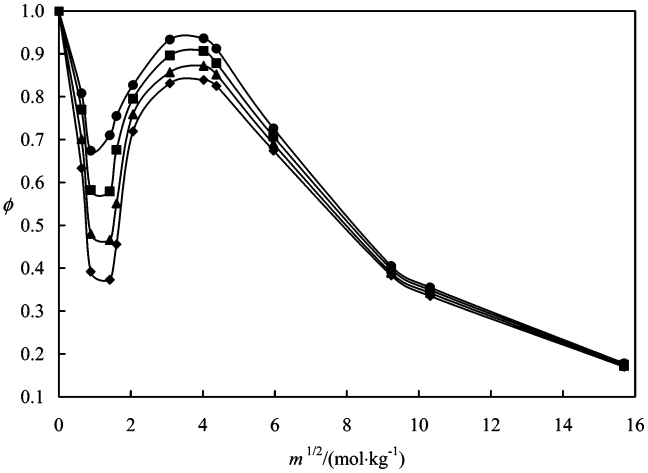

Figure 9. Plot of osmotic coefficient ϕ of CH_3OH + [BMIM][OctS] mixture vs molality $m^{1/2}$ of CH_3OH: ◆, 298.15 K; ▲, 303.15 K; ■, 308.15 K; ●, 313.15 K.

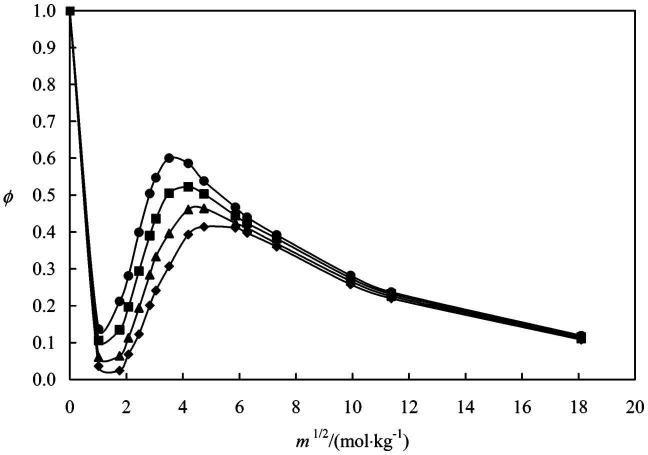

Figure 10. Plot of osmotic coefficient ϕ of C_2H_5OH + [BMIM][OctS] mixture vs molality $m^{1/2}$ of C_2H_5OH: ◆, 298.15 K; ▲, 303.15 K; ■, 308.15 K; ●, 313.15 K.

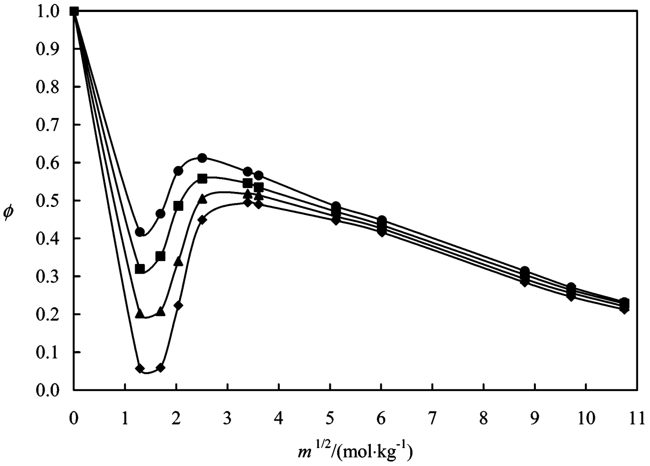

Figure 11. Plot of osmotic coefficient ϕ of C_3H_7OH + [BMIM][OctS] mixture vs molality $m^{1/2}$ of C_3H_7OH: ◆, 298.15 K; ▲, 303.15 K; ■, 308.15 K; ●, 313.15 K.

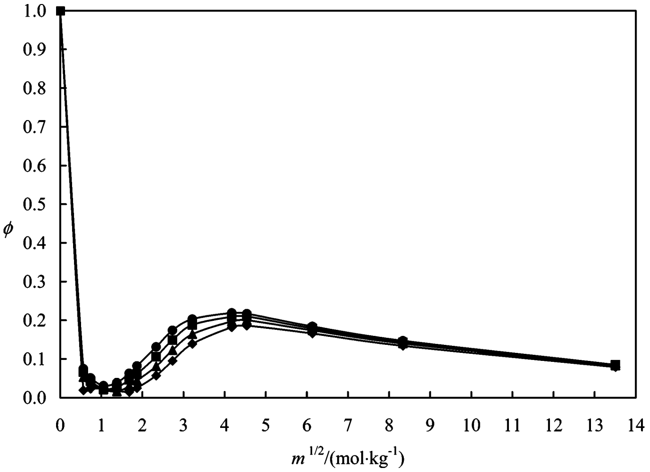

Figure 12. Plot of osmotic coefficient ϕ of C_6H_6 + [BMIM][OctS] mixture vs molality $m^{1/2}$ of C_6H_6: ◆, 298.15 K; ▲, 303.15 K; ■, 308.15 K; ●, 313.15 K.

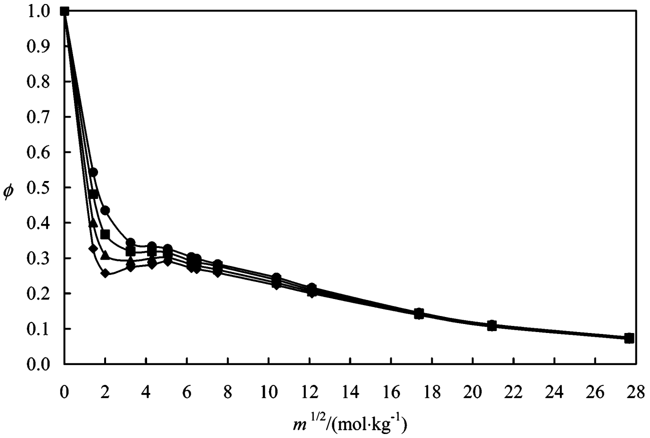

Figure 13. Plot of osmotic coefficient ϕ of CH_3OH + [OMIM][BF_4] mixture vs molality $m^{1/2}$ of CH_3OH: ◆, 298.15 K; ▲, 303.15 K; ■, 308.15 K; ●, 313.15 K.

The plots of eq 3 of ILs with alcohols and benzene versus the mole fractions x_1 of solvent are shown in Figures 1 to 8.

The activity of the solvent (a_s) and osmotic coefficients (ϕ) were calculated from the experimental vapor pressure values using the following equations:

$$\ln a_s = \ln(p/p^*) + (B_s - V_s^*)(p - p^*)/RT \qquad (4)$$

$$\phi = -\ln a_s/(\nu m M_s) \qquad (5)$$

where p and p^* are the vapor pressures of the solution and pure solvent, respectively; B_s and V_s^* are the second virial coefficient of solvent vapor and molar volume of pure liquid solvent, respectively; ν is the sum of stoichiometric numbers of anion and cation ($\nu_- + \nu_+$); m is molality of salt; and M_s is the molecular weight of solvent, respectively. The second term on the right-hand side of eq 4 takes into account the nonideality of the solvent vapor using the virial equation. The obtained values for a_s and ϕ are tabulated in Table 5. The values of p^*, B_s, and V_s^* required for calculations were taken from refs 12, 14, and 15 and are shown in Table 2. The plots of eq 5 of ILs with alcohols and benzene versus the molality of solvent are shown in Figures 9 to 16.

Values of γ_i^∞ in [OMIM][BF_4] at 298 K extrapolated from the present VLE results agree well with our previous results obtained by GC techniques[9] for ethanol and propanol (see Table 4), indicating consistency of both methods. The deviation in case of methanol arises from some inherent problems involved with methanol by using the GC technique, discussed in the ref 9. The deviation in case of benzene arises most probably from an insufficient extrapolation based on VLE data with mole fractions not small enough to justify an extrapolation within the uncertainty of experimental error of the GC method.[9] Values

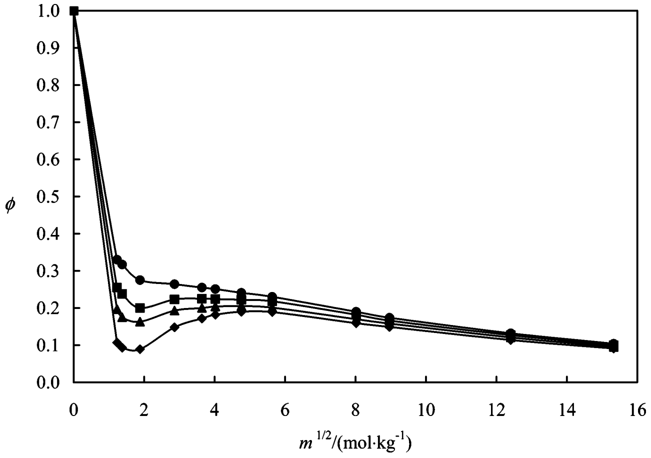

Figure 14. Plot of osmotic coefficient ϕ of C_2H_5OH + [OMIM][BF_4] mixture vs molality $m^{1/2}$ of C_2H_5OH: ◆, 298.15 K; ▲, 303.15 K; ■, 308.15 K; ●, 313.15 K.

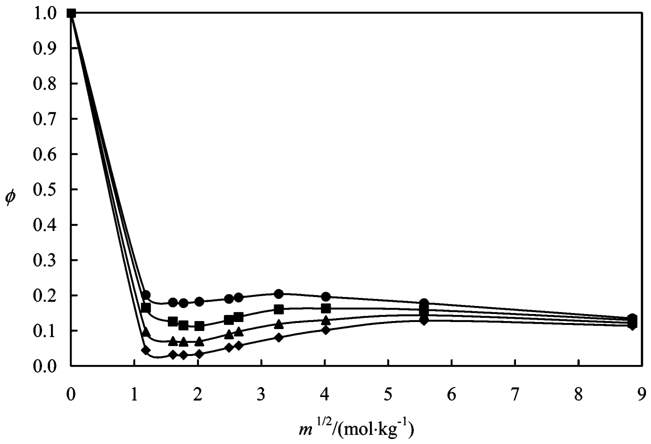

Figure 15. Plot of osmotic coefficient ϕ of C_3H_7OH + [OMIM][BF_4] mixture vs molality $m^{1/2}$ of C_3H_7OH: ◆, 298.15 K; ▲, 303.15 K; ■, 308.15 K; ●, 313.15 K.

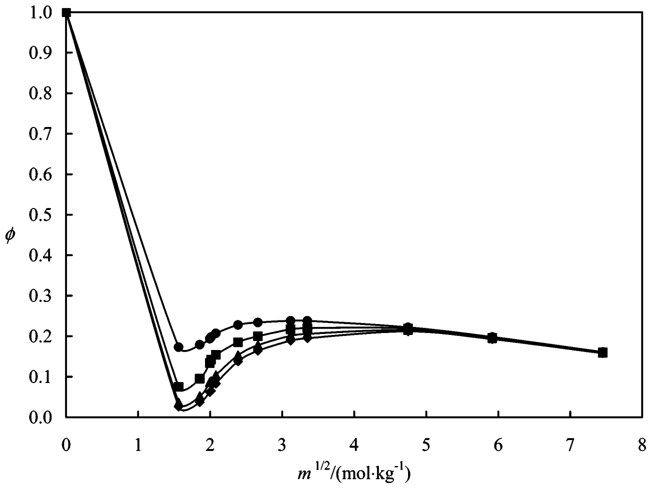

Figure 16. Plot of osmotic coefficient ϕ of C_6H_6 + [OMIM][BF_4] mixture vs molality $m^{1/2}$ of C_6H_6: ◆, 298.15 K; ▲, 303.15 K; ■, 308.15 K; ●, 313.15 K.

of γ_i^∞ for methanol and benzene in [BMIM][OctS] at 298 K (see Table 4) extrapolated from our VLE results agree in acceptable way with the GC-results.

Values of γ_1 decrease with temperature for all mixtures (except for the mixture methanol + [BMIM][OctS]. In case of ethanol + [BMIM][OctS] and methanol + [OMIM][BF_4], γ_1 passes a maximum at high mole fractions of the solvents. Such a behavior is similar to the results obtained for [BMIM][NTf_2] investigated in our previous work.[5] In case of benzene in [BMIM][OctS], γ_1 is > 1 in the whole range of concentration. Generally, values of γ_1 in [OMIM][BF_4] are higher for all solvents, indicating a less favorable interactional energy between the mixing partners. An unusual behavior occurs in case of the system benzene + [OMIM][BF_4], where the change of sign concerning the temperature dependence of γ_1 is observed leading to a crossing point of γ_1 at $x \approx 0.2$. On the other side γ_i^∞ of benzene at 298 K obtained from GC is 1.19 (see Table 4), which is distinctly outside the experimental error for both methods. This system requires a more careful investigation concerning the temperature dependence of γ_1 in particular on smaller x values. Heats of dilution measurements of the benzene + [OMIM][BF_4] system are currently under study and hopefully will clear this special situation.

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