Thermodynamic Properties of Mixtures Containing Ionic Liquids. Activity Coefficients of Ethers and Alcohols in 1-Methyl-3-Ethyl-Imidazolium Bis(Trifluoromethyl-sulfonyl) Imide Using the Transpiration Method

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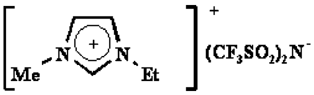
Vapor−liquid equilibria of binary mixtures containing high-boiling solutes methoxy-benzene, (hydroxymethyl)-benzene, 1,2-ethanediol, and 1,4-butanediol and ionic liquid [EMIM][NTf$_2$] were studied by using the transpiration method. VLE measurements were carried out over the whole concentration range at different temperatures between 298 K and 363 K. Activity coefficients γ_i of these solvents in the ionic liquid have been determined from these data and are described formally by using the NRTL equation. In addition, vapor pressures of pure solutes methoxy-benzene, (hydroxymethyl)-benzene, 1,2-ethanediol, and 1,4-butanediol have been measured as a function of temperature, and their enthalpies of vaporization have been obtained.

Introduction

The use of ionic liquids (ILs) as solvents for a broad range of chemical processes is potentially one of the most significant developments of the past decade. In contrast to molten salts, which have very high melting points and are highly corrosive, ionic liquids are organic salts that are liquids under ambient conditions. Ionic liquids are thermally stable and odorless, and many are unaffected by moisture. They have no detectable vapor pressure and are immiscible or partially miscible with saturated hydrocarbon solvents, dialkyl ethers, and water (which makes the extraction of organic products simple and efficient). Because of this combination of properties, ionic liquids are candidates for recyclable “green” solvents. Knowledge of specific properties will provide fundamental insight into the unique behavior of this novel class of solvents. A diverse range of ionic liquids is commercially available.[7] However, little information is available on their physical properties. This work continues our study of the thermodynamic properties of mixtures of solutes in ILs.[1−5] Activity coefficients covering the whole range of composition for mixtures containing high-boiling compounds (such as aldehydes and ketones) and ionic liquids were reported recently.[6] With the present work, we continue to fill the gap of information on this class of ionic liquid mixtures.

We have performed measurements of activity coefficient γ_i of four solutes in the ionic liquid 1-methyl-3-ethyl-imidazolium bis(trifluoromethyl-sulfonyl) imide [EMIM]-[NTf$_2$]:



A series of mixtures of the solutes methoxy-benzene, (hydroxymethyl)-benzene, 1,2-ethanediol, and 1,4-butanediol with [EMIM][NTf$_2$], have been studied over the temperature range of (298 to 363) K. Vapor pressures of the pure individual alcohols and ether, required for the calculation of the activity coefficients, as well as enthalpies of vaporization of these compounds have been obtained by using the transpiration method (Table 1).

Experimental Section

Materials. The samples of methoxybenzene (or anisol), (hydroxymethyl)-benzene (or benzyl alcohol), 1,2-ethanediol, and 1,4-butanediol were purchased from Aldrich and Merck and dried and purified by fractional distillation. The degree of purity was controlled using a Hewlett-Packard gas chromatograph 5890 series II equipped with a flame-ionization detector, autosampler, and Hewlett-Packard 3390A integrator. The carrier gas (nitrogen) flow was 0.726 dm^3·min^{-1}. An HP-5 capillary column (stationary phase cross-linked 5% PH ME silicone) was used with a column length of 30 m, an inside diameter of 0.32 mm, and a film thickness of 0.25 m. The standard temperature program of the GC was $T = 333$ K for 3 min followed by a heating rate of 10 K·min^{-1} to $T = 523$ K. No impurities (greater than mass fraction 0.0005) could be detected in the samples used for the investigation. The ionic liquid [EMIM][NTf$_2$] was synthesized according to the literature procedure.[8] Before use, the sample was dissolved in excess methanol and filtered. Then it was subjected to vacuum evaporation at 333 K over 24 h to remove possible traces of solvents and moisture. Samples of ionic liquid used in the experiment have been checked regularly concerning water content using Karl Fischer titration. In all cases, the content of water was less than 100 ppm. All samples have been stored in a dry atmosphere of N$_2$ before use.

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10.1021/je0497799 CCC: $30.25

Table 1. Results for the Vapor Pressure p and $\Delta_l^g H_m$ of Pure Compounds Obtained by the Transpiration Method

T/K	m/mg	V_{N_2}/dm^3	p/Pa	$p_{exptl} - p_{calcd}$/Pa	$\Delta_l^g H_m$/kJ·mol^{-1}	T/K	m/mg	V_{N_2}/dm^3	p/Pa	$p_{exptl} - p_{calcd}$/Pa	$\Delta_l^g H_m$/kJ·mol^{-1}
Methoxy-benzene, $\Delta_l^g H_m(298.15\ K) = (46.59 \pm 0.22)$ kJ·mol^{-1}											
eq 2: $a = 269.809$ J·mol^{-1}K^{-1}, $b = -65\ 160.559$ J·mol^{-1}, $\Delta_l^g C_p = 62.3$ J·mol^{-1}K^{-1}											
278.3	4.88	0.96	122.0	0.1	47.83	296.3	4.90	0.28	410.9	−10.9	46.70
281.3	4.47	0.70	152.4	0.6	47.64	299.3	5.75	0.26	518.8	8.9	46.52
284.3	4.85	0.61	189.3	1.1	47.45	302.2	6.24	0.24	610.6	0.8	46.34
287.3	5.49	0.56	231.7	−0.2	47.26	306.2	6.38	0.19	765.0	−10.5	46.09
290.3	5.57	0.46	285.1	0.5	47.08	309.2	8.62	0.21	929.2	5.1	45.90
293.3	5.21	0.35	345.2	−2.0	46.89	312.3	6.21	0.13	1113.9	10.9	45.71
(Hydroxymethyl)-benzene, $\Delta_l^g H_m(298.15\ K) = (65.46 \pm 0.38)$ kJ·mol^{-1}											
eq 2: $a = 307.387$ J·mol^{-1}K^{-1}, $b = -85\ 350.413$ J·mol^{-1}, $\Delta_l^g C_p = 66.7$ J·mol^{-1}K^{-1}											
282.2	0.89	7.49	2.72	−0.1	66.53	305.2	1.29	1.23	23.77	0.6	65.00
285.2	0.98	6.08	3.68	−0.1	66.33	308.1	0.95	0.75	28.95	−0.5	64.80
288.2	1.00	4.40	5.16	0.1	66.13	311.2	0.88	0.53	37.79	−0.2	64.60
291.2	1.35	4.46	6.88	0.2	65.93	314.1	1.16	0.57	46.68	−1.1	64.40
294.1	1.27	3.23	8.90	0.1	65.74	317.1	1.25	0.46	60.77	0.5	64.20
297.2	1.02	2.02	11.48	−0.1	65.53	320.1	1.06	0.32	74.55	−1.2	64.00
300.2	1.19	1.74	15.49	0.4	65.33	323.0	0.84	0.20	94.70	0.7	63.81
303.2	1.08	1.25	19.59	0.0	65.13						
1,2-Ethanediol, $\Delta_l^g H_m(298.15\ K) = (65.40 \pm 0.32)$ kJ·mol^{-1}											
eq 2: $a = 289.087$ J·mol^{-1}K^{-1}, $b = -80\ 163.333$ J·mol^{-1}, $\Delta_l^g C_p = 49.5$ J·mol^{-1}K^{-1}											
308.2	1.24	1.86	26.39	−0.3	64.91	310.2	1.97	2.51	31.07	−0.4	64.81
313.2	2.40	2.36	40.27	0.3	64.66	316.2	1.81	1.45	49.50	−1.1	64.51
328.1	1.63	0.52	124.4	1.7	63.92	318.2	1.88	1.24	59.97	0.9	64.41
303.2	2.17	4.79	17.99	0.4	65.16	320.2	1.96	1.14	67.97	−0.7	64.32
323.2	2.21	1.04	84.64	−1.3	64.17	331.2	2.09	0.54	152.3	−0.5	63.77
326.2	1.65	0.62	105.3	−1.7	64.02	333.2	3.75	0.83	179.2	3.6	63.67
306.2	1.98	3.44	22.75	0.1	65.01	336.2	1.98	0.36	216.4	0.9	63.52
1,4-Butanediol, $\Delta_l^g H_m(298.15\ K) = (78.95 \pm 0.92)$ kJ·mol^{-1}											
eq 2: $a = 325.131$ J·mol^{-1}K^{-1}, $b = -97\ 614.424$ J·mol^{-1}, $\Delta_l^g C_p = 62.6$ J·mol^{-1}K^{-1}											
329.2	0.48	0.94	13.85	−0.9	77.01	348.2	1.21	0.48	69.52	1.8	75.82
332.3	0.79	1.13	18.99	−0.2	76.82	351.2	0.97	0.31	84.55	−0.1	75.63
335.2	1.12	1.25	24.37	0.0	76.63	353.2	1.07	0.28	103.1	5.1	75.51
338.2	0.90	0.76	32.20	1.1	76.45	356.2	0.99	0.22	120.6	−1.1	75.32
341.2	0.82	0.57	39.40	−0.1	76.26	358.3	0.93	0.18	142.1	0.8	75.19
343.2	0.93	0.54	47.54	1.4	76.13	361.2	0.91	0.15	167.1	−5.8	75.01
346.3	0.95	0.43	59.71	1.1	75.94	363.2	1.03	0.15	189.0	−9.3	74.88

Table 2. VLE in the System (Methoxy-benzene + [EMIM][NTf$_2$])

T/K	x_1	p_1^{exptl}/Pa	p_1^{NRTL}/Pa	γ_1^{NRTL}	ln γ_1^{NRTL}	T/K	x_1	p_1^{exptl}/Pa	p_1^{NRTL}/Pa	γ_1^{NRTL}	ln γ_1^{NRTL}
298.6	0.000	0.00	0.00	1.591	0.464	298.6	0.679	431.62	403.51	1.188	0.172
	0.200	155.51	152.46	1.521	0.419		0.796	430.15	436.23	1.096	0.091
	0.377	261.75	267.95	1.420	0.351		0.920	496.64	469.12	1.020	0.019
	0.569	345.76	363.70	1.278	0.245		1.000	500.11	500.11	1.000	0.000
303.6	0.000	0.00	0.00	1.812	0.594	303.6	0.661	580.89	606.63	1.364	0.311
	0.174	192.98	204.81	1.748	0.558		0.783	640.17	641.01	1.216	0.195
	0.232	285.00	268.59	1.719	0.542		0.917	670.31	650.40	1.053	0.052
	0.493	529.33	509.11	1.535	0.429		1.000	673.07	673.07	1.000	0.000
308.6	0.000	0.00	0.00	2.140	0.761	308.6	0.764	875.72	847.19	1.243	0.217
	0.146	247.23	259.38	1.986	0.686		0.914	913.59	860.04	1.054	0.053
	0.185	341.20	320.78	1.945	0.665		1.000	892.11	892.11	1.000	0.000
	0.642	753.94	805.51	1.406	0.341						
313.6	0.000	0.00	0.00	2.724	1.002	313.6	0.621	1035.40	1088.07	1.486	0.396
	0.118	312.06	335.48	2.409	0.879		0.740	1159.89	1138.35	1.306	0.267
	0.143	414.76	395.21	2.351	0.855		0.911	1156.25	1143.64	1.065	0.063
	0.370	892.65	826.05	1.895	0.639		1.000	1178.31	1178.31	1.000	0.000
318.6	0.000	0.00	0.00	3.455	1.240	318.6	0.598	1402.91	1449.89	1.572	0.452
	0.088	395.31	400.39	2.952	1.083		0.713	1607.42	1526.47	1.387	0.327
	0.108	465.41	474.49	2.859	1.050		0.907	1546.61	1523.16	1.088	0.084
	0.303	1095.63	1015.30	2.174	0.776		1.000	1543.31	1543.31	1.000	0.000
323.6	0.000	0.00	0.00	4.648	1.536	323.6	0.572	1738.92	1783.24	1.555	0.441
	0.059	492.44	464.67	3.960	1.376		0.686	1925.27	1839.40	1.338	0.291
	0.076	558.03	573.82	3.792	1.333		0.904	1950.05	1898.54	1.048	0.047
	0.239	1180.83	1269.14	2.644	0.972		1.000	2004.25	2004.25	1.000	0.000

Vapor Pressure Measurements of Pure-Component Systems. The vapor pressure and enthalpies of vaporization of alcohols and ether were determined using the method of transpiration in a saturated N_2 stream and by applying the Clausius−Clapeyron equation. About 0.5 g of the sample was mixed with glass beads and placed in a thermostated U-shaped tube having a length of 20 cm and a diameter of 0.5 cm. Glass beads with a diameter of 1 mm provide a surface large enough for rapid vapor−liquid equilibration. At constant temperature (±0.1 K), a nitrogen stream was passed through the U tube, and the transported amount of gaseous material was collected in a cooling trap. The flow rate of the nitrogen stream was measured using a soap bubble flowmeter and optimized to reach the saturation equilibrium of the transporting gas at each temperature under study. The flow rate of the nitrogen stream in the saturation tube should not be too slow in order to avoid the transport of material from the U tube by diffusion. However, the flow rate should be not too fast in order to reach the saturation of the nitrogen stream with a compound. We tested our apparatus at different carrier gas flow rates to check the lower boundary of the flow rate

Table 3. VLE in the System ((Hydroxymethyl)-benzene + [EMIM][NTf$_2$])

T/K	x_1	p_1^{exptl}/Pa	p_1^{NRTL}/Pa	γ_1^{NRTL}	$\ln \gamma_1^{\text{NRTL}}$	T/K	x_1	p_1^{exptl}/Pa	p_1^{NRTL}/Pa	γ_1^{NRTL}	$\ln \gamma_1^{\text{NRTL}}$
298.6	0.000	0.00	0.00	1.937	0.661	298.6	0.549	8.19	7.93	0.982	−0.018
	0.049	1.14	1.14	1.586	0.461		0.670	10.42	9.72	0.986	−0.014
	0.154	2.87	2.76	1.217	0.196		0.851	11.66	12.48	0.996	−0.004
	0.270	3.89	4.21	1.060	0.058		0.963	13.90	14.17	1.000	0.000
	0.395	5.83	5.80	0.998	−0.002		1.000	13.02	14.72	1.000	0.000
	0.482	7.16	6.99	0.984	−0.016						
303.6	0.000	0.00	0.00	2.378	0.866	303.6	0.539	12.35	11.56	0.956	−0.045
	0.048	1.88	1.87	1.734	0.550		0.668	15.53	14.58	0.973	−0.028
	0.151	3.99	4.03	1.190	0.174		0.850	17.64	18.95	0.994	−0.006
	0.265	5.95	5.97	1.007	0.007		0.963	20.92	21.58	1.000	0.000
	0.391	7.94	8.36	0.954	−0.047		1.000	19.90	22.42	1.000	0.000
	0.478	10.53	10.19	0.951	−0.051						
308.6	0.000	0.00	0.00	1.974	0.680	308.6	0.527	18.62	17.85	0.954	−0.047
	0.046	2.57	2.53	1.547	0.436		0.550	20.43	18.65	0.957	−0.044
	0.144	5.94	5.85	1.148	0.138		0.666	21.93	22.99	0.973	−0.027
	0.183	6.62	6.97	1.074	0.071		0.849	29.06	29.94	0.994	−0.006
	0.259	8.70	9.11	0.993	−0.007		0.963	31.65	34.14	1.000	0.000
	0.473	17.38	15.94	0.949	−0.052		1.000	30.25	35.47	1.000	0.000
313.6	0.000	0.00	0.00	2.392	0.872	313.6	0.514	27.38	24.85	0.967	−0.033
	0.045	4.07	4.05	1.820	0.599		0.663	32.80	32.40	0.978	−0.022
	0.134	8.67	8.70	1.299	0.261		0.848	42.30	42.11	0.995	−0.005
	0.252	13.06	13.35	1.059	0.057		0.963	45.19	48.05	1.000	0.000
	0.382	18.55	18.69	0.981	−0.020		1.000	45.36	49.93	1.000	0.000
	0.467	21.99	22.55	0.968	−0.032						
318.6	0.000	0.00	0.00	2.393	0.872	318.6	0.498	40.20	36.13	0.998	−0.002
	0.042	5.82	5.84	1.927	0.656		0.540	42.25	39.02	0.993	−0.007
	0.123	13.13	12.89	1.445	0.368		0.660	48.14	47.49	0.990	−0.010
	0.245	19.94	20.47	1.148	0.138		0.846	59.51	61.31	0.997	−0.003
	0.376	27.73	28.28	1.034	0.033		0.963	67.53	69.96	1.000	0.000
	0.459	30.21	33.52	1.005	0.005		1.000	67.17	72.67	1.000	0.000
323.6	0.000	0.00	0.00	2.445	0.894	323.6	0.535	60.97	57.60	1.047	0.046
	0.039	8.71	8.35	2.105	0.744		0.655	68.57	68.59	1.018	0.018
	0.112	18.05	19.37	1.687	0.523		0.844	83.95	86.93	1.002	0.002
	0.371	43.54	43.57	1.142	0.133		0.962	96.10	98.98	1.000	0.000
	0.448	48.51	50.05	1.087	0.083		1.000	98.27	102.84	1.000	0.000
	0.480	56.58	52.83	1.070	0.067						

Table 4. VLE in the System (1,2-Ethanediol + [EMIM][NTf$_2$])

T/K	x_1	p_1^{exptl}/Pa	p_1^{NRTL}/Pa	γ_1^{NRTL}	$\ln \gamma_1^{\text{NRTL}}$	T/K	x_1	p_1^{exptl}/Pa	p_1^{NRTL}/Pa	γ_1^{NRTL}	$\ln \gamma_1^{\text{NRTL}}$
339.6	0.000	0.00	0.00	2.672	0.983	339.6	0.629	246.26	255.90	1.535	0.428
	0.133	87.93	89.17	2.534	0.930		0.713	249.64	256.56	1.357	0.305
	0.294	176.04	176.87	2.268	0.819		0.860	251.50	252.30	1.107	0.101
	0.436	239.12	227.81	1.971	0.679		0.951	261.38	256.14	1.016	0.015
	0.545	253.85	249.09	1.723	0.544		1.000	273.38	265.22	1.000	0.000
343.6	0.000	0.00	0.00	2.857	1.050	343.6	0.596	332.24	329.87	1.541	0.433
	0.128	115.35	120.23	2.619	0.963		0.612	320.06	331.20	1.507	0.410
	0.283	244.43	230.92	2.276	0.822		0.848	331.62	335.44	1.102	0.097
	0.413	304.44	291.27	1.964	0.675		0.948	353.03	345.03	1.014	0.014
	0.522	306.08	319.86	1.707	0.535		1.000	357.00	358.95	1.000	0.000
348.6	0.000	0.00	0.00	2.851	1.048	348.6	0.491	455.91	470.77	1.914	0.649
	0.122	154.14	164.79	2.701	0.994		0.552	460.36	487.26	1.761	0.566
	0.268	342.76	326.92	2.437	0.891		0.832	452.64	481.89	1.155	0.144
	0.367	439.70	407.71	2.216	0.796		0.944	512.00	483.19	1.021	0.021
	0.384	434.78	418.76	2.176	0.777		1.000	494.08	501.13	1.000	0.000
353.6	0.000	0.00	0.00	3.315	1.199	353.6	0.494	637.20	656.76	1.985	0.686
	0.115	218.76	236.00	3.063	1.119		0.813	604.61	648.42	1.192	0.175
	0.251	494.27	454.79	2.703	0.994		0.940	681.03	644.33	1.025	0.025
	0.348	605.80	563.64	2.423	0.885		1.000	677.55	669.13	1.000	0.000
	0.455	618.30	640.17	2.101	0.742						
358.6	0.000	0.00	0.00	3.752	1.322	358.6	0.423	845.16	879.21	2.417	0.882
	0.108	302.27	322.12	3.467	1.243		0.790	806.38	869.36	1.279	0.246
	0.235	637.36	619.89	3.072	1.122		0.936	872.85	832.00	1.034	0.033
	0.305	817.24	742.94	2.833	1.041		1.000	921.01	860.09	1.000	0.000
	0.416	880.08	873.70	2.441	0.892						
363.6	0.000	0.00	0.00	3.792	1.333	363.6	0.376	1167.75	1208.72	2.662	0.979
	0.101	380.66	433.76	3.547	1.266		0.762	1169.93	1263.69	1.374	0.318
	0.219	960.47	846.76	3.198	1.163		0.931	1221.86	1170.98	1.042	0.042
	0.261	1065.44	965.14	3.061	1.119		1.000	1241.41	1206.35	1.000	0.000
	0.345	1125.28	1154.06	2.774	1.020						

at which the contribution of the vapor condensed in the trap by diffusion becomes comparable to that transpired. In our apparatus, the contribution due to diffusion was negligible at a flow rate up to 6.6 cm^3·min^{-1}. The upper limit for our apparatus where the flow of nitrogen could already disturb the equilibration was at a flow rate of 49.2 cm^3·min^{-1}. Thus, we carried out the experiments in the flow rate interval of (16.8 to 31.2) cm^3·min^{-1}, which ensured

Table 5. VLE in the System (1,4-Butanediol + [EMIM][NTf$_2$])

T/K	x_1	p_1^{exptl}/Pa	p_1^{NRTL}/Pa	γ_1^{NRTL}	ln γ_1^{NRTL}
339.6	0.000	0.00	0.00	7.296	1.987
	0.059	11.91	11.72	5.066	1.623
	0.152	18.18	19.44	3.280	1.188
	0.184	21.86	20.86	2.902	1.065
	0.333	24.29	24.60	1.889	0.636
	0.362	26.00	25.10	1.775	0.574
	0.398	24.90	25.69	1.651	0.501
343.6	0.000	0.00	0.00	7.971	2.076
	0.053	15.95	15.75	5.594	1.722
	0.136	24.36	26.28	3.649	1.294
	0.172	30.36	28.59	3.147	1.146
	0.307	35.16	33.36	2.050	0.718
	0.346	35.19	34.25	1.867	0.624
	0.387	31.82	35.11	1.712	0.538
348.6	0.000	0.00	0.00	9.441	2.245
	0.043	23.86	23.10	6.772	1.913
	0.110	35.79	39.09	4.504	1.505
	0.156	45.27	44.24	3.608	1.283
	0.202	48.51	47.41	2.991	1.096
	0.271	52.70	50.44	2.371	0.863
	0.330	50.13	52.31	2.016	0.701
353.6	0.000	0.00	0.00	8.719	2.165
	0.087	51.12	49.58	5.349	1.677
	0.143	64.18	64.32	4.204	1.436
	0.181	67.54	71.04	3.662	1.298
	0.238	77.65	78.42	3.073	1.123
	0.299	92.41	84.36	2.630	0.967
	0.313	75.45	85.49	2.551	0.937
	0.529	105.12	99.25	1.750	0.560
	0.556	98.98	100.46	1.688	0.523
358.6	0.000	0.00	0.00	12.668	2.539
	0.067	73.89	75.28	7.279	1.985
	0.095	97.54	88.85	6.086	1.806
	0.132	91.60	100.43	4.970	1.603
	0.137	103.23	101.70	4.842	1.577
	0.209	105.66	114.09	3.560	1.270
	0.267	128.40	120.60	2.941	1.079
	0.510	147.77	139.98	1.786	0.580
	0.540	138.95	141.83	1.710	0.537
339.6	0.790	34.65	32.72	1.060	0.058
	0.855	34.91	34.36	1.029	0.028
	0.923	36.29	36.35	1.008	0.008
	0.965	36.59	37.75	1.002	0.002
	0.969	38.92	37.90	1.001	0.001
	0.980	36.30	38.30	1.001	0.001
	1.000	35.38	39.06	1.000	0.000
343.6	0.788	48.29	44.42	1.064	0.062
	0.853	45.19	46.56	1.031	0.031
	0.922	49.38	49.26	1.009	0.009
	0.964	51.14	51.16	1.002	0.002
	0.968	52.59	51.35	1.002	0.002
	0.980	49.01	51.92	1.001	0.001
	1.000	47.75	52.97	1.000	0.000
348.6	0.785	68.72	66.24	1.074	0.071
	0.849	68.95	69.18	1.037	0.036
	0.920	72.24	73.04	1.011	0.011
	0.963	76.24	75.84	1.002	0.002
	0.967	77.60	76.13	1.002	0.002
	0.980	74.11	77.02	1.001	0.001
	1.000	69.45	78.56	1.000	0.000
353.6	0.720	114.45	105.28	1.365	0.311
	0.782	94.66	105.65	1.262	0.233
	0.846	100.10	105.22	1.162	0.150
	0.918	104.99	104.41	1.062	0.060
	0.962	108.81	104.76	1.017	0.017
	0.967	111.22	104.90	1.013	0.013
	0.979	105.20	105.46	1.006	0.006
	1.000	99.95	107.10	1.000	0.000
358.6	0.709	158.13	148.97	1.367	0.313
	0.778	141.19	149.76	1.253	0.225
	0.841	144.85	149.49	1.158	0.147
	0.916	147.66	148.92	1.059	0.058
	0.961	155.86	149.90	1.016	0.016
	0.966	149.53	150.16	1.012	0.012
	0.979	149.18	151.10	1.005	0.005
	1.000	142.39	153.57	1.000	0.000

that the transporting gas was in saturated equilibrium with the coexisting liquid phase in the saturation tube. The amount of condensed substance was determined by GC analysis using an external standard (hydrocarbon n-C_nH_{2n+2}). The saturation vapor pressure p_i^{sat} at each temperature T_i was calculated from the amount of product collected within a definite period of time. Assuming that Dalton's law of partial pressures applied to the nitrogen stream saturated with substance i of interest is valid, values of p_i^{sat} were calculated with

$$p_i^{\text{sat}} = \frac{m_i R T_{\text{a}}}{M_i V} \qquad V = V_{\text{N}_2} + V_i \qquad (V_{\text{N}_2} \gg V_i) \quad (1)$$

where R = 8.31451 J·K^{-1}·mol^{-1}, m_i is the mass of transported compound, M_i is the molar mass of the compound, and V_i is its volume contribution to the gaseous phase. V_{N_2} is the volume of transporting gas, and T_{a} is the temperature of the soap bubble meter. The volume of transporting gas V_{N_2} was determined from the flow rate and time measurements. Data for p_i^{sat} have been obtained as a function of temperature and were fitted using the following equation:[9]

$$R \ln p_i^{\text{sat}} = a + \frac{b}{T} + \Delta_{\text{l}}^{\text{g}} C_p \ln \frac{T}{T_0} \qquad (2)$$

where a and b are adjustable parameters and $\Delta_{\text{l}}^{\text{g}} C_{\text{p}}$ is the difference in the molar heat capacities of the gas and the liquid phases, respectively. T_0 appearing in eq 2 is an arbitrarily chosen reference temperature (which has been chosen to be 298.15 K). Consequently, from eq 2 the expression for the vaporization enthalpy at temperature T is derived:

$$\Delta_{\text{l}}^{\text{g}} H_{\text{m}}(T) = -b + \Delta_{\text{l}}^{\text{g}} C_p T \qquad (3)$$

Values of $\Delta_{\text{l}}^{\text{g}} C_p$ have been derived from the isobaric molar heat capacities of the liquid, C_p^{l}, of ketones and from values of the isobaric molar heat capacities, C_p^{g}, of the gaseous species calculated according to a procedure developed by Chickos.[10] All results together with parameters a and b are listed in Table 1.

VLE Measurements of the Binary Mixtures (Solute + IL). Activity coefficients covering the whole range of concentration in a mixture of an ionic liquid and an organic solute can be measured using a dynamic method. This method is based on the so-called transpiration technique described above, which is particularly suitable in such cases where the vapor pressure of the solute is low. About (0.3 to 0.5) g of the IL was weighted in a glass flask together with a certain amount of a solute in order to obtain a desired mole fraction of the liquid phase. About 7 g of glass beads (having a size of 1 mm) were added to the content of the glass flask. Glass beads coated with the initial mixture were placed in the transpiration tube quantitatively. A slow stream of N_2 gas flowing through the tube continuously elutes the vapor phase in the glass tubing. Because of the negligible vapor pressure of the ionic liquid, the vapor phase consists exclusively of the solute and is condensed in a cooling trap. The mass of solute collected within a certain time interval is determined by dissolving it in a suitable solvent with a certain amount of internal standard (hydrocarbon). This solution is analyzed using a gas chromatograph equipped with an autosampler. The uncertainty of the amount of solute determined by GC analysis was assessed to be within (1−3)%. The peak area of the solute related to the peak of the external standard (hydrocarbon n-C_nH_{2n+2}) is a direct measure of the mass of the

Table 6. Comparison of Data for the Enthalpy of Vaporization $\Delta_g^l H_m$ at 298.15 K

technique	T/K	$\Delta_l^g H_m$/kJ·mol^{-1}	ref	technique	T/K	$\Delta_l^g H_m$/kJ·mol^{-1}	ref
			Methoxy-benzene				
ebulliometer	346.5−426.9	47.86 ± 0.18	Dreisbach, 1949	ebulliometer	365−430	45.8	Reich, 1993
		39.4	Glaser, 1957	calorimeter	298.15	46.84 ± 0.22	Fenwick, 1975
ebulliometer	383.1−437.3	48.38 ± 0.08	Collerson, 1965	transpiration	278.3−312.3	46.59 ± 0.22	this work
static manometer	363−383	38.15 ± 0.40	Lebedeva, 1972				
			(Hydroxymethyl)-benzene				
ebulliometer		60.29 ± 0.42	Mathews, 1926	ebulliometer	404.1−507.4	62.46 ± 0.30	Ambrose, 1990
ebulliometer	312.0−424.8	63.0 ± 2.2	Gardner, 1937	transpiration	282.2−323.0	65.46 ± 0.38	this work
ebulliometer	395.7−478.6	62.08 ± 0.27	Dreisbach, 1949				
			1,2-Ethanediol				
ebulliometer	323.2−473.2	64.8 ± 0.3	Jones, 1952	ebulliometer	374.0−495.4	63.70 ± 0.05	Ambrose, 1981
ebulliometer	363−403	68.2	Schierholz, 1935	calorimeter	298.15	65.6 ± 0.3	Knauth, 1989
static manometer	333−443	63.6	Gardner, 1972	transpiration	308.2−336.2	65.40 ± 0.32	this work
			1,4-Butanediol				
static manometer	419−490	77.2	Gardner, 1972	calorimeter	298.15	78.3 ± 0.3	Eusebio, 2003
ebulliometer	416.3−501.5	76.13 ± 0.54	Palczewska,1984	transpiration	329.2−363.2	78.95 ± 0.92	this work
calorimeter	298.15	79.3 ± 0.5	Knauth, 1989				

Table 7. Parameters of the NRTL Equation

T/K	$g_{12} - g_{22}$/ kJ mol^{-1}	$g_{21} - g_{11}$/ kJ mol^{-1}	α	T/K	$g_{12} - g_{22}$/ kJ mol^{-1}	$g_{21} - g_{11}$/ kJ mol^{-1}	α
			Methoxy-benzene + [EMIM][NTf$_2$]				
298.65	4.31925	−0.6567	0.5	313.55	7.76919	0.8612	0.5
303.55	7.34170	−0.2144	0.5	318.55	9.09675	1.6507	0.5
308.55	7.19381	0.1814	0.5	323.55	5.95974	2.1646	0.5
			(Hydroxymethyl)-benzene + [EMIM][NTf$_2$]				
298.65	−1.74147	4.11416	0.5	313.55	−1.93743	5.08351	0.5
303.65	−2.01489	5.19008	0.5	318.65	−1.67074	4.60096	0.5
308.65	−2.10974	4.92718	0.5	323.65	−1.02769	3.64881	0.5
			1,2-Ethanediol + [EMIM][NTf$_2$]				
339.65	10.9296	−2.26446	0.2	353.65	11.5160	−1.73750	0.2
343.65	9.64323	−1.91042	0.2	358.65	12.8783	−1.48613	0.2
348.65	11.5479	−2.16919	0.2	363.65	13.8182	−1.50935	0.2
			1,4-Butanediol + [EMIM][NTf$_2$]				
339.55	2.10100	4.16248	0.5	353.45	9.10323	4.42941	0.5
343.45	2.25930	4.40652	0.5	358.45	8.74119	5.55040	0.5
348.45	2.64094	4.83005	0.5				

solute condensed into the cooling trap provided a calibration run has been made. From this information, the partial pressure of the solute in the glass tubing can be determined (i.e., the ideal gas law can be applied provided that the vapor pressure of the substance is low enough). Real gas corrections arising from interactions of the vapor with the carrier gas turned out to be negligible. Because the method is a dynamic one, extreme care has to be taken to ensure that thermodynamic equilibrium conditions have been fulfilled by adjusting the gas flow to small enough values. If the amount of condensed solute is small compared to its content in the liquid phase inside the tubing, then the change of concentration in the liquid mixture is negligible during such an experiment, and the partial pressure of the solute can be assigned to the known composition of the liquid mixture that is in thermodynamic equilibrium with the vapor phase. This method was carefully checked[6] by measuring the vapor−liquid equilibrium of the binary mixture (n-pentanol + decane), where reliable VLE data exist in the literature.[11]

Measurements of activity coefficients covering the whole range of concentration of solute (1) + ionic liquid (2) mixtures have been performed. A series of measurements that include methoxy-benzene, (hydroxymethyl)benzene, 1,2-ethanediol, and 1,4-butanediol mixed with an ionic liquid have been studied. Partial pressures of solutes are presented in Tables 2 to 5; the partial pressure of the ionic liquid was not detectable. We checked every system under study for the repeatability of the data and it was governed within (1−3)% by the accuracy of the GC analysis.

Results and Discussion

Vapor Pressure and Enthalpies of Vaporization of Pure Substances. Most of the vapor pressure values for anisol, benzyl alcohol, and diols that are reported in the literature were measured using a dynamic recirculation still. That is why they are referenced to elevated temperatures above 363 K. In general, the transpiration method used in this work provides reliable experimental vapor pressures in the temperature range around ambient temperature. Therefore, a direct comparison of our vapor pressures with those available from the literature is not possible. However, one way to relate the literature data to our measurements is to compare the enthalpies of vaporization at the reference temperature, 298.15 K. For this purpose, we treated the $p-T$ results available in the literature using eqs 2 and 3 and calculated $\Delta_l^g H_m$ (298.15 K) for the sake of comparison with our results (Table 6). As can be seen from Table 6, enthalpies of vaporization derived from both methods (static and transpiration) are in very close agreement within the boundaries of their experimental uncertainties.

Data Correlation of Binary Systems Using the NRTL Equation. The values of γ_1 of different solutes in [EMIM][NTf$_2$] obtained at four different temperatures are listed in Tables 2 to 5.

$$p_1 = p_{0,1} x_1 \gamma_1^{\mathrm{NRTL}} \tag{4}$$

with

$$\ln \gamma_1^{\mathrm{NRTL}} = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] \tag{5}$$

where $G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$ with $\tau_{ij} = (g_{ij} - g_{jj})/RT$ and $\alpha_{ij} = \alpha_{ji} = \alpha$ ($i, j = 1, 2$; $i \neq j$). Table 7 contains the parameters α_{ij} and $(g_{ij} - g_{jj})$. Figures 1 to 4 show the experimental results for the partial pressures of the solutes and activity coefficients γ_1 of the solutes mixed with [EMIM][NTf$_2$] in comparison with the calculated results of the NRTL model according to eq 5 with parameters taken from Table 6. The scattering of the experimental data is about 5% of the maximal pressure of the pure solutes, which is not surprising considering the low values of absolute pressures obtained in the experiments. The NRTL equation is able to fit all of the results within the experimental errors. The temperature dependence of ln γ_i indicates that ln γ_1 increases with increasing temperature. However, because of the relatively large scattering of the data this temper-

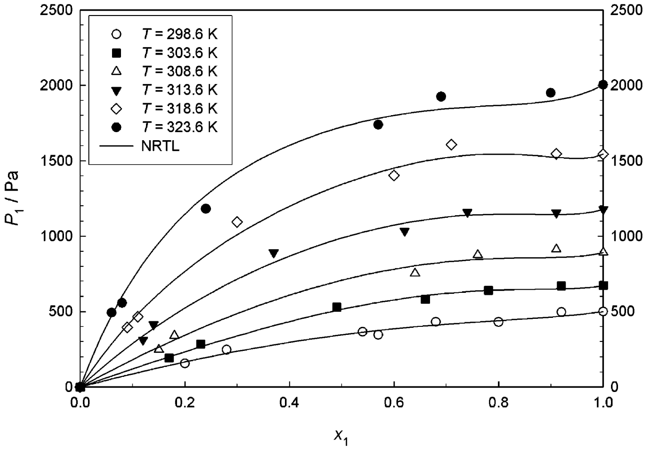

Figure 1. Partial pressure data of methoxy-benzene in the mixture with [EMIM][NTf$_2$] as a function of x_1 (methoxy-benzene).

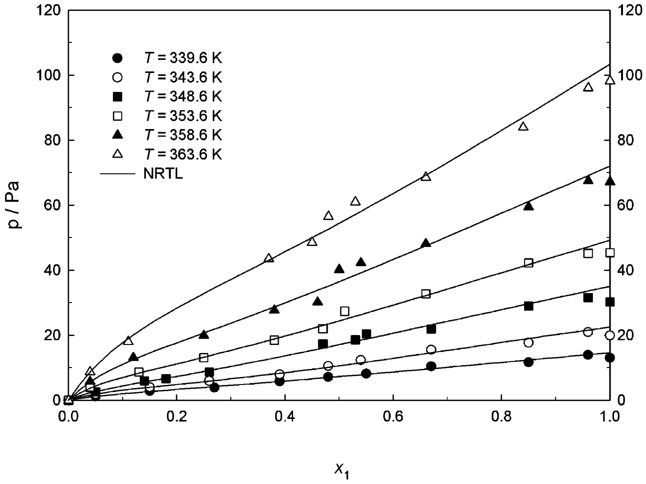

Figure 2. Partial pressure data of (hydroxymethyl)-benzene in the mixture with [EMIM][NTf$_2$] as a function of x_1 ((hydroxymethyl)-benzene).

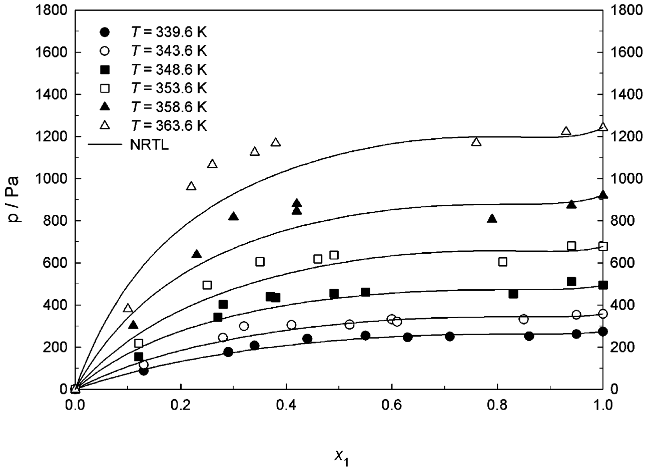

Figure 3. Partial pressure data of 1,2-ethanediol in the mixture with [EMIM][NTf$_2$] as a function of x_1 (1,2-ethanediol).

ature dependence of ln γ_1 is not significant enough to derive enthalpies of mixing.

List of Symbols

$\Delta_l^g H_m$	molar enthalpy of vaporization
T_a	ambient temperature
p	vapor pressure
C_p^l	molar heat capacities of liquid at constant pressure
C_p^g	molar heat capacities of gas at constant pressure
$\Delta_l^g C_p$	difference of the molar heat capacities at constant pressure for the gaseous and liquid phases, respectively
γ_i	activity coefficient of component i
τ_{ij}	interaction parameters of the NRTL equation
α_{ij}	interaction parameters of the NRTL equation

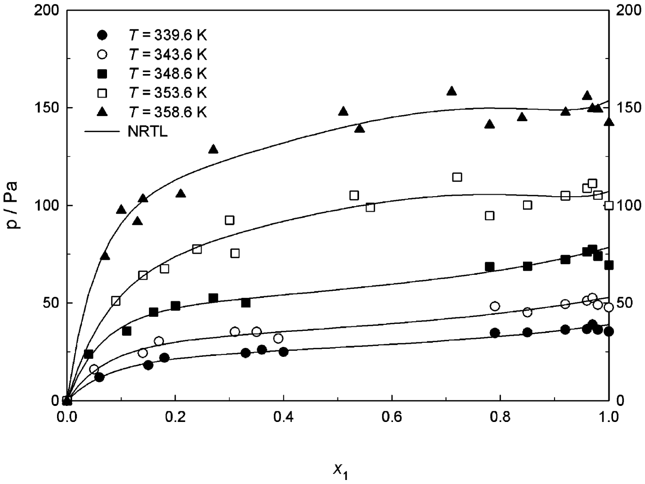

Figure 4. Partial pressure data of 1,4-butanediol in the mixture with [EMIM][NTf$_2$] as a function of x_1 (1,4-butanediol).

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Received for review June 15, 2004. Accepted November 4, 2004. T.V.V. gratefully acknowledges a research scholarship from the DAAD (Deutscher Akademischer Austauschdienst).

JE0497799