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Thermodynamic Properties of Mixtures Containing Ionic Liquids. 7. Activity Coefficients of Aliphatic and Aromatic Esters and Benzylamine in 1-Methyl-3-ethylimidazolium Bis(trifluoromethylsulfonyl) Imide Using the Transpiration Method

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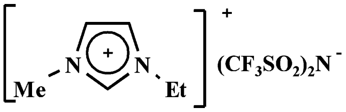
Vapor−liquid equilibria of binary mixtures containing the high boiling solutes (dimethyl adipate, ethyl benzoate, and benzylamine) with the ionic liquid 1-methyl-3-ethylimidazolium bis(trifluoromethylsulfonyl) imide [EMIM][NTf$_2$] were studied using the transpiration method. VLE measurements were carried out over the whole concentration range at temperatures between 298 K and 318 K. Activity coefficients (γ_i) of these solvents in the ionic liquid were determined from these data and are correlated by the NRTL equation. In addition, vapor pressures of the pure solutes dimethyl adipate and ethyl benzoate have been measured as a function of temperature, and their enthalpies of vaporization have been derived.

Introduction

The application of ionic liquids (ILs) for separation processes is promising because of their nonvolatile nature. This facilitates solvent recovery using techniques such as flash distillation or stripping. The quality of separation is governed by activity coefficients of organics in ILs. This work continues our study of thermodynamic properties of mixtures of solutes in ILs.[1−9] Activity coefficients, covering the whole range of composition for mixtures containing high boiling compounds (such as aldehydes, ketones, ethers, alcohols) and ILs were reported recently.[10,11] With the present work, we continue to fill in the gap of information on IL mixtures. In this work, we have performed measurements of γ_i of three solutes in the IL 1-methyl-3-ethylimidazolium bis(trifluoromethylsulfonyl) imide [EMIM][NTf$_2$]:



A series of mixtures of the solutes dimethyl adipate, ethyl benzoate, and benzylamine with the solvent−ionic liquid [EMIM][NTf$_2$] has been studied over the temperature range (298 to 318) K. Vapor pressures of the pure dimethyl adipate and ethyl benzoate 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 (see Table 1). Vapor pressures of the pure benzylamine have been published recently.[12]

Experimental Section

Materials. The samples of esters and benzylamine studied were purchased from Aldrich and Fluka. The degree of purity was controlled using a Hewlett-Packard gas chromatograph 5890 series II equipped with a flame ionization detector, an autosampler, and a Hewlett-Packard 3390A integrator. The carrier gas (nitrogen) flow was 12.1 cm^3·s^{-1}. A capillary column HP-5 (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 μm. The standard temperature program of the GC was $T = 333$ K for 180 s followed by a heating rate of 0.167 K·s^{-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.[13] Before using, the sample was dissolved in an excess of 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 experiments 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 dry atmosphere of N$_2$ before use.

Vapor Pressure Measurements of Pure Component Systems. The vapor pressure and enthalpies of vaporization of the esters were determined using the method of transpiration in a saturated N$_2$ stream[14,15] and 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 diameter of 1 mm provide a surface that is sufficient enough for the 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 in order to reach the saturation equilibrium of the transporting gas at each temperature under study. On one hand, the flow rate of nitrogen stream in the saturation tube should be not too slow in order to avoid the transport of material from the U-tube due to diffusion.

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

T / K[a]	m / mg[b]	V_{N_2} / dm^3[c]	p / Pa[d]	$p_{exp} - p_{calc}$ / Pa	$\Delta_l^g H_m$ / kJ·mol^{-1}
Dimethyl Adipate: $\Delta_l^g H_m$ (298.15 K) = (67.14 ± 0.30)kJ·mol^{-1} $\ln(p/\text{Pa}) = 39.9 - 11475.0/(T/\text{K}) - 11.4 \ln((T/\text{K})/298.15)$					
293.2	0.73	4.12	2.53	0.00	67.62
296.2	0.90	3.82	3.36	0.01	67.33
299.2	1.11	3.60	4.43	0.01	67.05
302.2	1.07	2.62	5.86	0.09	66.77
305.2	1.01	1.95	7.40	−0.08	66.48
308.2	1.35	1.95	9.91	0.26	66.20
310.2	1.76	2.23	11.33	−0.07	66.01
313.3	1.53	1.51	14.54	−0.13	65.71
316.2	1.35	1.08	17.94	−0.55	65.44
319.3	1.18	0.718	23.56	0.03	65.14
322.2	1.49	0.754	28.31	−1.02	64.87
325.3	1.71	0.647	37.78	0.84	64.58
328.2	1.85	0.575	45.92	0.32	64.30
331.2	1.43	0.359	57.04	0.62	64.02
334.2	1.75	0.359	69.81	0.33	63.73
Ethyl Benzoate: $\Delta_l^g H_m$ (298.15 K) = (61.14 ± 0.25) kJ·mol^{-1} $\ln(p/\text{Pa}) = 39.3 - 10777.4/(T/\text{K}) - 11.5 \ln((T/\text{K})/298.15)$					
283.9	1.10	2.56	7.1	0.2	62.50
289.0	1.74	2.55	11.3	0.3	62.01
292.0	1.29	1.49	14.3	−0.1	61.73
295.0	1.63	1.47	18.3	−0.3	61.44
294.1	2.16	2.04	17.4	0.2	61.53
286.9	1.63	2.88	9.3	0.2	62.21
298.1	1.70	1.17	23.9	−0.2	61.14
299.1	1.50	0.974	25.4	−0.7	61.05
301.2	1.81	0.954	31.2	0.2	60.85
304.2	2.00	0.843	39.0	−0.3	60.56
307.2	1.98	0.687	47.2	−2.5	60.28
310.1	2.08	0.571	59.7	−2.3	60.00
312.3	2.32	0.532	71.6	−1.4	59.79
315.3	1.86	0.355	86.2	−4.6	59.50
317.3	4.20	0.652	105.5	0.7	59.31
320.3	4.51	0.571	129.7	0.4	59.02
323.4	4.53	0.448	165.6	5.8	58.73
326.4	4.01	0.326	201.6	6.3	58.44
329.5	4.27	0.285	245.2	6.2	58.15
332.5	4.39	0.245	294.4	5.1	57.86

[a] Temperature of saturation. N_2 gas flow 0.22 to 0.69 cm^3·s^{-1}. [b] Mass of transferred sample condensed at T = 243 K. [c] Volume of nitrogen used to transfer mass (m) of sample. [d] Vapor pressure at temperature (T) calculated from m and the residual vapor pressure at T = 243 K.

Table 2. Comparison of Data for the Enthalpy of Vaporization $\Delta_l^g H_m$ at 298.15 K

technique	T / K	$\Delta_l^g H_m$ (T = 298.15 K) / kJ·mol^{-1}	ref
Dimethyl Adipate			
torsion-effusion	293.3−323.2	55.9 ± 2.0	20
not available	418−501	72.9	19
not available	382−500	71.8	19
transpiration	293.2−334.2	67.14 ± 0.30	this work
Ethyl Benzoate			
static manometer	344.1−440.6	61.9 ± 0.3	21
ebulliometry	369.2−531.1	63.1 ± 0.3	22
transpiration	283.9−332.5	61.1 ± 0.3	this work

On the other hand, the flow rate should be not too fast in order to reach saturation of the nitrogen stream with a compound. We tested our apparatus at different flow rates of the carrier gas in order to check the lower boundary of the flow below which the contribution of the vapor condensed in the trap by diffusion becomes comparable to the transpired one. In our apparatus, the contribution due to diffusion was negligible at a flow rate up to 0.11 cm^3·s^{-1}. The upper limit for our apparatus where the speed of nitrogen could already disturb the equilibration was at a flow rate of 0.82 cm^3·s^{-1}. Thus, we carried out the experiments in the flow rate interval of (0.28 to 0.52) cm^3·s^{-1}, which ensured 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 the substance i of interest is valid, values of $p_i^{sat_i}$ were calculated assuming:

$$p_i^{sat} = m_i R T_a / V M_i \quad V = V_{N_2} + V_i \quad (V_{N_2} \gg V_i) \qquad (1)$$

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

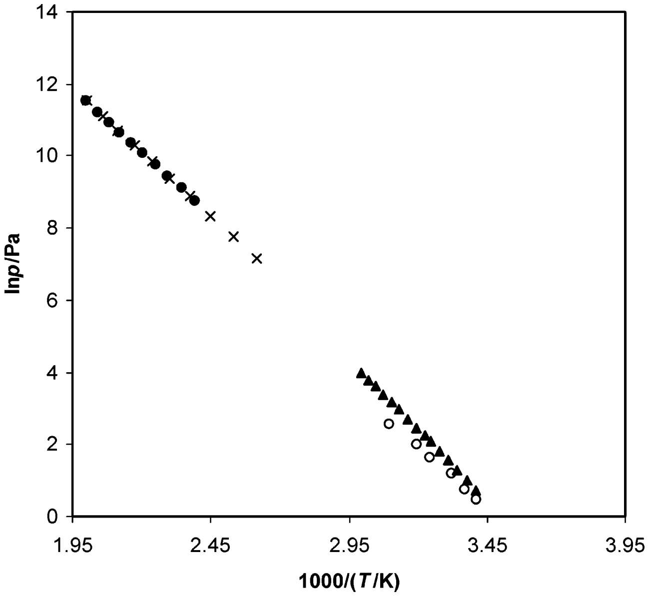

Figure 1. Experimental data of the vapor pressures of the dimethyl adipate. ▲, this work; ●, ref 19; ×, ref 19; ○, ref 20.

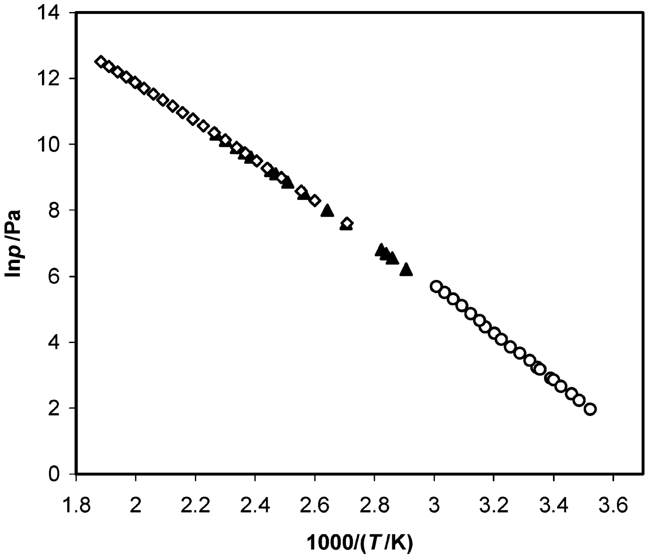

Figure 2. Experimental data of the vapor pressures of the ethyl benzoate. ○, this work; ▲, ref 21; ◇, ref 22.

Table 3. VLE in the System (Dimethyl Adipate + [EMIM][NTf$_2$])

$\frac{T}{\text{K}}$	x_1	$\frac{p_1^{\text{exptl}}}{\text{Pa}}$	$\frac{p_1^{\text{NRTL}}}{\text{Pa}}$	γ_1^{NRTL}
298.65	0.000	0.00	0.00	0.577
	0.044	0.05	0.11	0.608
	0.138	0.36	0.39	0.677
	0.224	0.74	0.69	0.742
	0.311	1.13	1.04	0.809
	0.457	1.50	1.73	0.912
	0.548	2.30	2.19	0.965
	0.690	2.97	2.91	1.018
	0.811	3.43	3.45	1.026
	0.907	3.81	3.81	1.012
	1.000	4.23	4.15	1.000
305.55	0.000	0.00	0.00	0.562
	0.044	0.09	0.19	0.585
	0.137	0.60	0.65	0.637
	0.223	1.18	1.13	0.686
	0.308	1.84	1.67	0.736
	0.454	2.66	2.75	0.821
	0.543	3.43	3.48	0.869
	0.690	4.58	4.76	0.936
	0.811	5.72	5.83	0.976
	0.907	6.93	6.64	0.994
	1.000	6.56	7.37	1.000
308.55	0.000	0.00	0.00	0.607
	0.044	0.20	0.32	0.627
	0.136	1.08	1.06	0.670
	0.220	1.78	1.81	0.710
	0.303	2.84	2.64	0.751
	0.450	3.92	4.29	0.824
	0.538	5.37	5.40	0.867
	0.689	7.10	7.43	0.932
	0.810	9.68	9.11	0.972
	0.906	10.3	10.41	0.993
	1.000	10.	11.58	1.000
313.55	0.000	0.00	0.00	0.735
	0.043	0.38	0.55	0.751
	0.135	1.75	1.79	0.785
	0.216	3.07	2.98	0.815
	0.296	4.81	4.22	0.844
	0.445	5.83	6.74	0.895
	0.532	7.93	8.31	0.922
	0.688	11.09	11.21	0.963
	0.809	14.57	13.49	0.986
	0.905	15.12	15.26	0.996
	1.000	15.08	16.93	1.000
318.65	0.000	0.00	0.00	0.743
	0.043	0.69	0.84	0.761
	0.133	2.71	2.75	0.799
	0.211	4.30	4.53	0.831
	0.282	7.19	6.26	0.859
	0.437	9.21	10.36	0.916
	0.524	13.32	12.77	0.942
	0.684	16.97	17.34	0.979
	0.807	22.00	20.78	0.995
	0.904	22.64	23.37	0.999
	1.000	22.38	25.87	1.000

Table 4. VLE in the System (Ethyl Benzoate + [EMIM][NTf$_2$])

$\frac{T}{\text{K}}$	x_1	$\frac{p_1^{\text{exptl}}}{\text{Pa}}$	$\frac{p_1^{\text{NRTL}}}{\text{Pa}}$	γ_1^{NRTL}
298.65	0.000	0.00	0.00	3.675
	0.112	7.34	7.65	2.712
	0.245	15.16	12.72	2.069
	0.339	12.98	15.12	1.776
	0.508	17.34	18.19	1.426
	0.588	20.23	19.32	1.308
	0.720	21.67	20.92	1.157
	0.852	22.66	22.50	1.052
	0.952	22.85	24.06	1.006
	0.979	25.60	24.62	1.001
	1.000	24.84	25.11	1.000
305.55	0.000	0.00	0.00	2.969
	0.102	8.85	8.92	2.415
	0.202	14.71	15.07	2.055
	0.212	16.26	15.59	2.026
	0.310	20.17	20.08	1.784
	0.484	25.08	26.14	1.488
	0.581	29.23	28.76	1.364
	0.716	32.25	31.58	1.216
	0.850	33.21	33.55	1.087
	0.952	34.32	35.02	1.014
	0.979	35.57	35.64	1.003
	1.000	37.07	36.30	1.000
308.55	0.000	0.00	0.00	2.877
	0.091	11.18	11.06	2.401
	0.173	18.58	18.35	2.104
	0.182	18.82	19.11	2.074
	0.271	24.52	25.28	1.845
	0.452	35.22	34.92	1.530
	0.573	40.95	39.89	1.380
	0.711	44.63	44.27	1.233
	0.848	46.45	47.11	1.100
	0.951	48.72	48.84	1.017
	0.958	45.15	49.01	1.013
	1.000	54.62	50.50	1.000
313.55	0.000	0.00	0.00	2.789
	0.080	14.92	15.21	2.414
	0.135	25.77	23.35	2.208
	0.151	23.62	25.46	2.154
	0.230	34.32	34.57	1.917
	0.417	49.36	49.52	1.515
	0.563	58.55	57.42	1.301
	0.706	62.06	63.55	1.149
	0.846	70.65	69.40	1.047
	0.950	74.86	74.85	1.006
	0.958	73.68	75.32	1.004
	1.000	79.48	78.33	1.000
318.65	0.000	0.00	0.00	3.237
	0.069	21.43	21.62	2.740
	0.183	46.99	45.88	2.197
	0.374	69.80	71.40	1.675
	0.552	87.27	87.18	1.384
	0.700	97.55	96.55	1.209
	0.844	103.56	103.57	1.076
	0.949	105.16	109.44	1.011
	0.957	113.83	110.00	1.008
	1.000	114.31	114.04	1.000

meter. The volume of transporting gas (V_{N_2}) was determined from the flow rate and time measurements. The flow rate was maintained constant with help of the high precision needle valve (Hoke, C1335G6 μ_BM-ITA). The accuracy of the volume (V_{N_2}) measurements from flow rate was established to be (± 0.001 dm^3) with help of series of experiments, where the volume of nitrogen was measured with a gas-clock or by water withdrawing using a calibrated gasometer. Data of p_i^{sat} have been obtained as a function of temperature and were fitted using following equation:[14]

$$R\ln\frac{p_i^{\text{sat}}}{p_0} = a + \frac{b}{T} + \Delta_{\text{l}}^{\text{g}}C_{\text{p}}\ln\left(\frac{T}{T_0}\right) \qquad (2)$$

where a and b are adjustable parameters and $\Delta_{\text{l}}^{\text{g}}C_{\text{p}}$ is the difference of the molar heat capacities of the gaseous and the liquid phase, respectively. T_0 appearing in eq 2 is an arbitrarily chosen reference temperature (which has been chosen to be 298.15 K) and p_0 = 1 Pa. Consequently, from eq 2 the expression for the vaporization enthalpy at temperature (T) is derived:

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

Values of $\Delta_{\text{l}}^{\text{g}}C_{\text{p}}$ have been obtained from the isobaric molar heat capacities of the liquid esters (C_{p}^{l}) and from their gaseous values of the isobaric molar heat capacities (C_{p}^{g}) calculated

Table 5. VLE in the System (Benzylamine + [EMIM][NTf$_2$])

T / K	x_1	p_1^{exptl} / Pa	p_1^{NRTL} / Pa	γ_1^{NRTL}
298.65	0.000	0.00	0.00	1.687
	0.124	18.04	17.91	1.527
	0.193	27.34	26.64	1.455
	0.300	37.51	38.78	1.365
	0.362	44.45	45.33	1.322
	0.440	52.88	53.26	1.277
	0.570	66.60	65.81	1.218
	0.656	73.16	73.89	1.189
	0.741	83.80	81.90	1.166
	0.876	94.67	94.01	1.133
	1.000	94.34	94.77	1.000
305.65	0.000	0.00	0.00	2.765
	0.109	31.78	32.08	2.213
	0.185	42.49	48.10	1.953
	0.288	66.83	65.33	1.704
	0.347	75.91	73.75	1.600
	0.429	80.37	84.78	1.484
	0.561	101.84	101.14	1.357
	0.640	111.93	110.81	1.301
	0.736	121.83	122.13	1.248
	0.873	135.21	136.33	1.174
	1.000	133.64	132.99	1.000
308.65	0.000	0.00	0.00	4.233
	0.080	48.33	48.42	3.231
	0.172	70.19	81.16	2.540
	0.271	104.12	104.96	2.076
	0.326	116.74	115.40	1.900
	0.415	131.83	130.57	1.690
	0.548	152.37	151.77	1.486
	0.619	163.85	162.82	1.412
	0.728	174.76	179.49	1.323
	0.871	196.29	197.05	1.215
	1.000	187.91	186.25	1.000
313.65	0.000	0.00	0.00	7.980
	0.042	66.41	66.41	6.043
	0.153	107.84	141.44	3.561
	0.249	169.11	170.07	2.637
	0.296	177.76	180.80	2.356
	0.395	215.45	200.94	1.966
	0.532	225.75	227.78	1.653
	0.591	232.86	238.97	1.561
	0.718	248.75	260.42	1.401
	0.868	277.43	271.76	1.208
	1.000	262.37	259.10	1.000
318.65	0.000	0.00	0.00	6.624
	0.132	177.43	179.15	3.736
	0.219	224.85	229.32	2.892
	0.262	260.81	247.57	2.609
	0.368	283.34	283.91	2.134
	0.511	329.00	324.80	1.756
	0.552	326.21	335.40	1.679
	0.704	356.80	368.27	1.445
	0.865	386.27	378.28	1.208
	1.000	363.86	362.08	1.000

Table 6. Parameters of the NRTL Equation

T / K	$g_{12}-g_{22}$ / kJ·mol^{-1}	$g_{22}-g_{11}$ / kJ·mol^{-1}	α
Dimethyl Adipate + [EMIM][NTf$_2$]			
298.65	8.576	−5.118	0.239
303.55	6.682	−5.501	0.190
308.55	4.715	−4.124	0.275
313.55	4.002	−3.517	0.253
318.65	4.638	−3.475	0.312
Ethyl Benzoate + [EMIM][NTf$_2$]			
298.65	3.057	1.925	0.690
303.55	4.575	1.600	0.764
308.55	5.145	1.609	0.768
313.55	2.837	1.298	0.665
318.65	4.094	1.830	0.751
Benzylamine + [EMIM][NTf$_2$]			
298.65	26.820	0.942	0.400
305.65	18.888	2.004	0.469
308.65	20.527	2.964	0.416
313.65	13.631	4.270	0.474
318.65	12.795	3.677	0.468

according to a procedure developed by Chickos and coworkers.[16,17] All results together with the parameters a and b are listed in Table 1. The experimental data were approximated with the linear equation $\ln p = f\,(T^{-1})$ (see Table 1) using the method of least squares. The error in the enthalpy of vaporization was defined as average deviation of experimental results from this linear correlation.

Vapor pressure of the pure benzylamine was measured in our previous work[12] in the temperature range (283.4 to 313.3) K using the transpiration method. The following equation (see eq 2)

$$\ln(p/\text{Pa}) = 33.3 - \frac{8567.3}{(T/\text{K})} - 7.75\ln\left(\frac{T/\text{K}}{298.15}\right)$$

for the temperature dependence of vapor pressure of benzylamine has been used in this work.

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 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) was 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 eluates continuously the vapor phase in the glass tubing. Due to 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 certain amount of internal standard (hydrocarbon). This solution is analyzed using a gas chromatograph equipped with autosampler. Uncertainty of the solute amount determined by GC analysis was assessed to be within (1 to 3) %. The peak area of the solute related to the peak of the external standard (hydrocarbon *n*-decane or *n*-dodecane) is a direct measure of the mass of the 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 are negligible. Since 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 values small enough. If the amount of solute condensed is small as compared to its contents in the liquid phase inside the tubing, 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 being in thermodynamic equilibrium with the vapor phase. This method was carefully checked[10,11] with agreement within (1 to 3) % by measuring the vapor−liquid equilibrium of the binary mixture (*n*-pentanol + decane), where reliable VLE data exist in the literature.[18]

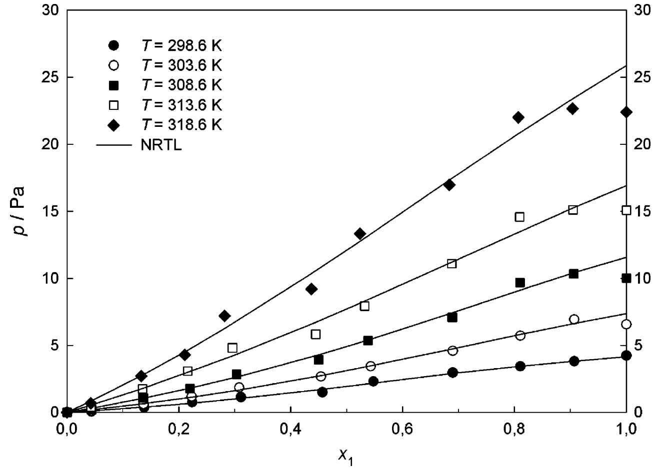

Figure 3. Partial pressure data of dimethyl adipate in the mixture with [EMIM][NTf$_2$] as function of x_1 (dimethyl adipate).

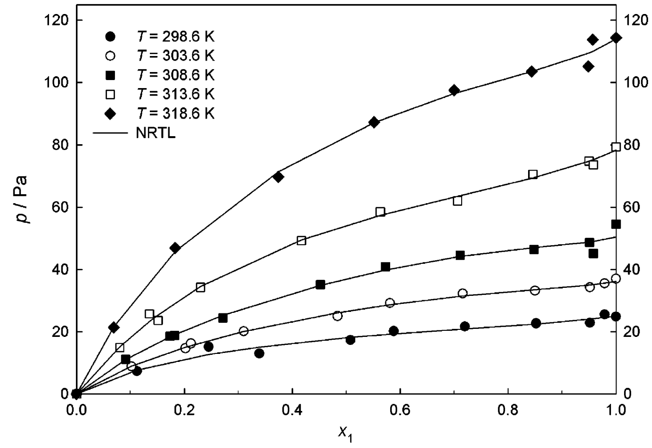

Figure 4. Partial pressure data of ethyl benzoate in the mixture with [EMIM][NTf$_2$] as function of x_1 (ethyl benzoate).

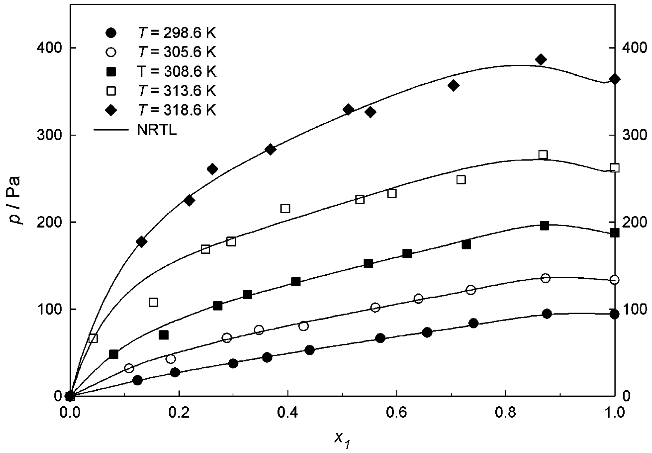

Figure 5. Partial pressure data of benzylamine in the mixture with [EMIM][NTf$_2$] as function of x_1 (benzylamine).

Measurements of activity coefficients covering the whole range of concentration of solute (1) + ionic liquid (2) mixtures have been performed. A series of solutes dimethyl adipate, ethyl benzoate, and benzylamine mixed with ionic liquid has been studied. Partial pressures of solutes are presented in Tables 3 to 5, the partial pressure of the ionic liquid was not detectable. We checked each system under study for the reproducibility of the data which was found to be within an uncertainty of the GC analysis at the level of (1 to 3) %.

Results and Discussion

Vapor Pressure and Enthalpies of Vaporization of Pure Substances. As a rule, vapor pressure values for high-boiling organic solutes that are reported in the literature were measured using dynamic recirculation still at elevated temperatures above 363 K (see Table 2). Any extrapolation of the vapor pressure to the ambient temperatures is accompanied with a large uncertainty. For this reason, additional measurements of vapor pressures of pure components in the temperature range relevant to the determination of activity coefficients are required. In general, the transpiration method used in this work provides reliable experimental vapor pressure in the temperature range not too from ambient temperatures. Thus, any direct comparison of our vapor pressures with those available from the literature is hardly possible. A possible relationship to the literature data is the comparison of the enthalpies of vaporization at the reference temperature 298.15 K. For this purpose, we treated the vapor pressure data available in the literature using eqs 2 and 3 and calculated $\Delta_l^g H_m(298.15\ \mathrm{K})$ for the sake of comparison with our results (see Table 2). It can bee seen from the Table 2 that enthalpies of vaporization of dimethyl adipate are in disagreement. However, it has to be considered that the origin of data for dimethyl adipate presented in the comprehensive compilation by Stephenson and Malanowski[19] is unclear, methods of measurements are unknown as well as errors of measurements and purities of compounds. Thus, comparison with our data remains questionable. Recently, a torsion effusion apparatus was used for measuring vapor pressures of the pure dimethyl adipate.[20] The comparison of the experimental results with ours is given in Figure 1. The deviations of the results at the lower temperatures are obvious, and we do not have an explanation for this fact. The vapor pressure data for ethyl benzoate from static,[21] ebulliometric,[22] and transpiration method are generally in acceptable agreement (see Figure 2). As presented in Table 2, enthalpies of vaporization derived from these methods are also in agreement within (1 to 2) kJ·mol^{-1}. Such agreement is considered to be acceptable taking into account the simplified method of exptrapolation[16,17] of vaporization enthalpies to the reference temperature (298.15 K) using calculated values of $\Delta_l^g C_p$.

Data Correlation of Binary Systems Using the NRTL Equation. The values of activity coefficients γ_1 of different solutes in [EMIM][NTf$_2$] obtained at different temperatures are listed in Tables 3 to 5. It turned out[10,11] that the NRTL equation gives the best empirical description of the activity coefficients. Table 6 contains the parameters a and $(g_{ij} - g_{jj})$ used in the expression for the partial pressure of the solute (index 1):

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

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 $G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$, $\tau_{ij} = (g_{ij} - g_{jj})/RT$ and $\alpha_{ij} = \alpha_{ji} = \alpha$ ($i, j = 1, 2;\ i \neq j$). It turned out that the parameter α had also to be fitted separately for each system and temperature to obtain an optimized description of activity coefficients. Table 6 contains the parameters α_{ij} and $(g_{ij} - g_{jj})$ obtained by fitting γ_1^{NRTL} to the experimental VLE data. Figures 3 to 5 show the experimental results for the partial pressures 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 by the experiments. The NRTL equation is able to fit all the results within the experimental uncertainties. The results obtained in this work reveal that activity coefficients in mixtures can be determined using the transpiration method. However, due to the low vapor pressure in the present systems, the accuracy of the method is not as high as in systems when conventional vapor pressure measurements at distinctly higher pressures have been performed. The temperature dependence of ln γ_i indicates that ln γ_1 increases with increasing temperature. However, due to the relatively large scattering of the data, this temperature dependence of ln γ_1 is not significant enough to derive quantitatively enthalpies of mixing.

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