Industrial & Engineering Chemistry Research

Supporting Information

Separation of 2-Phenylethanol from Water by Liquid-Liquid Extraction with Ionic Liquids: New Experimental Data and Modeling with Modern Thermodynamic Tools

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Synthesis of $[C_6C_1Pyr][NTf_2]$

The bromide salt needed for further reaction was synthesized according to well known path. To a 35.11 g of *N*-methylpyrrolidine (0.4124 mol, Sigma-Aldrich 97%, Reagent Plus, used as received) 90.74 g of bromohexane (0.5497 mol, 33% excess, Sigma-Aldrich 98%, used as received) in 100 cm^3 of acetonitrile (Avantor Chemicals) was added. Mixture was placed in oil bath and stirred in the temperature T = 353.2 K for 24h. Afterwards, acetonitrile was added and solution was heated until all crystals were dissolved. Next, the 200 cm^3 of ethyl acetate (Avantor Chemicals) was added to the mixture. After cooling to room temperature, the crystals were filtered and dried in vacuum at T = 348 K. The amount of 92.65 g of white crystalline powder was obtained. Reaction yield 89.8%. ^{1}H NMR: δ_H(400 MHz; D_2O): 0.695(3 H, t, $^3J_{H,H}$ = 6.4 Hz), 1.113 (6 H, m), 1.521 (2 H, m), 2.074 (4 H, m), 2.911 (3 H, s), 3.192 (2 H, m), 3.361 (4 H, m). ^{13}C NMR: δ_C(100 MHz; $CDCl_3$): 13.213, 21.001, 21.895, 23.301, 25.392, 30.632, 47.894, 64.122, 64.455.

To a solution of 48.47 g *N*-hexyl-*N*-methylpyrrolidinium bromide (0.1937 mol, synthesized) in 50 cm^3 water a solution of 59.07 g lithium bis(trifuloromethane)sulfonylimide (0.2058 mol, Sigma-Aldrich 99%, 6% excess, used as received) in 50 cm^3 of water was added. The second heavier phase forms immediately. Next, the 100 cm^3 of dichloromethane was added. Mixture was stirred at room temperature for 4 h and phases were separated by draining. Then organic phase was extracted with 10 times 25 cm^3 of water (removal of residual lithium chloride). Product was further cleaned by activated carbon. Solvents were removed in rotary evaporator and product was further dried under vacuum at T = 353 K for 48h. Product was obtained as a 81.33 g of pale yellow liquid. Yield 93.2%. ^{1}H NMR: δ_H(400 MHz; CDCl3): 0.777 (3 H, t, $^3J_{H,H}$ = 6.4 Hz), 1.221 (6 H, m), 1.637 (2 H, m), 2.127 (4 H, m), 2.895 (3 H, s), 3.160 (2 H, m), 3.383 (4 H, m). ^{13}C NMR: δ_C(100 MHz; CDCl3): 13.323, 21.095, 21.902, 23.320, 25.401, 30.616, 47.875, 64.107, 64.429, 119.511 (q, $^1J_{CF}$ = 319 Hz). Elemental analysis: Found: C, 34.47% ; N, 6.18%; H, 5.52%, S 14.01%. Calculated for $C_{13}H_{24}N_2S_2O_4F_6$: C, 34.66%; N, 6.22%; H, 5.37%, S 14.24%.

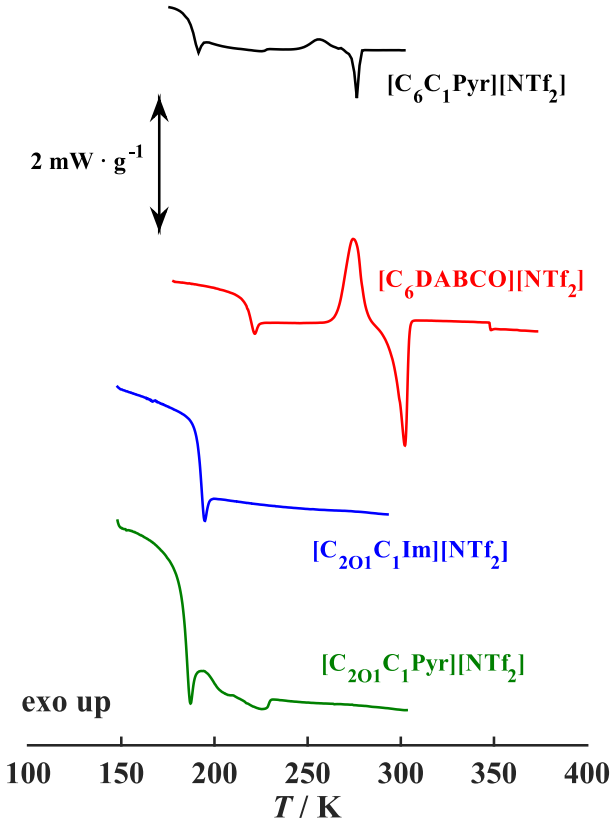

Figure S1. DSC themograms of the studied ionic liquids.

Table S1. Operational Conditions in the Gas Chromatograph for the Compositional Analysis of the Liquid Phases in Equilibrium.

Element	Characteristic	Description
Column	Type	Elite-5 PerkinElmer DB-5
		(5% diphenyl/95% Dimethyl Polysiloxane) Elite-5 Perkin Elmer,
		length 30 m, inner diameter 0.53 mm, film thickness: 1.50 μm
	Flow	5 mL/min
	Carrier gas	Helium
Oven	Temperature program	373 K, 6 min *to* (318 K/min) 473 K, 4 min
Injector	Injection volume	0.5 mL
	Split ratio	3:1
	Temperature progam	473 K
Detector	Type	Flame ionization detector (FID), thermal conductivity detector (TCD)
	Temperature	523 K (FID), 493 K (TCD)

Table S2. The Hildebrand's Solubility Parameters (δ_H) of the Investigated ILs as a Function of Temperature (T).[a]

$[C_6C_1Pyr][NTf_2]$		$[C_6DABCO][NTf_2]$		$[C_{2O1}C_1Im][NTf_2]$		$[C_{2O1}C_1Pyr][NTf_2]$	
T / K	δ_H / MPa$^{1/2}$	T / K	δ_H / MPa$^{1/2}$	T / K	δ_H / MPa$^{1/2}$	T / K	δ_H / MPa$^{1/2}$
298.2	21.10	313.15	20.15	332.65	20.83	318.15	20.28
322.9	20.13	323.15	19.90	342.75	20.50	328.15	20.04
333.0	19.83	333.15	19.64	353.15	20.17	338.15	19.78
343.1	19.60	343.15	19.36			348.15	19.50
		353.15	19.05			358.15	19.20
		363.15	18.72			368.15	18.88

[a] Obtained based on the literature data on $\gamma_{2,1}^{\infty}$: $[C_6C_1Pyr][NTf_2]$, W. E. Acree Jr. et al., *J. Chem. Eng. Data* **2012**, *57*, 3510–3518; $[C_6DABCO][NTf_2]$, Marcinkowski et al., *J. Chem. Thermodyn.* **2014**, *71*, 84–90; $[C_{2O1}C_1Im][NTf_2]$, A. L. Revelli et al. *J. Chem. Eng. Data* **2010**, *55*, 2434–2443; $[C_{2O1}C_1Pyr][NTf_2]$, Marciniak and Wlazlo, *J. Chem. Thermodyn.* **2012**, *54*, 90–96.

Table S3. Linear Solvation-Energy Relationship (LSER) Analysis of Literature Infinite Dilution Activity Coefficients Data Used to Estimate Infinite Dilution Activity Coefficient of PEA in the Investigated ILs at T = 308.15 K.[a]

Ionic liquid	c	e	s	a	b	l	$\log K_{L,2}$	$\gamma^{\infty}_{2,1}$
$[C_6C_1Pyr][NTf_2]$	−0.360	-0.1673	2.090	2.004	0.595	0.689	5.429	1.100
$[C_6DABCO][NTf_2]$	−0.682	0.0049	1.938	2.149	0.876	0.734	5.548	0.945
$[C_{2O1}C_1Im][NTf_2]$	−0.348	0.1264	2.298	2.128	0.690	0.552	5.307	1.843
$[C_{2O1}C_1Pyr][NTf_2]$	−0.524	0.0696	2.366	2.334	0.487	0.627	5.416	1.314

[a] Infinite dilution activity coefficient of solute "2" in solvent "1" (denoted by $\gamma^{\infty}_{2,1}$) is transformed into gas-to-solvent partition coefficient by using the following relationship:

$$K_{L,2} = \frac{RT}{P_2^{sat} V_1 \gamma^{\infty}_{2,1}}$$

where R stands for gas contant, P_2^{sat} is the solute's vapour pressure and V_1 denotes the solvent's molar volume. LSER relationship expresses $K_{L,2}$ as a linear combinations of the following contributions:

$$\log K_{L,2} = c + e\mathbf{E} + s\mathbf{S} + a\mathbf{B} + b\mathbf{B} + l\mathbf{L}$$

where **E**, **S**, **A**, **B**, **L** are molecular descriptors of the solute, whereas c, e, s, a, b, l are solvent-specific (here, IL-specific) coefficients determined by means of linear regression analysis (for more details, see: M. H. Abraham, *Chem. Soc. Rev.* 1990, 22, 73–83). The coefficients given in the table were obtained based on the literature data on $\gamma^{\infty}_{2,1}$: $[C_6C_1Pyr][NTf_2]$, W. E. Acree Jr. et al., *J. Chem. Eng. Data* **2012**, *57*, 3510–3518; $[C_6DABCO][NTf_2]$, Marcinkowski et al., *J. Chem. Thermodyn.* **2014**, *71*, 84–90; $[C_{2O1}C_1Im][NTf_2]$, A. L. Revelli et al. *J. Chem. Eng. Data* **2010**, *55*, 2434–2443; $[C_{2O1}C_1Pyr][NTf_2]$, Marciniak and Wlazlo, *J. Chem. Thermodyn.* **2012**, *54*, 90–96. Common set of the molecular solvents, i.e. such that for which $\gamma^{\infty}_{2,1}$ data were available in each IL, was used in the parameters determinations, namely: *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, cyclohexane, cycloheptane, benzene, toluene, *p*-xylene, ethanol, 1-propanol, 2-propanol, 2-pentanone, 3-pentanone, pyridine, acetonitrile. Molecular descriptors of PEA were taken from literature (Sprunger et al., *J. Chromatogr. A* **2007**, *1175*, 162–173): **E** = 0.78, **S** = 0.83, **A** = 0.30, **B** = 0.66, **L** = 4.628.

Table S4. Experimental Density (ρ) of the Studied ILs at P = 0.1 MPa as a Function of Temperature (T).

T / K	ρ / kg · m^3			
	[C_6C_1Pyr][NTf_2]	[C_6DABCO][NTf_2]	[$C_{2O1}C_1$Im][NTf_2]	[$C_{2O1}C_1$Pyr][NTf_2]
288.2	1340.7		1587.0	1462.8
293.2	1336.4		1582.0	1458.0
298.2	1332.0		1577.0	1453.2
303.2	1327.7		1572.0	1448.5
308.2	1323.4	1365.3	1567.0	1443.8
313.2	1319.1	1361.0	1562.1	1439.1
318.2	1314.9	1356.8	1557.2	1434.4
323.2	1310.6	1352.5	1552.3	1429.8
328.2	1306.4	1348.3	1547.4	1425.2
333.2	1302.2	1344.0	1542.6	1420.5
338.2	1297.9	1339.8	1537.8	1415.9
343.2	1293.6	1335.7	1532.9	1411.4
348.2		1331.5	1528.2	1406.8
353.2	1285.4	1327.3	1523.4	1402.3
358.2	1281.3	1323.2	1518.6	1397.7
363.2	1277.1	1319.1	1513.9	1393.2

Table S5. Experimental (Solid + Liquid) Equilibrium Data (IL Mole Fraction x_1 vs. Equilibrium Temperature T) at P = 0.1 MPa for the Binary Systems {[C_6DABCO][NTf_2] (1) + PEA (2)}.

x_1	T / K	x_1	T / K
1.0000	306.3	0.9403	298.4
0.9977	305.6	0.9319	296.7
0.9936	304.3	0.9218	295.2
0.9877	303.3	0.9014	293.1
0.9766	301.7	0.8841	291.3
0.9613	299.6	0.8590	284.9
0.9536	299.5		

Table S6. Experimental (Solid + Liquid)/(Liquid + Liquid) Equilibrium Data (IL Mole Fraction x_1 vs. Equilibrium Temperature T) at P = 0.1 MPa for the Investigated Binary Systems {IL (1) + Water (2)}.

$[C_6DABCO][NTf_2]$		$[C_{2O1}C_1Im][NTf_2]$		$[C_{2O1}C_1Pyr][NTf_2]$	
x_1	T / K	x_1	T / K	x_1	T / K
1.0000[a]	306.3	0.7011	305.6	0.7387	300.7
0.9682[a]	303.8	0.6880	308.1	0.7264	305.4
0.9232[a]	299.4	0.6749	310.3	0.7120	310.4
0.8870[a]	295.6	0.6600	313.1	0.7006	315.5
0.8514[a]	294.2	0.6488	315.4	0.6883	319.4
0.8157[a]	291.9	0.6415	317.1	0.6784	324.0
0.7835[a]	289.8	0.6302	319.0	0.6597	330.8
0.7562[a]	286.9	0.6179	321.3	0.6413	337.5
0.7362[a]	285.4	0.6118	323.0	0.6301	342.0
0.7135[a]	284.2	0.6032	324.8	0.6144	348.4
0.6662[a]	282.5	0.5937	327.0	0.000803[c]	298.2
0.5307	308.2	0.5897	328.1	0.000931[c]	308.2
0.5212	315.5	0.5830	329.7	0.001015[c]	318.2
0.5100	319.5	0.5757	331.1	0.001121[c]	328.2
0.4936	325.2	0.5646	333.3		
0.4786	331.9	0.5583	334.8		
0.4635	336.4	0.5499	336.3		
0.4447	343.4	0.5355	338.7		
0.4220	348.3	0.5235	341.1		
0.3986	353.6	0.5131	343.5		
0.3780	358.6	0.5010	345.9		
0.3517	364.9	0.4895	348.2		
0.3281	370.4	0.4781	351.1		
0.000219[b]	308.4	0.004268[c]	298.2		
0.000230[b]	318.4	0.004769[c]	308.2		
0.000245[b]	328.4	0.005353[c]	318.2		
0.000281[b]	338.3	0.006652[c]	328.2		

[a] (Solid + liquid) equilibrium.

[b] Water-rich phase composition. Measured with UV-Vis.

[c] Water-rich phase composition. Measured based on conductivity.

Table S7. Experimental (Liquid + Liquid) Equilibrium Data (Water-Rich Phase Mole Fractions x_1' and x_2' vs. IL-Rich Phase Mole Fractions x_1'' and x_2'') for the Investigated Ternary Systems {IL (1) + PEA (2) + Water (3)} at T = 308.15 K and P = 0.1 MPa.

Water-rich phase		IL-rich phase		Water-rich phase		IL-rich phase	
x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
[C_6C_1Pyr][NTf_2]				[C_6DABCO][NTf_2]			
0.000	0.000	0.742	0.000	0.000	0.000	0.531	0.000
0.000	0.001	0.564	0.111	0.000	0.000	0.447	0.088
0.000	0.001	0.453	0.210	0.000	0.001	0.394	0.150
0.000	0.001	0.422	0.246	0.000	0.001	0.311	0.223
0.000	0.002	0.368	0.284	0.000	0.001	0.298	0.241
0.000	0.002	0.354	0.303	0.000	0.002	0.262	0.286
0.000	0.002	0.298	0.338	0.000	0.002	0.237	0.313
0.000	0.002	0.245	0.376	0.000	0.004	0.207	0.347
0.000	0.003	0.243	0.385	0.000	0.003	0.175	0.386
0.000	0.003	0.231	0.395	0.000	0.003	0.136	0.427
0.000	0.003	0.222	0.403	0.000	0.004	0.067	0.500
0.000	0.003	0.177	0.436	0.000	0.003	0.046	0.528
0.000	0.003	0.119	0.481	0.000	0.004	0.023	0.552
0.000	0.003	0.141	0.462	0.000	0.004	0.000	0.582
0.000	0.003	0.073	0.516	[$C_{2O1}C_1$Pyr][NTf_2]			
0.000	0.004	0.012	0.563	0.000	0.000	0.720	0.000
0.000	0.004	0.041	0.537	0.000	0.001	0.627	0.074
0.000	0.004	0.000	0.582	0.000	0.001	0.555	0.130
[$C_{2O1}C_1$Im][NTf_2]				0.000	0.002	0.500	0.164
0.000	0.000	0.688	0.000	0.000	0.002	0.417	0.234
0.000	0.001	0.580	0.107	0.000	0.002	0.436	0.207
0.000	0.001	0.486	0.205	0.000	0.003	0.371	0.270
0.000	0.002	0.439	0.239	0.000	0.003	0.327	0.302
0.000	0.002	0.384	0.277	0.000	0.003	0.288	0.329
0.000	0.002	0.370	0.296	0.000	0.003	0.271	0.333
0.000	0.002	0.312	0.332	0.000	0.003	0.233	0.368
0.000	0.003	0.283	0.354	0.000	0.003	0.172	0.418

Table S7. (continued)

0.000	0.003	0.263	0.372	0.000	0.004	0.112	0.465
0.000	0.003	0.243	0.389	0.000	0.004	0.070	0.499
0.000	0.003	0.233	0.397	0.000	0.004	0.000	0.582
0.000	0.003	0.187	0.431				
0.000	0.003	0.149	0.457				
0.000	0.003	0.126	0.477				
0.000	0.003	0.080	0.513				
0.000	0.004	0.043	0.544				
0.000	0.004	0.013	0.569				
0.000	0.004	0.000	0.582				