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Supporting Information

Extraction of 2-Phenylethanol (PEA) from Aqueous Solution Using Ionic Liquids: Synthesis, Phase Equilibrium Investigation, Selectivity in Separation and Thermodynamic Models

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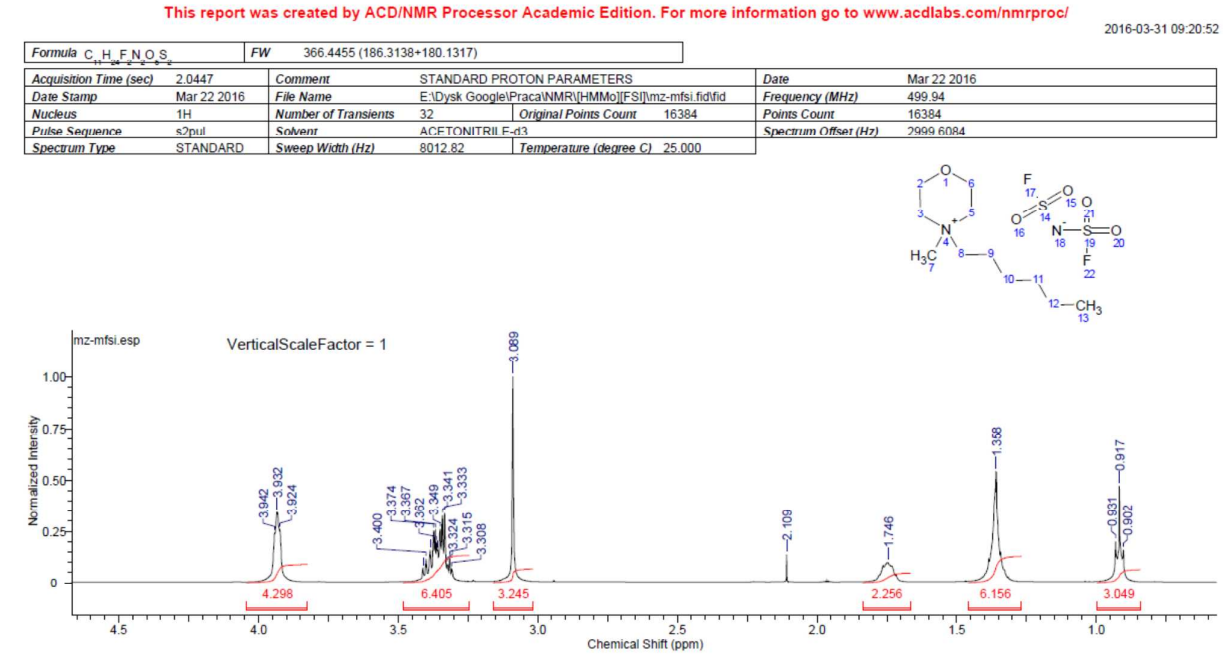
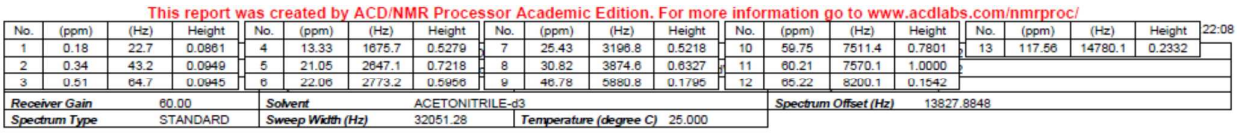
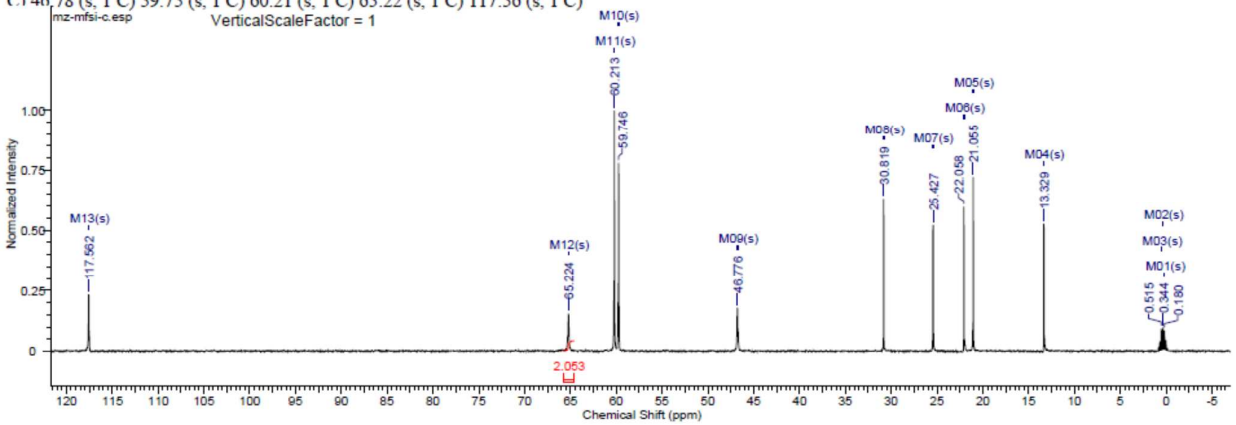
Report S1. Synthetize of [HMMOR][FSI].

1H NMR





13C NMR (126 MHz, ACETONITRILE-d_3) δ ppm 0.18 (s, 1 C) 0.34 (s, 1 C) 0.51 (s, 1 C) 13.33 (s, 1 C) 21.05 (s, 1 C) 22.06 (s, 1 C) 25.43 (s, 1 C) 30.82 (s, 1 C) 46.78 (s, 1 C) 59.75 (s, 1 C) 60.21 (s, 1 C) 65.22 (s, 1 C) 117.56 (s, 1 C)



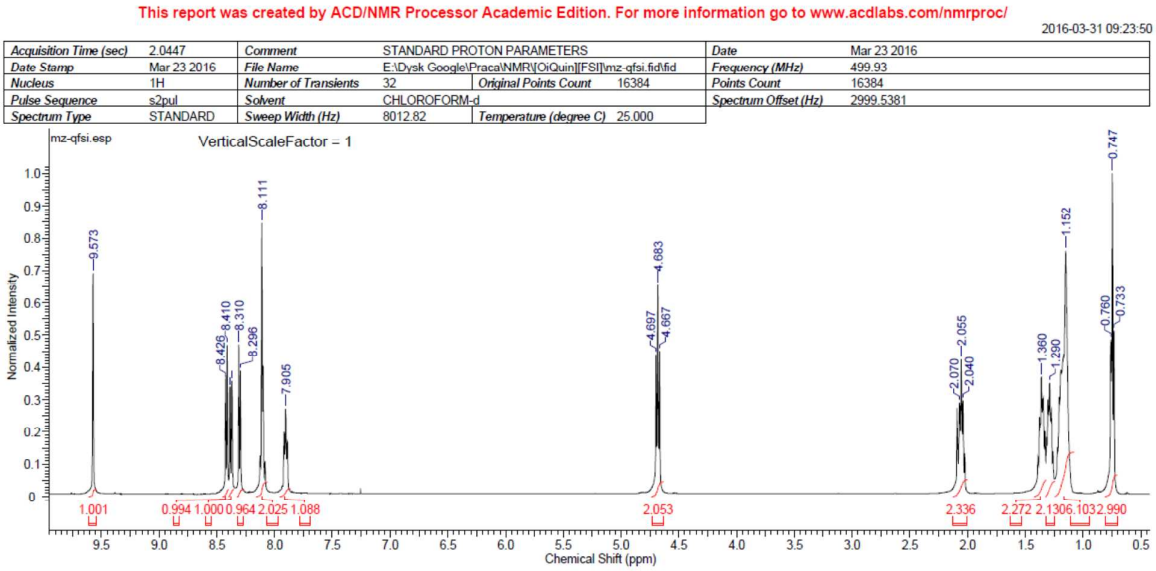
13C NMR

^{1}H NMR: δ_H(500 MHz; CD_3CN): 0.917 (3 H, t, $^3J_{H,H}$ = 7.34 Hz), 1.358 (6 H, m), 1.746 (2 H, m), 3.089 (3 H, s), 3.349 (6 H, m), 3.932 (4 H, m).

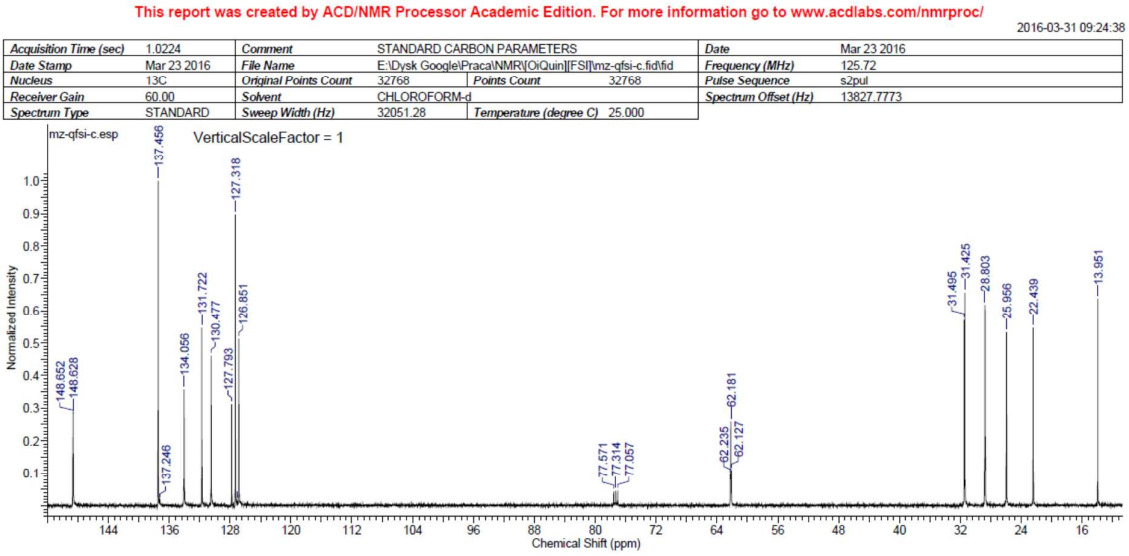
^{13}C NMR: δ_C(100 MHz; CD_3CN): 13.329, 21.055, 22.058, 25.427, 30.819, 46.776, 59.746, 60.213, 65.224.

Elemental analysis: Found: C, 36.16 ; N, 7.5; H, 6.57, S 17.50 %. Calc. for $C_{11}H_{24}N_2S_2O_5F_2$: C, 36.05; N, 7.64; H, 6.60, S 17.50 %.

Report S2. Synthetize of [OiQuin][FSI].



1H NMR



13C NMR

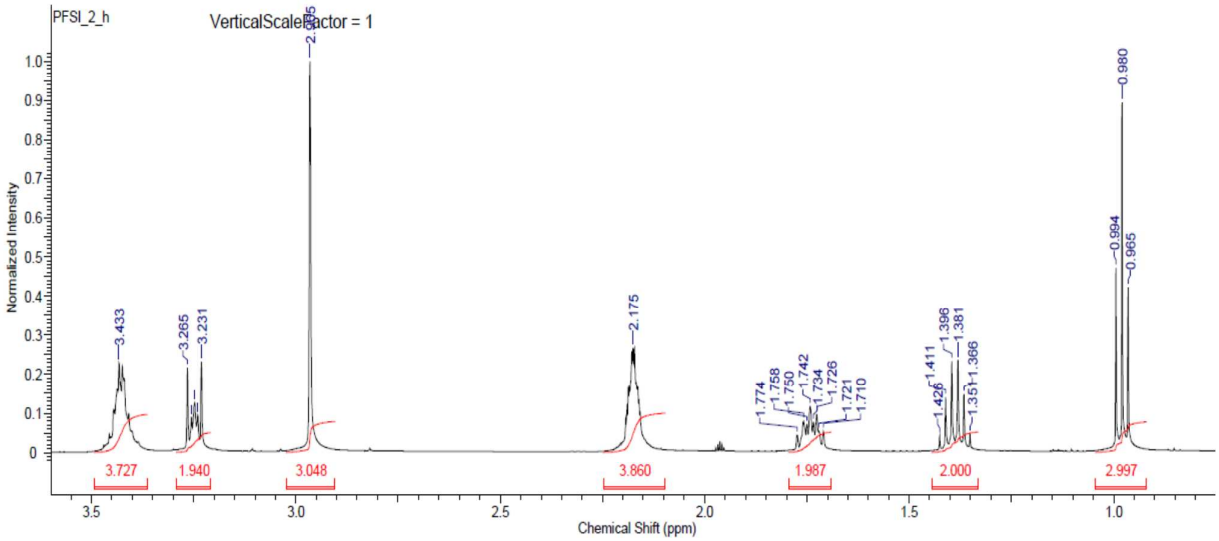
^{1}H NMR: δ_H(500 MHz; D_2O): 0.747 (3 H, t, $^3J_{H,H}$ = 6.85 Hz), 1.167 (6 H, m), 1.290 (2 H, quin, $^3J_{H,H}$ = 7.83 Hz), 1.360 (2 H, quin, $^3J_{H,H}$ = 7.34 Hz), 2.055 (2 H, quin, $^3J_{H,H}$ = 7.34 Hz),

4.683 (2 H, t, $^{3}J_{H,H}$ = 7.83 Hz), 7.905 (1H, m), 8.111 (2H, m), 8.303 (1H, d, $^{3}J_{H,H}$ = 6.85 Hz), 8.378 (1H, d, $^{3}J_{H,H}$ = 8.31 Hz), 8.418 (1H, d, $^{3}J_{H,H}$ = 7.83 Hz), 9.573 (1H, s).

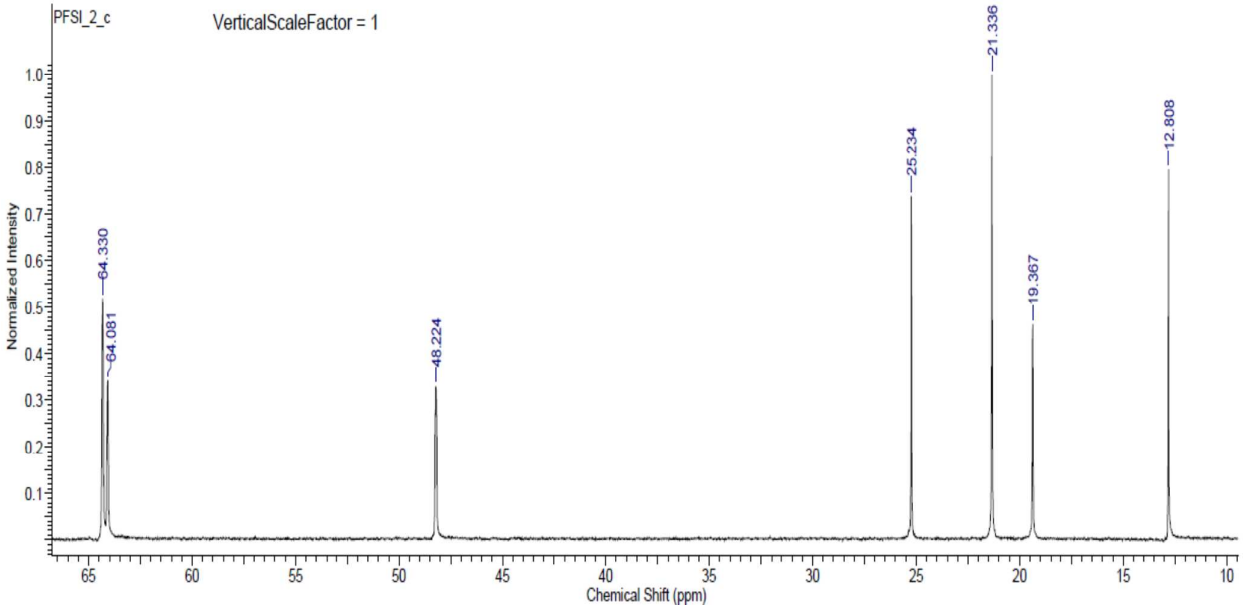
^{13}C NMR: δ_C(100 MHz; D_2O): 13.951, 22.439, 25.956, 28.803, 31.425, 31.495, 62.181, 126.851, 127.318, 127.793, 130.477, 131.722, 134.056, 137.456, 148.628, 148.652.

Elemental analysis: Found: C, 48.38; N, 6.48; H, 5.73, S 15.29 %. Calc. for $C_{17}H_{24}N_2S_2O_4F_2$: C, 48.33; N, 6.63; H, 5.73, S 15.18 %.

Report S3. Synthetize of [BMPYR][FSI].



1H NMR



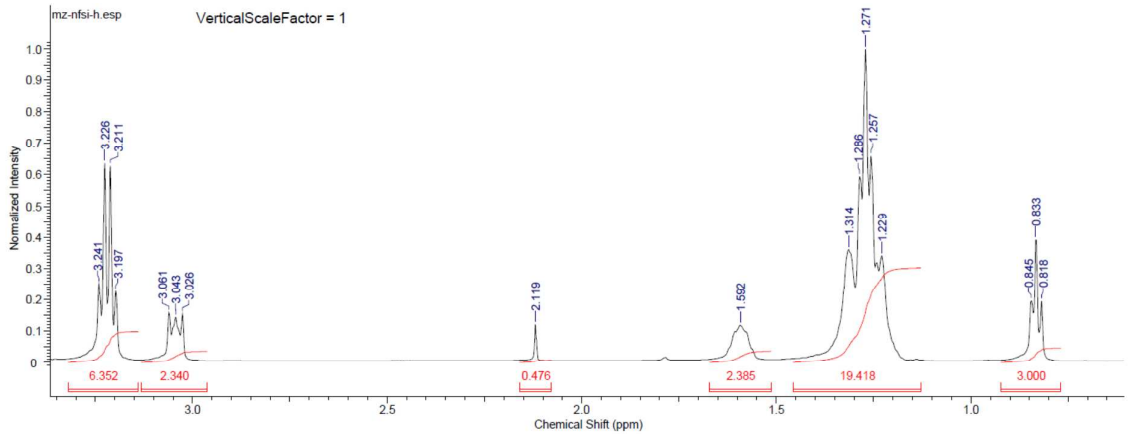
13C NMR

^{1}H NMR: δ_H(500 MHz; CD_3CN): 0.980 (3 H, t, $^{3}J_{H,H}$ = 7.34 Hz), 1.388 (2 H, hex, $^{3}J_{H,H}$ = 7.34 Hz), 1.742 (2 H, m), 2.175 (4H, m), 2.965 (3 H, s), 3.247 (2 H, m), 3.433 (4 H, m).

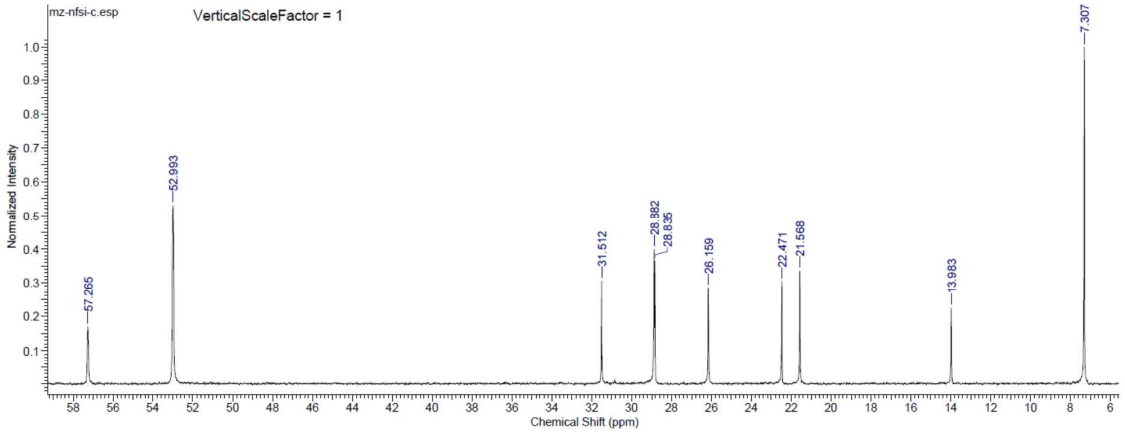
^{13}C NMR: δ_C(100 MHz; CD_3CN): 12.808, 19.367, 21.336, 25.234, 48.224, 64.081, 64.330.

Elemental analysis: Found: C, 33.44; N, 8.68; H, 6.20, S 19.74 %. Calc. for $C_9H_{20}N_2S_2O_4F_2$: C, 33.53; N, 8.69; H, 6.25, S 19.85 %.

Report S4. Synthetize of $[N_{2228}][FSI]$.



1H NMR



13C NMR

^{1}H NMR: δ_H(500 MHz; $CDCl_3$): 0.833 (3 H, t, $^{3}J_{H,H}$ = 7.34 Hz), 1.229 - 1.314 (20 H, m), 1.592 (2 H, m), 3.043 (2H, m), 3.218 (6 H, q, $^{3}J_{H,H}$ = 7.34 Hz).

^{13}C NMR: δ_C(100 MHz; $CDCl_3$): 7.307, 13.983, 21.568, 22.471, 26.159, 28.835, 28.882, 31.512, 52.993, 57.265.

Elemental analysis: Found: C, 42.65; N, 7.10; H, 8.13, S 16.25 %. Calc. for $C_{14}H_{32}N_2S_2O_4F_2$: C, 42.62; N, 7.10; H, 8.17, S 16.25%.

Report S5. Purity estimated from NMR analysis:

[HMMOR][FSI] 93% mol, 97.0% wt impurities: methylmorpholine 0.8% wt, hexylbromide 2% wt

[OiQuin][FSI] 92% mol, 97.0% wt impurities: isoquinoline 1.5% wt, octylbromide 1.3% wt

[BMPYR][FSI] 93.4% mol, 97.4% wt impurities: methylpyrrolidine 0.5% wt, butylbromide 2% wt

[N_{2228}][FSI] 93.5% mol, 97.5% wt impurities: triethylamine 0.9% wt, octylbromide 1.5% wt

During synthesis the organic phase was extracted with water ~10 x 15 ml the last portion was checked with 0.1M AgNO3 solution to detect any halide impurities. The analysis was not quantitative.

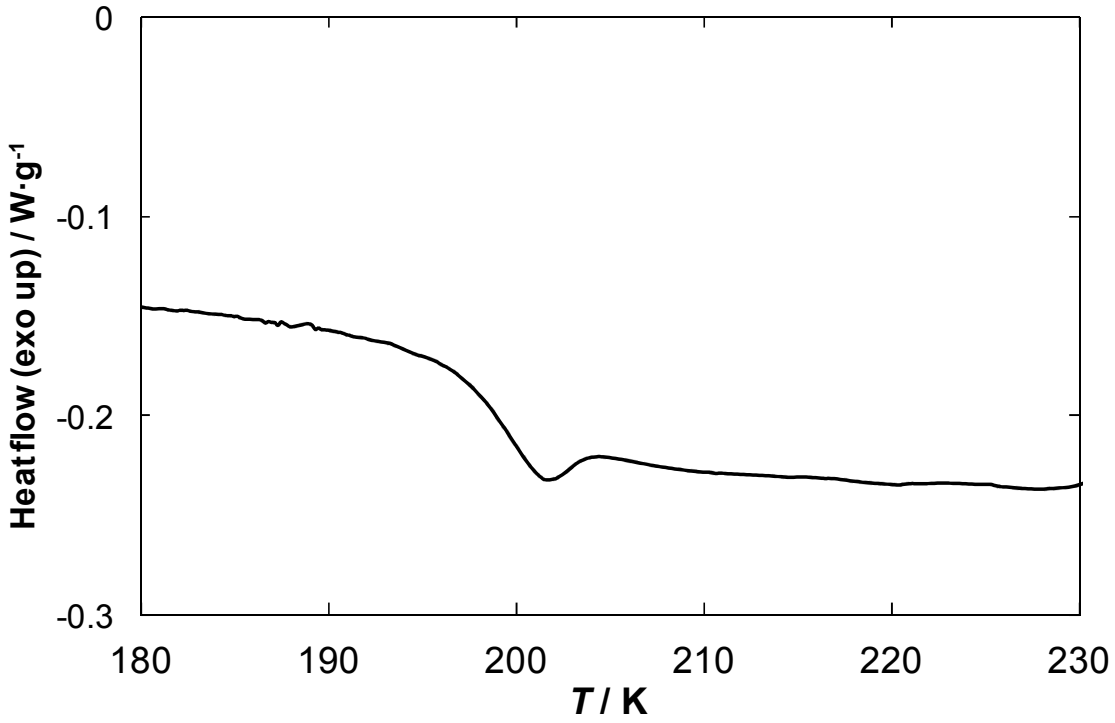


Figure S1. DSC diagram for [HMMOR][FSI].

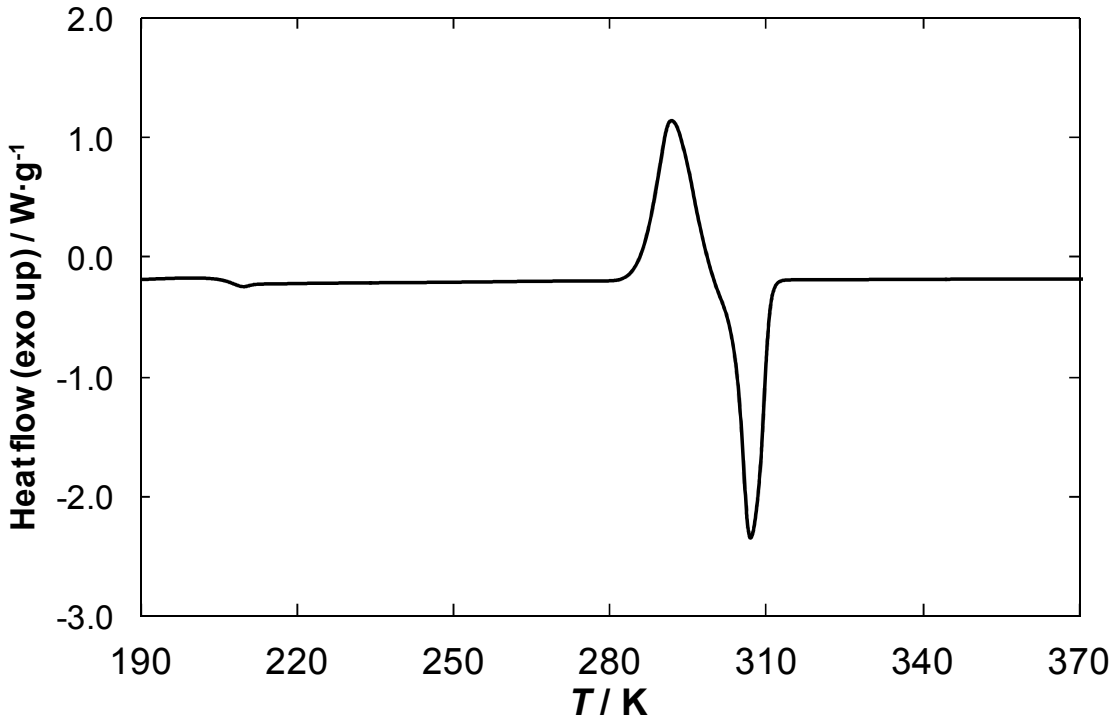


Figure S2. DSC diagram for [OiQuin][FSI].

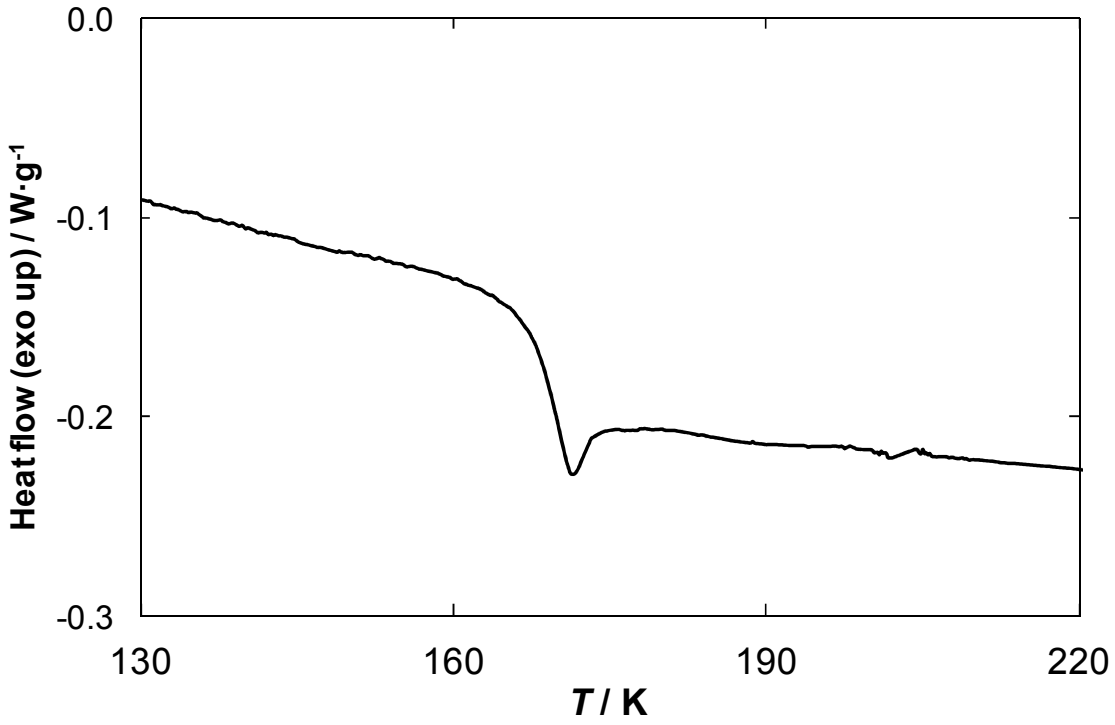


Figure S3. DSC diagram of pure [BMPYR][FSI].

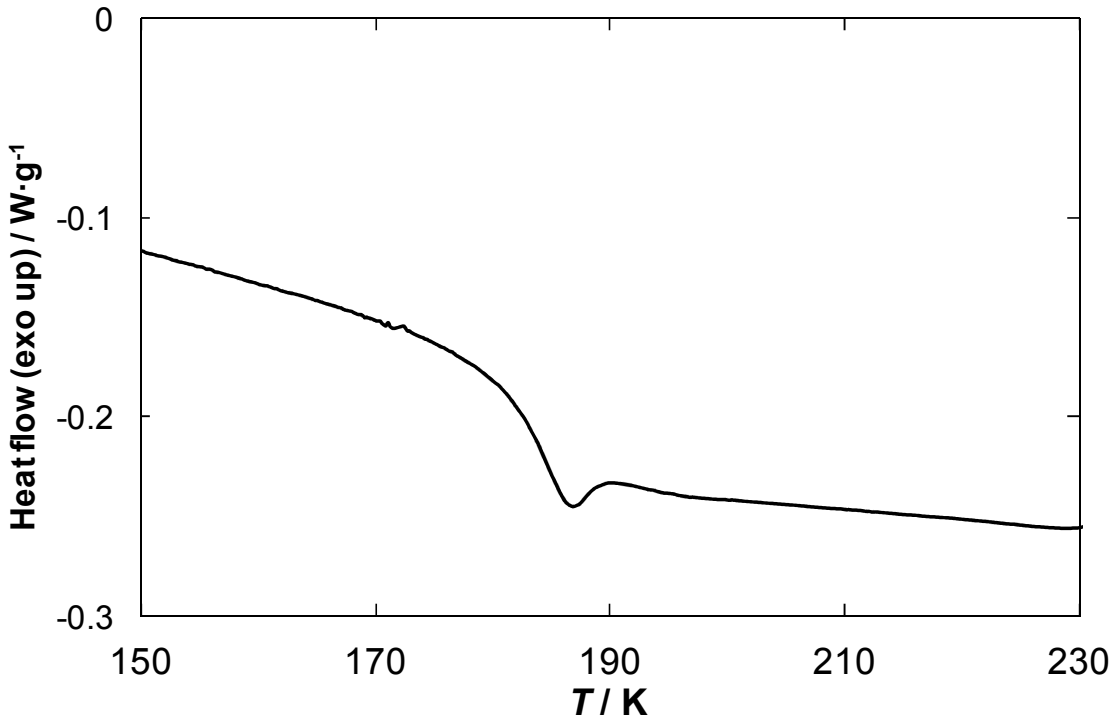


Figure S4. DSC diagram of pure $[N_{2228}][FSI]$.

Table S1. Density, ρ, Dynamic Viscosity, η and Surface Tension, σ of the ILs under Study as a Function of Temperature at p = 101 kPa[a]

T / K	[HMMOR][FSI]	[OiQuin][FSI]	[BMPYR][FSI]	[N_{2228}][FSI]
		ρ / (g·cm^{-3})		
298.15	1.2974	1.2612	1.3064	1.1646
303.15	1.2936	1.2574	1.3025	1.1611
308.15	1.2899	1.2537	1.2986	1.1576
313.15	1.2862	1.2499	1.2948	1.1541
318.15	1.2825	1.2462	1.2909	1.1507
323.15	1.2788	1.2424	1.2871	1.1472
328.15	1.2751	1.2387	1.2833	1.1437
333.15	1.2715	1.2350	1.2795	1.1403
338.15	1.2679	1.2314	1.2757	1.1369
343.15	1.2642	1.2277	1.2719	1.1334
348.15	1.2606	1.2240	1.2682	1.1300
353.15	1.2570	1.2204	1.2644	1.1266
358.15	1.2535	1.2168	1.2607	1.1233
		η / (mPa·s)		
298.15	369.8	319.9	60.24	194.8
303.15	274.1	231.4	50.49	150.5
308.15	209.1	184.8	42.65	117.8
313.15	161.5	140.7	36.57	94.46
318.15	127.1	109.6	31.65	76.57
323.15	102.6	86.45	27.47	62.48
328.15	82.49	71.67	24.07	52.01
333.15	67.72	56.51	21.23	43.13
338.15	56.13	46.68	18.75	35.40
343.15	47.22	38.97	16.76	30.32
348.15	40.24	32.62	12.71	26.24
353.15	34.31	28.02	13.51	22.65
358.15	28.11	23.59	12.45	22.05
		σ / (mN·m^{-1})		
298.15	32.02	28.73	35.04	28.83
303.15	31.64	28.46	34.61	28.56
308.15	31.29	28.23	34.17	28.28
313.15	30.92	27.97	33.72	28.00
318.15	30.60	27.70	33.25	27.76
323.15	30.26	27.45	32.80	27.50

328.15	29.90	27.18	32.31	27.24
333.15	29.54	26.93	31.89	27.01
338.15	29.23	26.71	31.47	26.77
343.15	28.91	26.45	31.01	26.49

[a]Standard uncertainities are: $u(\rho) = \pm 1.4 \cdot 10^{-3}$ g·cm^{-3}, $u(\eta) = \pm 0.5$ % , $u(\sigma) = \pm 0.04$ mN·m^{-1}; $u(T) = 0.1$ K; $u(p) = 1$kPa.

Table S2. Operating Conditions in the Gas Chromatograph for the Compositional Analysis of the Phases in Equilibrium for Ternary Systems {IL (1) + PEA (2) + Water (3)} at T = 308.15 K, p = 101 kPa

Element	Characteristic	Description
Column	Type	Elit-WAX PerkinElmer (Polyethylene Glycol), length 30 m, 0.53 mm internal diameter, 5 μm film thickness
	Flow	3 $cm^3 \cdot min^{-1}$
	Carrier gas	Helium
Oven	Temperature	343.15 K for 7.5 min
Injector	Injection volume	0.0005 cm^3
	Split ratio	2:1
	Temperature	473.15 K
Detector	Type	Flame ionization detector (TCD)
	Temperature	473.15 K

Table S3. Parameters of the Linear Dependence of Density as a Function of Temperature[a]

	$10^4 \cdot a_1$ /(g·cm^{-3}·K^{-1})	a_0 / (g·cm^{-3})
[HMMOR][FSI]	-7.286	1.514
[OiQuin][FSI]	-7.400	1.482
[BMPYR][FSI]	-7.626	1.534
[N_{2228}][FSI]	-6.891	1.370

[a] $\rho/(g \cdot cm^{-3}) = a_1 \cdot T/(K) + a_0$

Table S4. Fit Parameters of the VFT Equation, *C, D*, as Well as the Ideal Transition Temperature, T_0 for the Correlation of Dynamic Viscosity as a Function of Temperature for the Tested ILs[a]

ILs	T_0 / (K)	10^3 C / (mPa·s·K^{-1})	10^{-3} D / (K)
[HMMOR][FSI]	135.9	1.234	1.581
[OiQuin][FSI]	144.7	1.280	1.470
[BMPYR][FSI]	107.7	3.092	1.337
[N_{2228}][FSI]	120.2	0.887	1.680

[a] $\eta = CT^{0.5} exp\ (\frac{D}{T - T_0}\ )$

Table S5. Parameters of the Linear Dependence of Surface Tension as a Function of Temperature[a]

	$10^2 \cdot b_1$ / (mN·m^{-1}·K^{-1})	b_0 / (mN·m^{-1})
[HMMOR][FSI]	-6.930	52.653
[OiQuin][FSI]	-5.070	43.841
[BMPYR][FSI]	-9.001	61.890
[N_{2228}][FSI	-5.164	44.203

[a] $\sigma/(mN \cdot m^{-1}) = b_1 \cdot T/(K) + b_0$

Table S6. The Parachor, *P* for Ionic Liquids Under Study at Temperature Range *T* = (298.15 to 343.15) K at *p* = 101 kPa

	[HMMOR][FSI]	[OiQuin][FSI]	[BMPYR][FSI]	[N_{2228}][FSI]
		P / ($mN^{1/4}$·$m^{-1/4}$·cm^3·mol^{-1})		
298.15	671.9	775.6	600.4	785.0
303.15	671.8	776.1	600.3	785.5
308.15	671.9	776.8	600.2	786.0
313.15	671.8	777.4	600.0	786.4
318.15	672.0	777.8	599.7	787.0
323.15	672.1	778.4	599.4	787.5
328.15	672.0	778.8	599.0	788.1
333.15	671.9	779.3	598.8	788.8
338.15	672.0	780.1	598.6	789.4
343.15	672.1	780.5	598.1	789.7

$u(P) = \pm 0.1 (mN^{1/4} \cdot m^{-1/4} \cdot cm^3 \cdot mol^{-1})$.

Table S7. Experimental Liquid - Liquid Phase Equilibrium in {IL (1) + Water (2)} Binary Systems, p = 101 kPa[a]

x_1	T^{LLE}/K	x_1	T^{LLE}/K	x_1	T^{LLE}/K
		[HMMOR][FSI]			
0.7816	277.0	0.6454	308.7	0.000256	318.2[b]
0.7428	285.3	0.6255	314.3	0.000235	313.2[b]
0.7123	292.7	0.6051	320.3	0.000222	308.2[b]
0.6885	296.3	0.5965	324.8	0.000210	303.2[b]
0.6731	302.0	0.5708	330.9	0.000195	298.2[b]
0.6541	307.4	0.5127	344.6		
		[OiQuin][FSI]			
0.8826	275.7	0.7878	306.4	0.6656	336.6
0.8600	286.8	0.7619	313.3	0.015591	313.2[b]
0.8494	289.5	0.7500	318.0	0.015587	308.2[b]
0.8308	293.7	0.7165	324.3	0.015583	303.2[b]
0.8131	299.3	0.6948	329.5	0.015582	298.2[b]
0.8025	303.2	0.6821	333.7		
		[BMPYR][FSI]			
0.8344	281.3	0.7021	299.6	0.000378	313.2[b]
0.8019	285.8	0.6805	304.8	0.000368	308.2[b]
0.7785	291.6	0.6476	314.2	0.000363	303.2[b]
0.7510	296.9	0.6183	320.3	0.000356	298.2[b]
0.7247	299.6	0.000389	328.8[b]		
		[N_{2228}][FSI]			
0.9148	262.8	0.8507	289.4	0.7112	331.7
0.8950	272.0	0.8359	295.1	0.000047	318.2[b]
0.8780	276.0	0.8286	301.5	0.000044	313.2[b]
0.8722	280.1	0.8110	307.6	0.000040	308.2[b]
0.8641	282.6	0.7765	315.4	0.000037	303.2[b]
0.8534	287.8	0.7351	323.8	0.000035	298.2[b]

[a] Standard uncertainties are $u(x)$ = ±0.0005; $u(T)$ = ±0.2 K; $u(p)$ = ±0.1 kPa.
[b] $u(x)$ = ±0.000001, $u(T)$ = ±0.1 K; $u(p)$ = ±0.1 kPa in the conductivity method.

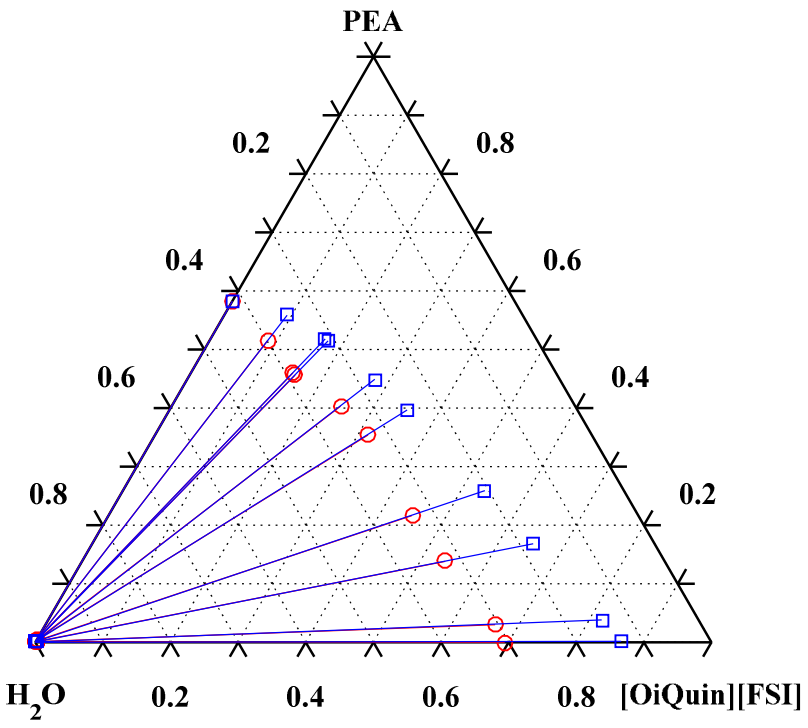


Figure S5. Experimental *versus* COSMO-RS predictions of LLE tie-lines for ternary system {[QiQuin][FSI] (1) + PEA (2) + water (3)} at T = 308.15 Kand pressure p = 101 kPa; (○—○) experimental data, (□—□) COSMO-RS predictions.

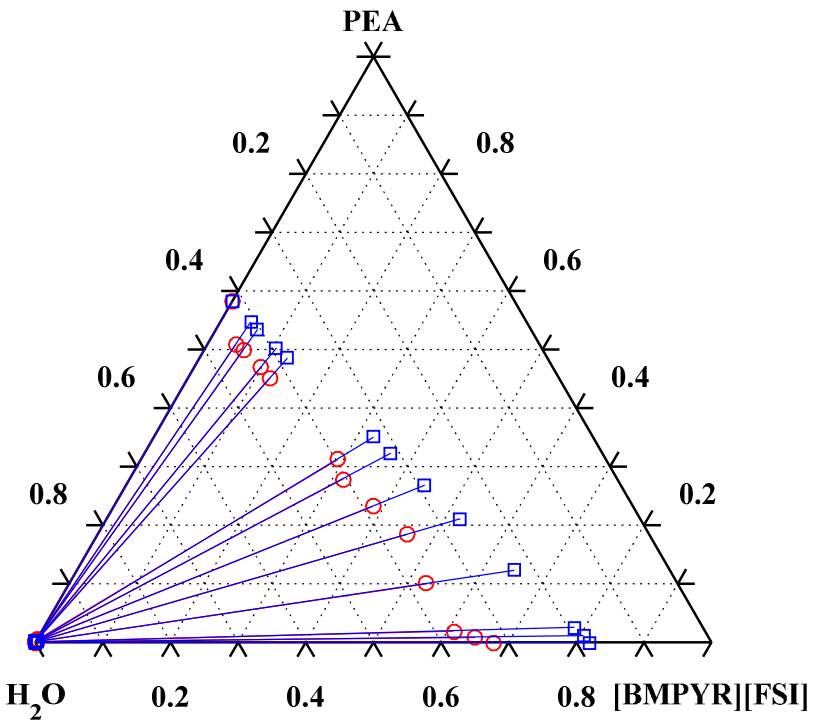


Figure S6. Experimental *versus* COSMO-RS predictionsof LLE tie-lines for ternary system {[BMPYR][FSI] (1) + 2-phenylethanol (PEA) (2) + water (3)} at T = 308.15 Kand pressure p = 101 kPa; (○—○) experimental data, (□—□) COSMO-RS predictions.

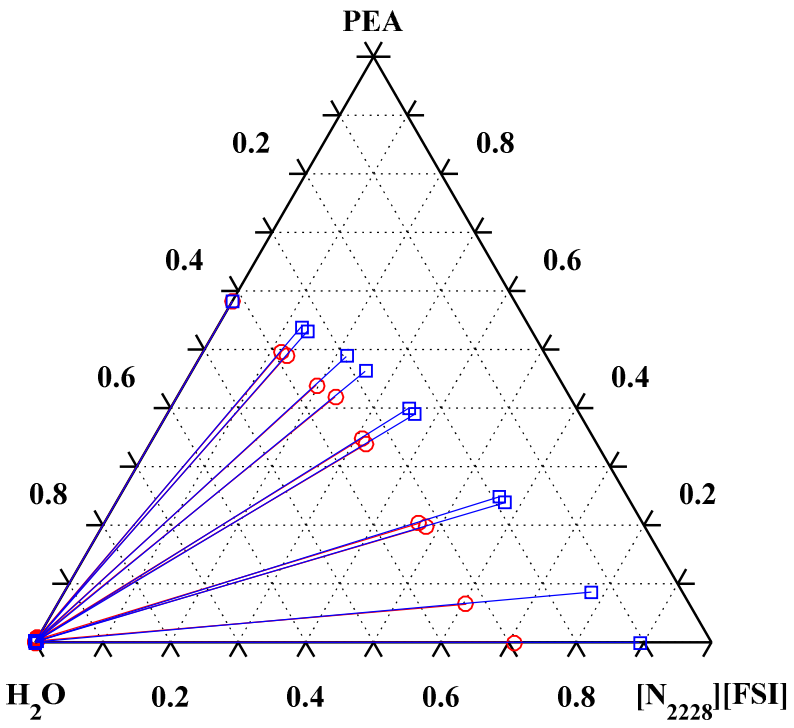


Figure S7. Experimental *versus* COSMO-RS predictions of LLE tie-lines for ternary system {[N_{2228}][FSI] (1) + 2-phenylethanol (PEA) (2) + water (3)} at T = 308.15 Kand pressure p = 101 kPa; (○—○) experimental data, (□—□) COSMO-RS predictions.