



**QUEEN'S
UNIVERSITY
BELFAST**

Liquid–Liquid Equilibria of Ionic Liquids–Water–Acetic Acid Mixtures

Wang, S., Liu, J., Hembre, R., Barnicki, S., Goodrich, P., Hughes, T-L., ... Hardacre, C. (2017). Liquid–Liquid Equilibria of Ionic Liquids–Water–Acetic Acid Mixtures. DOI: 10.1021/acs.jced.6b00692

Published in:

Journal of Chemical and Engineering Data

Document Version:

Peer reviewed version

Queen's University Belfast - Research Portal:

[Link to publication record in Queen's University Belfast Research Portal](#)

Publisher rights

This document is the Accepted Manuscript version of a Published Work that appeared in final form in Journal of Chemical and Engineering Data, copyright © 2017 American Chemical Society after peer review and technical editing by the publisher.

To access the final edited and published work see <http://pubs.acs.org/doi/abs/10.1021/acs.jced.6b00692>

General rights

Copyright for the publications made accessible via the Queen's University Belfast Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The Research Portal is Queen's institutional repository that provides access to Queen's research output. Every effort has been made to ensure that content in the Research Portal does not infringe any person's rights, or applicable UK laws. If you discover content in the Research Portal that you believe breaches copyright or violates any law, please contact openaccess@qub.ac.uk.

Supporting Information

Liquid-Liquid Equilibria of Ionic Liquids-Water-Acetic Acid Mixtures

Silu Wang,¹ Jingyi Liu,¹ Robert Hembre,² Scott Barnicki,² Peter Goodrich,¹ Terri-Louise Hughes,^{1,3} David W. Rooney,¹ Chester Sink,² Johan Jacquemin,^{1,*} Christopher Hardacre,^{1,3*}

¹The QUILL Research Centre, School of Chemistry and Chemical Engineering, Queen's University, Stranmillis Road, Belfast BT9 5AG, UK

²Eastman Chemical Company, 100 N. Eastman Road, Kingsport, TN 37662, USA

³School of Chemical Engineering & Analytical Science, University of Manchester, The Mill, Sackville Street, Manchester M13 9PL UK

*E-mail: c.hardacre@manchester.ac.uk, johan.jacquemin@qub.ac.uk

Table S1. Composition of the experimental tie-line ends, and values of the solute distribution ratios (β_x and β_w calculated from the mole and mass fractions, respectively) and selectivity (S) for the ternary system (water + acetic acid + MTBE) at 293.15 K and 313.15 K and at 101 kPa. The mole fractions of water, acetic acid and MTBE are represented by x_1 , x_2 and x_3 , respectively.

Water-rich phase			MTBE-rich phase			β_w	β_x	S
x_1	x_2	x_3	x_1	x_2	x_3			
$T = 293.15 \text{ K}$								
0.9890	0.0000	0.0110	0.0566	0.0000	0.9434	-	-	-
0.9739	0.0150	0.0111	0.1146	0.0643	0.8211	1.06	4.29	36.43
0.9397	0.0474	0.0129	0.2032	0.1532	0.6436	0.97	3.23	14.95
0.9246	0.0601	0.0153	0.3094	0.2041	0.4865	1.21	3.40	10.15
0.9077	0.0748	0.0175	0.3852	0.2151	0.3997	1.17	2.88	6.78
0.8943	0.0871	0.0186	0.4252	0.2181	0.3567	1.10	2.50	5.27
0.8864	0.0917	0.0219	0.4587	0.2180	0.3233	1.12	2.38	4.59
0.8798	0.0970	0.0232	0.4985	0.2177	0.2838	1.13	2.24	3.96
0.8398	0.1256	0.0346	0.5396	0.2195	0.2409	1.02	1.75	2.72
0.8280	0.1329	0.0391	0.5639	0.2200	0.2161	1.03	1.66	2.43
$T = 313.15 \text{ K}$								
0.9931	0.0000	0.0069	0.0466	0.0000	0.9534	-	-	-
0.9850	0.0075	0.0075	0.0674	0.0305	0.9021	0.93	4.07	59.43
0.9530	0.0394	0.0076	0.2098	0.1404	0.6498	1.04	3.56	16.19
0.9518	0.0397	0.0085	0.1794	0.1330	0.6876	0.95	3.35	17.77
0.9260	0.0582	0.0158	0.3071	0.1880	0.5049	1.14	3.23	9.74
0.8966	0.0845	0.0189	0.4786	0.2334	0.2880	1.32	2.76	5.17
0.8586	0.1121	0.0293	0.5652	0.2408	0.1940	1.28	2.15	3.26
0.8267	0.1331	0.0402	0.6127	0.2351	0.1522	1.21	1.77	2.38

$u(x_i) = 0.01$; $u(T) = 0.5 \text{ K}$; $u(p) = 2 \text{ kPa}$.

Table S2. Composition of the experimental tie-line ends, and values of the solute distribution ratios (β_x and β_w calculated from the mole and mass fractions, respectively) and selectivity (S) for the ternary system (water + acetic acid + MIBK) at 293.15 K and at 101 kPa. The mole fractions of water, acetic acid and MIBK are represented by x_1 , x_2 and x_3 , respectively.

Water-rich phase			MIBK-rich phase			β_w	β_x	S
x_1	x_2	x_3	x_1	x_2	x_3			
$T = 293.15$ K								
1.0000	0.0000	0.0000	0.0991	0.0000	0.9009	-	-	-
0.9697	0.0267	0.0036	0.1667	0.0758	0.7575	0.66	2.84	16.51
0.9630	0.0330	0.0040	0.2081	0.1208	0.6711	0.92	3.66	16.94
0.9361	0.0560	0.0079	0.2973	0.1622	0.5405	0.88	2.90	9.12
0.9138	0.0777	0.0085	0.3680	0.1991	0.4329	0.91	2.56	6.36
0.9072	0.0839	0.0089	0.4151	0.2075	0.3774	0.95	2.47	5.41
0.8921	0.0950	0.0129	0.4516	0.2258	0.3226	1.02	2.38	4.70
0.8877	0.0996	0.0127	0.4813	0.2305	0.2882	1.05	2.31	4.27
0.8618	0.1200	0.0182	0.5226	0.2261	0.2513	0.96	1.88	3.11
0.8560	0.1320	0.0120	0.5727	0.2238	0.2035	0.94	1.70	2.53
0.7800	0.1650	0.0550	0.6936	0.1908	0.1156	0.96	1.16	1.30

$u(x_i) = 0.01$; $u(T) = 0.5$ K; $u(p) = 2$ kPa.

Table S3. Composition of the experimental tie-line ends, and values of the solute distribution ratios (β_x and β_w calculated from the mole and mass fractions, respectively) and selectivity (S) for the ternary system (water + acetic acid + [P_{666,14}]Cl) at 293.15 K and at 101 kPa. The mole fractions of water, acetic acid and [P_{666,14}]Cl are represented by x_1 , x_2 and x_3 , respectively.

Water-rich phase			Ionic Liquid-rich phase			β_w	β_x	S
x_1	x_2	x_3	x_1	x_2	x_3			
1.000	0.000	0.000	0.826	0.000	0.174	-	-	-
0.998	0.002	0.000	0.497	0.112	0.391	4.64	56.00	112.45
0.998	0.002	0.000	0.499	0.046	0.455	1.68	23.00	46.00
0.995	0.005	0.000	0.496	0.080	0.424	1.25	16.00	32.10
0.992	0.008	0.000	0.499	0.073	0.428	0.71	9.13	18.14
0.984	0.016	0.000	0.471	0.277	0.252	2.07	17.31	36.17
0.980	0.020	0.000	0.490	0.235	0.275	1.34	11.75	23.50
0.920	0.080	0.000	0.498	0.377	0.125	1.04	4.71	8.71
0.883	0.117	0.000	0.470	0.345	0.185	0.54	2.95	5.54
0.833	0.167	0.000	0.481	0.384	0.135	0.57	2.30	3.98
0.833	0.167	0.000	0.530	0.360	0.110	0.61	2.16	3.39
0.824	0.176	0.000	0.521	0.385	0.094	0.68	2.19	3.46
0.820	0.180	0.000	0.510	0.394	0.096	0.68	2.19	3.52
0.811	0.189	0.000	0.527	0.390	0.083	0.70	2.06	3.18
0.806	0.194	0.000	0.519	0.391	0.090	0.66	2.02	3.13
0.789	0.211	0.000	0.494	0.395	0.111	0.56	1.87	2.99
0.773	0.227	0.000	0.509	0.411	0.080	0.66	1.81	2.75
0.758	0.241	0.001	0.502	0.410	0.088	0.61	1.70	2.57
0.749	0.250	0.001	0.540	0.388	0.072	0.64	1.55	2.15
0.728	0.272	0.000	0.520	0.413	0.067	0.65	1.52	2.13
0.714	0.286	0.000	0.525	0.420	0.055	0.70	1.47	2.00
0.698	0.302	0.000	0.544	0.399	0.057	0.64	1.32	1.70

$u(x_i) = 0.01$; $u(T) = 0.5$ K; $u(p) = 2$ kPa.

In the case of the (water + [P_{666,14}]Cl) binary system, a formation of an emulsion within the addition of water to this phosphonium-based ionic liquid was observed. This observation is in agreement with that already reported into the literature.^{1,2}

Table S4. Composition of the experimental tie-line ends, and values of the solute distribution ratios (β_x and β_w calculated from the mole and mass fractions, respectively) and selectivity (S) for the ternary system (water + acetic acid + [P_{666,14}][NTf₂]) at 293.15 K and at 101 kPa. The mole fractions of water, acetic acid and [P_{666,14}][NTf₂] are represented by x_1 , x_2 and x_3 , respectively.

Water-rich phase			Ionic Liquid-rich phase			β_w	β_x	S
x_1	x_2	x_3	x_1	x_2	x_3			
1.000	0.000	0.000	0.127	0.000	0.873	-	-	-
0.958	0.042	0.000	0.298	0.070	0.632	0.07	1.67	5.36
0.943	0.057	0.000	0.309	0.081	0.610	0.06	1.42	4.34
0.902	0.098	0.000	0.354	0.118	0.528	0.06	1.20	3.07
0.892	0.108	0.000	0.355	0.121	0.524	0.06	1.12	2.82
0.867	0.133	0.000	0.420	0.147	0.433	0.08	1.11	2.28

$u(x_i) = 0.01$; $u(T) = 0.5$ K; $u(p) = 2$ kPa.

In the case of the (water + [P_{666,14}][NTf₂]) binary system, a formation of an emulsion within the addition of water to this phosphonium-based ionic liquid was observed. This observation is in agreement with that already reported into the literature in the case of the [P_{666 14}][Cl].^{1,2}

Table S5. Composition of the experimental tie-line ends, and values of the solute distribution ratios (β_x and β_w calculated from the mole and mass fractions, respectively) and selectivity (S) for the ternary system (water + acetic acid + [C₂mim][NTf₂]) at 293.15 K and at 101 kPa. The mole fractions of water, acetic acid and [C₂mim][NTf₂] are represented by x_1 , x_2 and x_3 , respectively.

Water-rich phase			Ionic Liquid-rich phase			β_w	β_x	S
x_1	x_2	x_3	x_1	x_2	x_3			
0.9995	0.0000	0.0005	0.2954	0.0000	0.7046	-	-	-
0.9836	0.0139	0.0025	0.2342	0.0285	0.7373	0.14	2.05	8.61
0.9758	0.0217	0.0025	0.2164	0.0478	0.7358	0.15	2.20	9.93
0.9439	0.0538	0.0023	0.2952	0.1253	0.5795	0.21	2.33	7.45
0.9400	0.0577	0.0023	0.2965	0.1358	0.5677	0.21	2.35	7.46
0.9368	0.0606	0.0026	0.3072	0.1407	0.5521	0.22	2.32	7.08
0.9251	0.0720	0.0029	0.3685	0.1545	0.4770	0.23	2.15	5.39
0.9075	0.0892	0.0033	0.3957	0.1920	0.4123	0.28	2.15	4.94
0.8697	0.1249	0.0054	0.4827	0.2282	0.2891	0.34	1.83	3.29
0.8569	0.1363	0.0068	0.5133	0.2355	0.2512	0.37	1.73	2.88

$$u(x_i) = 0.01; u(T) = 0.5 \text{ K}; u(p) = 2 \text{ kPa}.$$

Table S6. Composition of the experimental tie-line ends, and values of the solute distribution ratios (β_x and β_w calculated from the mole and mass fractions, respectively) and selectivity (S) for the ternary system (water + acetic acid + [C₄mim][NTf₂]) at 293.15 K and at 101 kPa. The mole fractions of water, acetic acid and [C₄mim][NTf₂] are represented by x_1 , x_2 and x_3 , respectively.

Water-rich phase			Ionic Liquid-rich phase			β_w	β_x	S
x_1	x_2	x_3	x_1	x_2	x_3			
0.9995	0.0000	0.0005	0.2400	0.0000	0.7600	-	-	-
0.9945	0.0049	0.0006	0.2478	0.0178	0.7344	0.21	3.63	14.58
0.9835	0.0160	0.0005	0.2614	0.0414	0.6972	0.16	2.59	9.74
0.9690	0.0303	0.0007	0.3001	0.0700	0.6299	0.17	2.31	7.46
0.9301	0.0685	0.0014	0.3499	0.1200	0.5301	0.16	1.75	4.66
0.9086	0.0909	0.0005	0.4131	0.1697	0.4172	0.21	1.87	4.11
0.9014	0.0964	0.0022	0.4223	0.1756	0.4021	0.22	1.82	3.89
0.9013	0.0961	0.0026	0.4144	0.1713	0.4143	0.22	1.78	3.88
0.9009	0.0961	0.0030	0.4091	0.1777	0.4132	0.22	1.85	4.07
0.8793	0.1172	0.0035	0.4337	0.2048	0.3615	0.25	1.75	3.54
0.8694	0.1275	0.0031	0.4627	0.2267	0.3106	0.29	1.78	3.34
0.8582	0.1373	0.0045	0.4688	0.2247	0.3065	0.28	1.64	3.00
0.8090	0.1840	0.0070	0.5090	0.2370	0.2540	0.28	1.29	2.05

$u(x_i) = 0.01$; $u(T) = 0.5$ K; $u(p) = 2$ kPa.

Table S7. Composition of the experimental tie-line ends, and values of the solute distribution ratios (β_x and β_w calculated from the mole and mass fractions, respectively) and selectivity (S) for the ternary system (water + acetic acid + [C₄mim][NTf₂]) at 293.15 K and at 101 kPa. The mole fractions of water, acetic acid and [C₄mim][NTf₂] are represented by x_1 , x_2 and x_3 , respectively.

Water-rich phase			Ionic Liquid-rich phase			β_w	β_x	S
x_1	x_2	x_3	x_1	x_2	x_3			
0.9996	0.0000	0.0004	0.1735	0.0000	0.8265	-	-	-
0.9984	0.0012	0.0004	0.1764	0.0073	0.8163	0.31	6.08	34.43
0.9813	0.0183	0.0004	0.2096	0.0419	0.7485	0.13	2.29	10.72
0.9635	0.0361	0.0004	0.2209	0.0665	0.7126	0.11	1.84	8.03
0.9539	0.0455	0.0006	0.2476	0.0828	0.6696	0.12	1.82	7.02
0.9290	0.0705	0.0005	0.2802	0.1143	0.6055	0.13	1.62	5.38
0.9085	0.0909	0.0006	0.331	0.1517	0.5173	0.15	1.67	4.58
0.8970	0.1017	0.0013	0.354	0.1801	0.4659	0.18	1.77	4.49
0.8603	0.1376	0.0021	0.4129	0.2217	0.3654	0.22	1.61	3.36
0.8263	0.1707	0.0030	0.4584	0.2472	0.2944	0.25	1.45	2.61

$u(x_i) = 0.01$; $u(T) = 0.5$ K; $u(p) = 2$ kPa.

Table S8. Composition of the experimental tie-line ends, and values of the solute distribution ratios (β_x and β_w calculated from the mole and mass fractions, respectively) and selectivity (S) for the ternary system (water + acetic acid + [C₆mim][NTf₂]) at 293.15 K and at 101 kPa. The mole fractions of water, acetic acid and [C₆mim][NTf₂] are represented by x_1 , x_2 and x_3 , respectively.

Water-rich phase			Ionic Liquid-rich phase			β_w	β_x	S
x_1	x_2	x_3	x_1	x_2	x_3			
0.9998	0.0000	0.0002	0.1968	0.0000	0.8032	-	-	-
0.9941	0.0057	0.0002	0.2129	0.0329	0.7542	0.31	5.77	26.95
0.9753	0.0244	0.0003	0.2410	0.0655	0.6935	0.16	2.68	10.86
0.9706	0.0290	0.0004	0.2513	0.0805	0.6682	0.17	2.78	10.72
0.9453	0.0538	0.0009	0.2607	0.1111	0.6282	0.15	2.07	7.49
0.9392	0.0600	0.0008	0.2743	0.1207	0.6050	0.15	2.01	6.89
0.9193	0.0799	0.0008	0.2978	0.1506	0.5516	0.16	1.88	5.82
0.9090	0.0901	0.0009	0.3350	0.1798	0.4852	0.19	2.00	5.41
0.8993	0.1001	0.0006	0.3538	0.1868	0.4594	0.19	1.87	4.74
0.8882	0.1109	0.0009	0.3629	0.1995	0.4376	0.19	1.80	4.40
0.8713	0.1279	0.0008	0.3855	0.2131	0.4014	0.20	1.67	3.77
0.8444	0.1547	0.0009	0.4200	0.2479	0.3321	0.23	1.60	3.22
0.8401	0.1589	0.0010	0.4401	0.2575	0.3024	0.26	1.62	3.09
0.8268	0.1716	0.0016	0.4460	0.2699	0.2841	0.27	1.57	2.92
0.8157	0.1824	0.0019	0.4579	0.2750	0.2671	0.28	1.51	2.69
0.7806	0.2173	0.0021	0.5102	0.2801	0.2097	0.30	1.29	1.97

$u(x_i) = 0.01$; $u(T) = 0.5$ K; $u(p) = 2$ kPa.

Table S9. Composition of the experimental tie-line ends, and values of the solute distribution ratios (β_x and β_w calculated from the mole and mass fractions, respectively) and selectivity (S) for the ternary system (water + acetic acid + [C₈mim][NTf₂]) at 293.15 K and at 101 kPa. The mole fractions of water, acetic acid and [C₈mim][NTf₂] are represented by x_1 , x_2 and x_3 , respectively.

Water-rich phase			Ionic Liquid-rich phase			β_w	β_x	S
x_1	x_2	x_3	x_1	x_2	x_3			
0.9996	0.0000	0.0004	0.1759	0.0000	0.8241	-	-	-
0.9921	0.0075	0.0004	0.1859	0.0335	0.7806	0.22	4.47	23.84
0.9872	0.0124	0.0004	0.1913	0.0432	0.7655	0.18	3.48	17.98
0.9715	0.0281	0.0004	0.2247	0.0964	0.6789	0.20	3.43	14.83
0.9543	0.0453	0.0004	0.2587	0.1456	0.5957	0.22	3.21	11.86
0.9194	0.0797	0.0009	0.3341	0.2153	0.4506	0.25	2.70	7.43
0.8619	0.1375	0.0006	0.3914	0.2637	0.3449	0.25	1.92	4.22
0.8525	0.1470	0.0005	0.3940	0.2643	0.3417	0.24	1.80	3.89
0.8490	0.1501	0.0009	0.3973	0.2691	0.3336	0.24	1.79	3.83
0.8051	0.1932	0.0017	0.4573	0.2951	0.2476	0.29	1.53	2.69

$u(x_i) = 0.01$; $u(T) = 0.5$ K; $u(p) = 2$ kPa.

Table S10. Composition of the experimental tie-line ends, and values of the solute distribution ratios (β_x and β_w calculated from the mole and mass fractions, respectively) and selectivity (S) for the ternary system (water + acetic acid + [C₁₀mim][NTf₂]) at 293.15 K and at 101 kPa. The mole fractions of water, acetic acid and [C₁₀mim][NTf₂] are represented by x_1 , x_2 and x_3 , respectively.

Water-rich phase			Ionic Liquid-rich phase			β_w	β_x	S
x_1	x_2	x_3	x_1	x_2	x_3			
0.9998	0.0000	0.0002	0.1526	0.0000	0.8474	-	-	-
0.9934	0.0064	0.0002	0.1592	0.0353	0.8055	0.25	5.52	34.42
0.9823	0.0175	0.0002	0.1976	0.0872	0.7152	0.25	4.98	24.77
0.9622	0.0375	0.0003	0.2115	0.1017	0.6868	0.15	2.71	12.34
0.9004	0.0993	0.0003	0.2367	0.1825	0.5808	0.13	1.84	6.99
0.8567	0.1430	0.0003	0.3001	0.2414	0.4585	0.16	1.69	4.82
0.8177	0.1820	0.0003	0.3718	0.2917	0.3365	0.21	1.60	3.52
0.7979	0.2018	0.0003	0.3953	0.3063	0.2984	0.23	1.52	3.06
0.7345	0.2652	0.0003	0.4502	0.3209	0.2289	0.25	1.21	1.97

$$u(x_i) = 0.01; u(T) = 0.5 \text{ K}; u(p) = 2 \text{ kPa}.$$

Table S11. Composition of the experimental tie-line ends, and values of the solute distribution ratios (β_x and β_w calculated from the mole and mass fractions, respectively) and selectivity (S) for the ternary system (water + acetic acid + [C₄mpyrr][NTf₂]) at 293.15 K and at 101 kPa. The mole fractions of water, acetic acid and [C₄mpyrr][NTf₂] are represented by x_1 , x_2 and x_3 , respectively.

Water-rich phase			Ionic Liquid-rich phase			β_w	β_x	S
x_1	x_2	x_3	x_1	x_2	x_3			
1.0000	0.0000	0.0000	0.2194	0.0000	0.7806	-	-	-
0.9767	0.0233	0.0000	0.1681	0.0609	0.7710	0.15	2.61	15.19
0.9638	0.0362	0.0000	0.1760	0.0810	0.7430	0.14	2.24	12.25
0.9396	0.0604	0.0000	0.2028	0.1248	0.6724	0.14	2.07	9.57
0.9226	0.0771	0.0003	0.2685	0.1500	0.5815	0.16	1.95	6.69
0.9081	0.0916	0.0003	0.2996	0.1650	0.5354	0.16	1.80	5.46
0.8927	0.1066	0.0007	0.3011	0.1948	0.5041	0.18	1.83	5.42
0.8542	0.1444	0.0014	0.3584	0.2350	0.4066	0.21	1.63	3.88
0.8193	0.1777	0.0030	0.3724	0.2769	0.3507	0.24	1.56	3.43

$u(x_i) = 0.01$; $u(T) = 0.5$ K; $u(p) = 2$ kPa.

Table S12. Composition of the experimental tie-line ends, and values of the solute distribution ratios (β_x and β_w calculated from the mole and mass fractions, respectively) and selectivity (S) for the ternary system (water + acetic acid + [N₁₁₁₄][NTf₂]) at 293.15 K and at 101 kPa. The mole fractions of water, acetic acid and [N₁₁₁₄][NTf₂] are represented by x_1 , x_2 and x_3 , respectively.

Water-rich phase			Ionic Liquid-rich phase			β_w	β_x	S
x_1	x_2	x_3	x_1	x_2	x_3			
1.000	0.000	0.000	0.230	0.000	0.770	-	-	-
0.989	0.011	0.000	0.283	0.042	0.675	0.26	3.82	13.34
0.978	0.022	0.000	0.296	0.046	0.658	0.15	2.09	6.91
0.969	0.031	0.000	0.296	0.061	0.643	0.14	1.97	6.44
0.957	0.043	0.000	0.319	0.078	0.603	0.14	1.81	5.44
0.954	0.046	0.000	0.317	0.085	0.598	0.15	1.85	5.56
0.951	0.049	0.000	0.344	0.092	0.564	0.16	1.88	5.19
0.911	0.089	0.000	0.403	0.145	0.452	0.18	1.63	3.68
0.875	0.125	0.000	0.451	0.199	0.350	0.23	1.59	3.09
0.824	0.176	0.000	0.526	0.245	0.229	0.31	1.39	2.18

$u(x_i) = 0.01$; $u(T) = 0.5$ K; $u(p) = 2$ kPa.

Table S13. Relative deviation between experimental water solubility in IL data reported herein with published data expressed in water mole fraction in IL, x_1 at 101 kPa.

IL	This work ^a	x_1	Relative Deviation (%)
		Literature data	
[P ₆₆₆₁₄][Cl]	0.8261	0.814 ^b [3]	1.49
		0.818 ^c [4]	0.99
		0.829 ^c [5]	-0.35
		0.824 ^c [6]	0.25
[P ₆₆₆₁₄][NTf ₂]	0.1206	0.081 ^b [3]	48.9
		0.088 ^c [4]	37.1
		0.230 ^c [6]	-47.6
[C ₂ mim][NTf ₂]	0.2954	0.2357 ^b [7]	25.3
		0.2869 ^b [8]	2.96
		0.31 ^d [9]	-4.71
		0.2970 ^e [10]	-0.54
		0.3050 ^d [11]	-3.15
[C ₄ mim][NTf ₂]	0.2400	0.2484 ^b [7]	-3.38
		0.2443 ^b [8]	-1.76
		0.27 ^d [9]	-11.1
		0.2431 ^f [10]	-1.28
		0.3210 ^d [11]	-25.2
		0.2931 ^b [12]	-18.1
[C ₄ mmim][NTf ₂]	0.1735	-	
[C ₆ mim][NTf ₂]	0.1968	0.1978 ^b [8]	-0.51
		0.2703 ^b [12]	-27.2
		0.2117 ^g [13]	-7.04
[C ₈ mim][NTf ₂]	0.1759	0.1781 ^b [8]	-1.24
		0.2411 ^b [12]	-27.0
		0.1951 ^g [13]	-9.84
[C ₁₀ mim][NTf ₂]	0.1526	-	
[C ₄ mpyrr][NTf ₂]	0.2194	0.2260 ^h [10]	-2.92
		0.199 ^b [14]	10.3
[N ₁₁₁₄][NTf ₂]	0.2300	0.2043 ⁱ [10]	12.6
		0.2420 ^d [11]	-4.96

^a This work at 293.15 K: $u(x_i) = 0.01$; $u(T) = 0.5$ K; $u(p) = 2$ kPa. ^b at 293.15 K. ^c at 298.15 K. ^d at room temperature. ^e at 292.62 K. ^f at 290.13 K. ^g at 296.65 K. ^h at 290.35 K. ⁱ at 289.15 K.

Figure S1. $^1\text{H-NMR}$ of $[\text{C}_2\text{mim}][\text{NTf}_2]$ in $\text{d}_6\text{-DMSO}$.

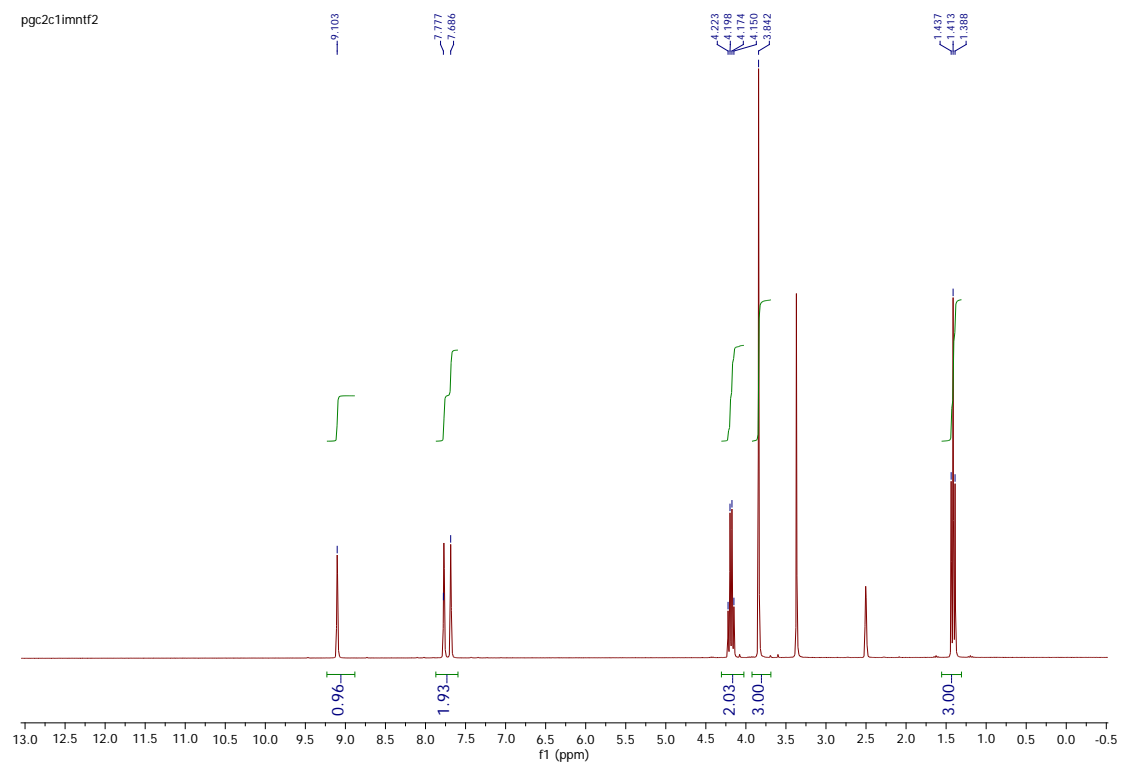


Figure S2. $^1\text{H-NMR}$ of $[\text{C}_4\text{mim}][\text{NTf}_2]$ in $\text{d}_6\text{-DMSO}$.

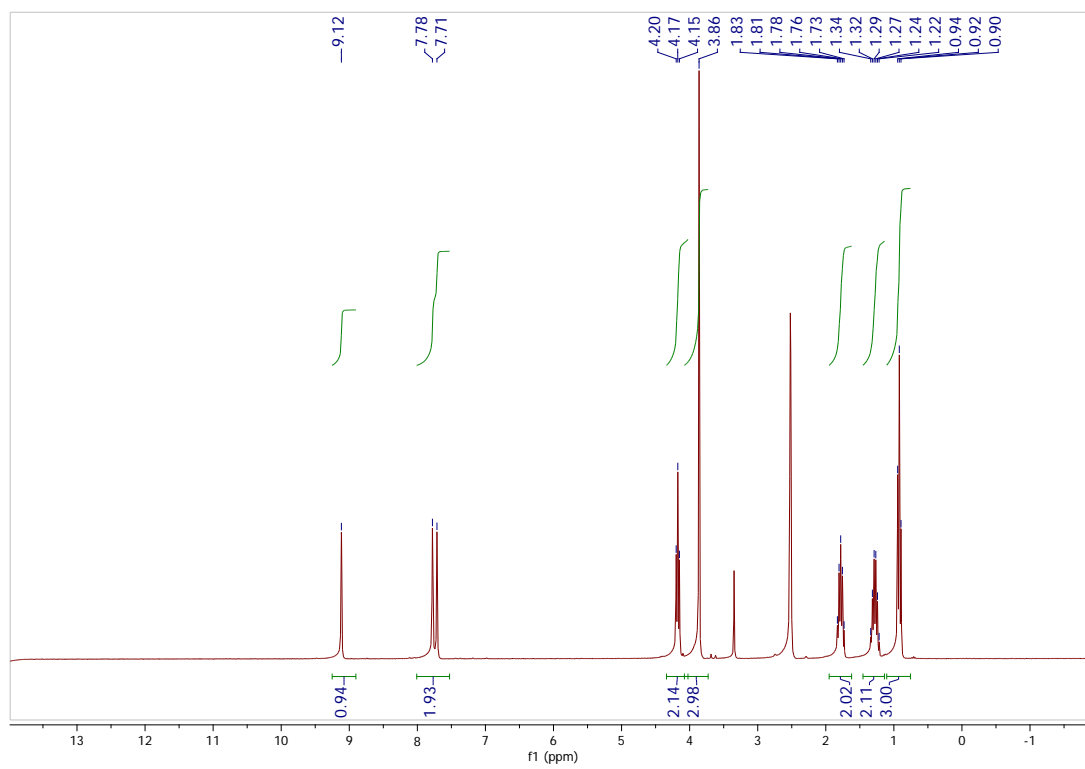


Figure S3. $^1\text{H-NMR}$ of $[\text{C}_4\text{mmim}][\text{NTf}_2]$ in $\text{d}_6\text{-DMSO}$.

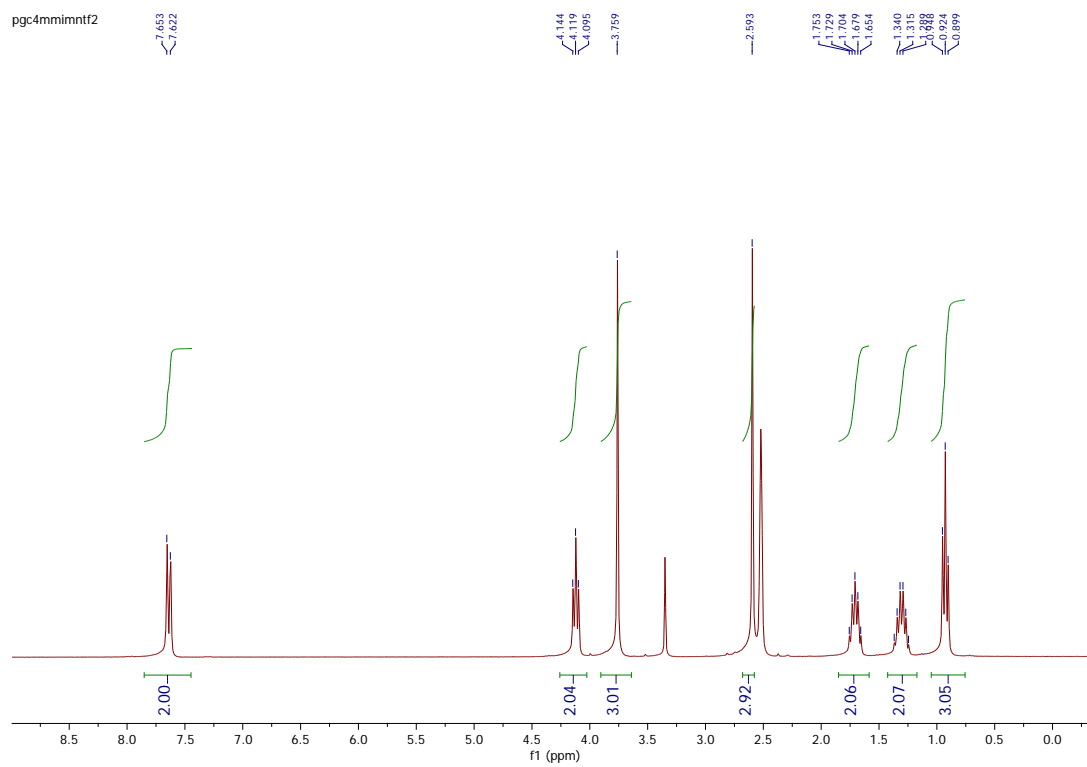


Figure S4. $^1\text{H-NMR}$ of $[\text{C}_6\text{mim}][\text{NTf}_2]$ in $\text{d}_6\text{-DMSO}$.

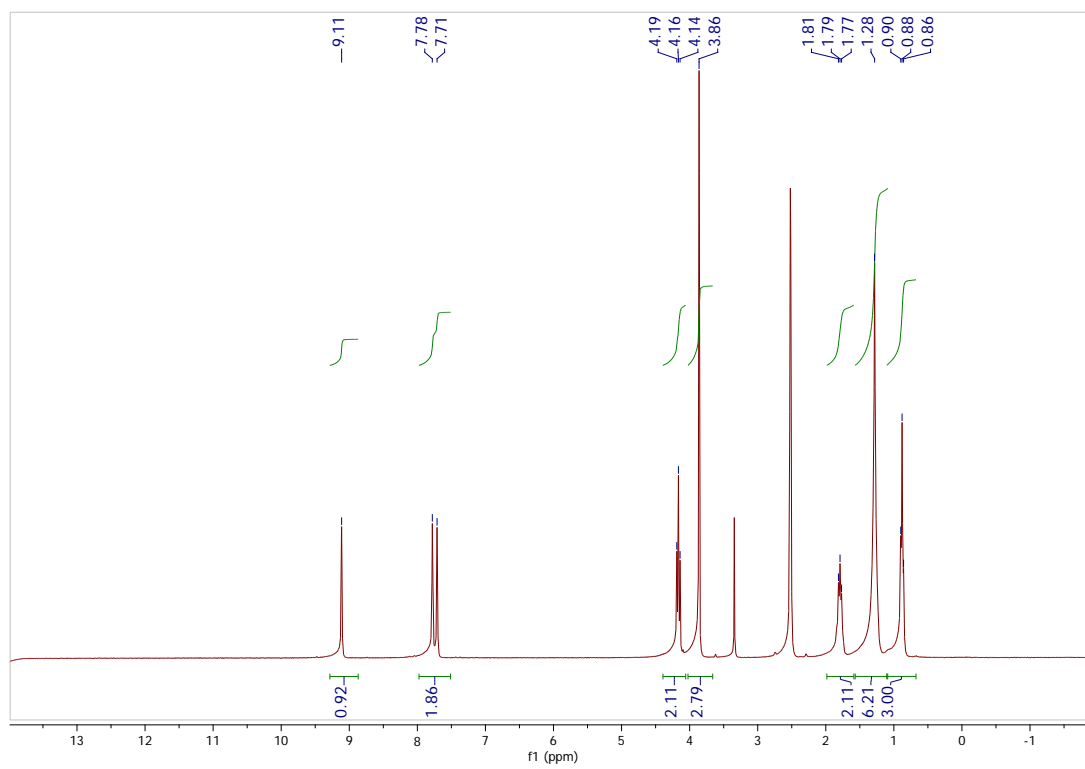


Figure S5. $^1\text{H-NMR}$ of $[\text{C}_8\text{mim}][\text{NTf}_2]$ in CDCl_3 .

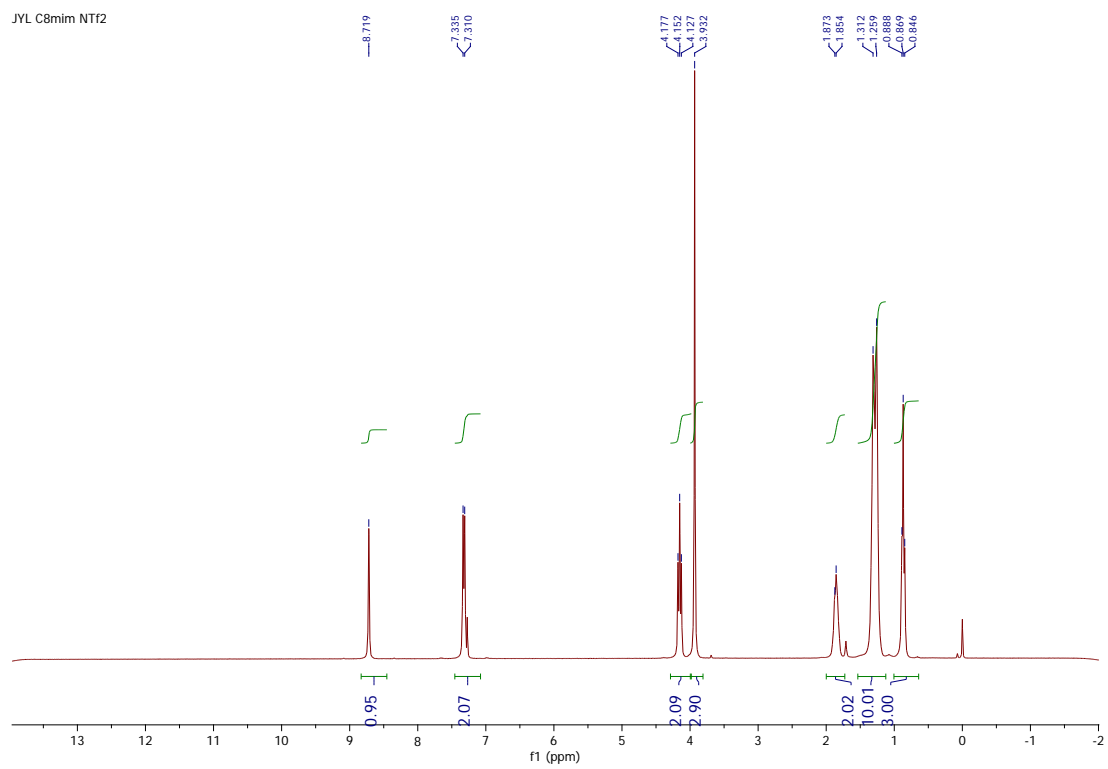


Figure S6. $^1\text{H-NMR}$ of $[\text{C}_{10}\text{mim}][\text{NTf}_2]$ in CDCl_3 .

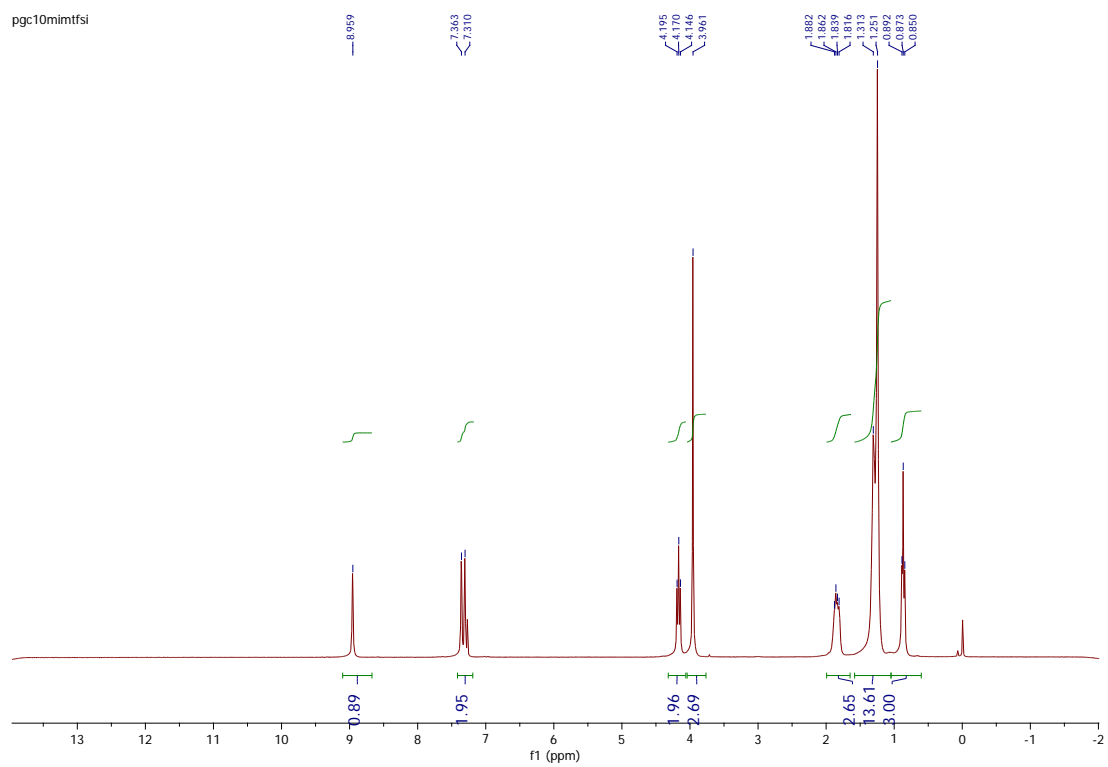


Figure S7. $^1\text{H-NMR}$ of $[\text{C}_4\text{mpyrr}][\text{NTf}_2]$ in $\text{d}_6\text{-DMSO}$.

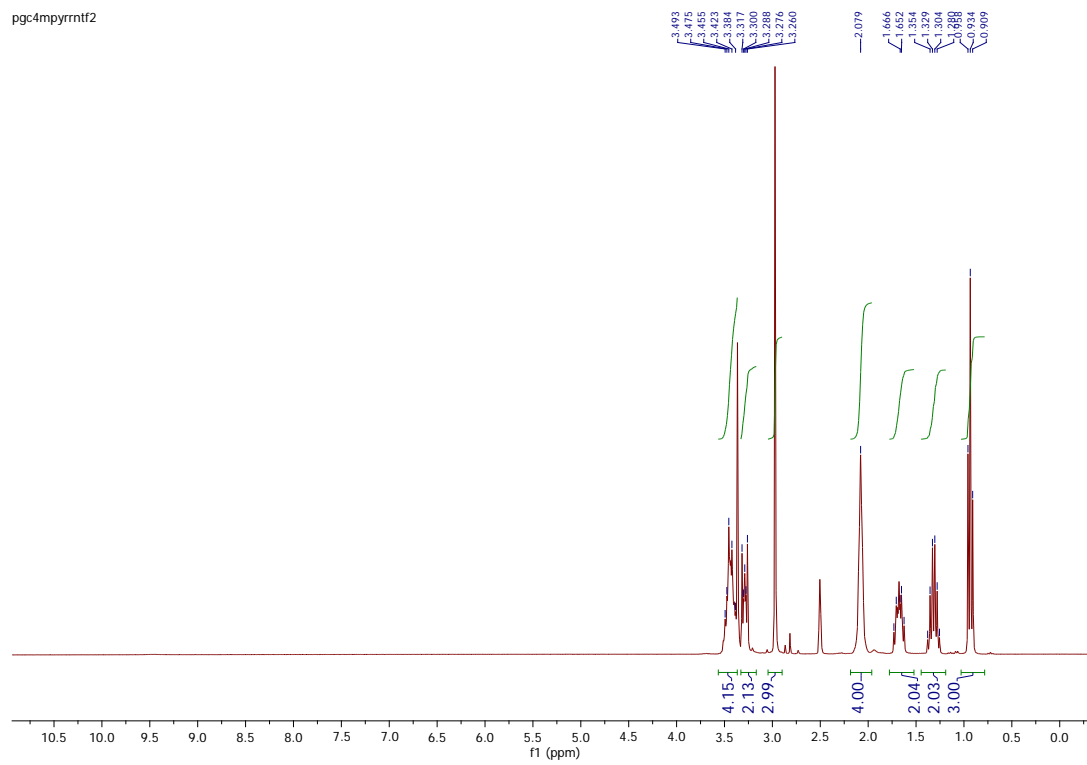


Figure S8. $^1\text{H-NMR}$ of $[\text{N}_{1114}][\text{NTf}_2]$ in $\text{d}_6\text{-DMSO}$.

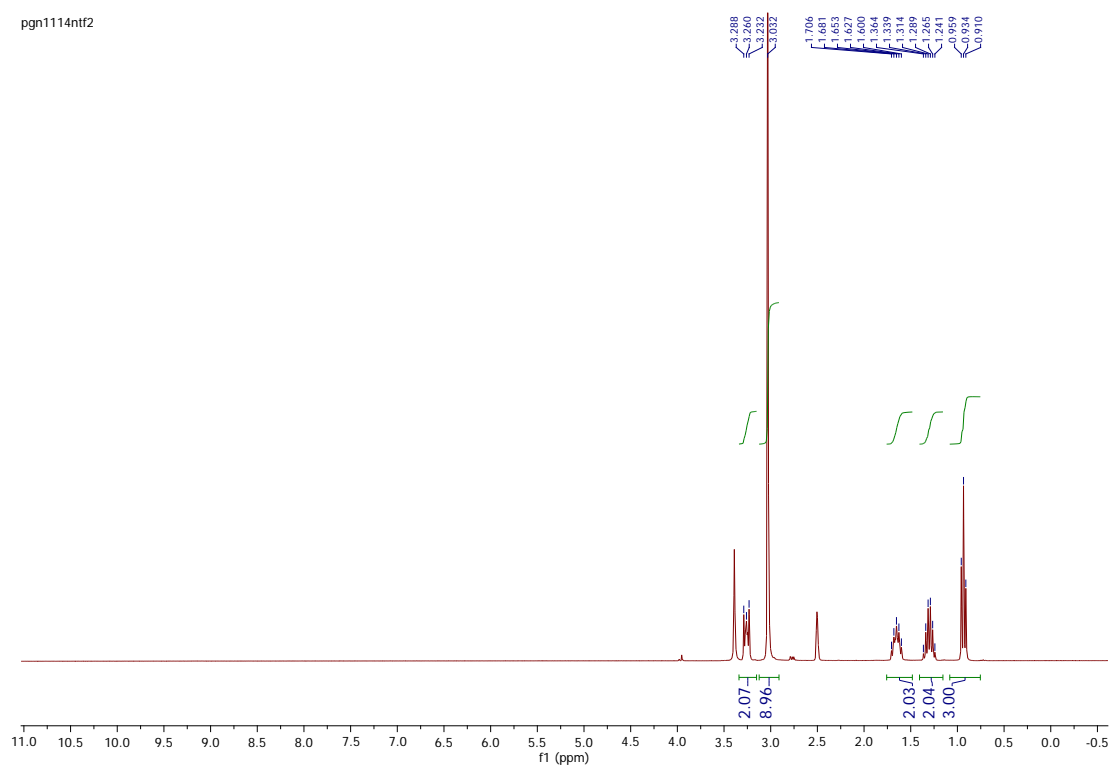


Figure S9. $^1\text{H-NMR}$ of $[\text{P}_{66614}][\text{NTf}_2]$ in CDCl_3 .

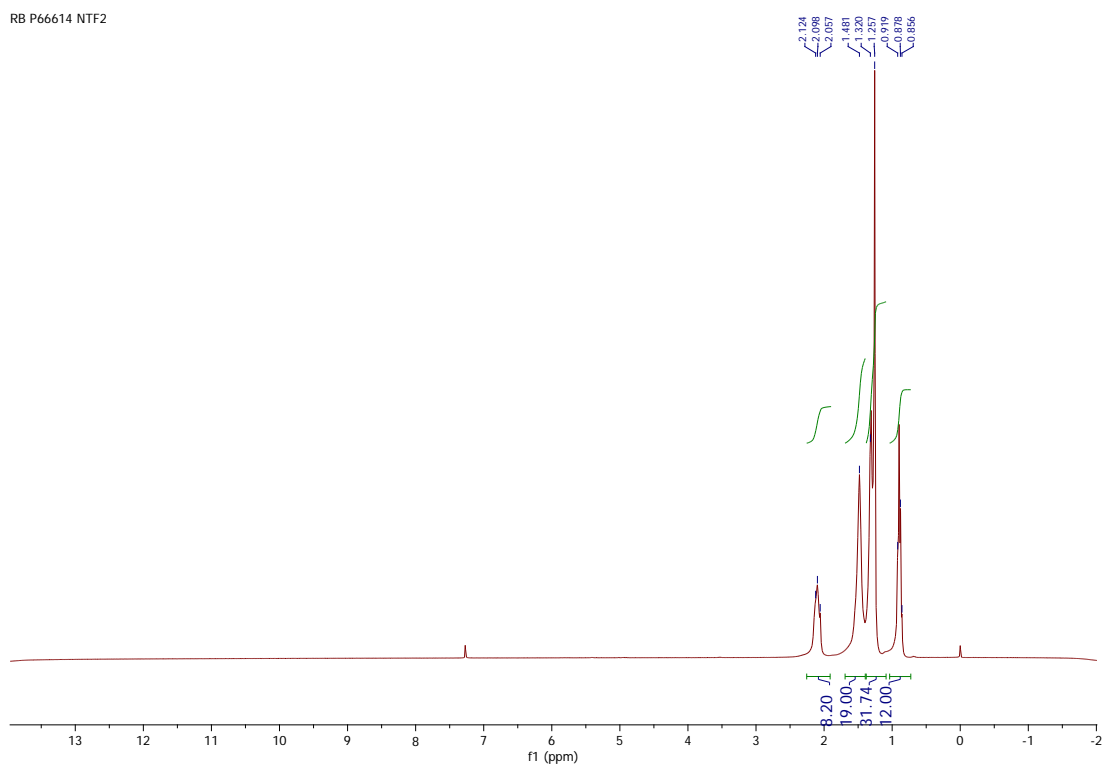


Figure S10. Equilibrium diagram of the ternary system (water + acetic acid + IL) at 293.15 K and at 101 kPa: ●, [P_{666,14}]Cl; □, [P_{666,14}][NTf₂].

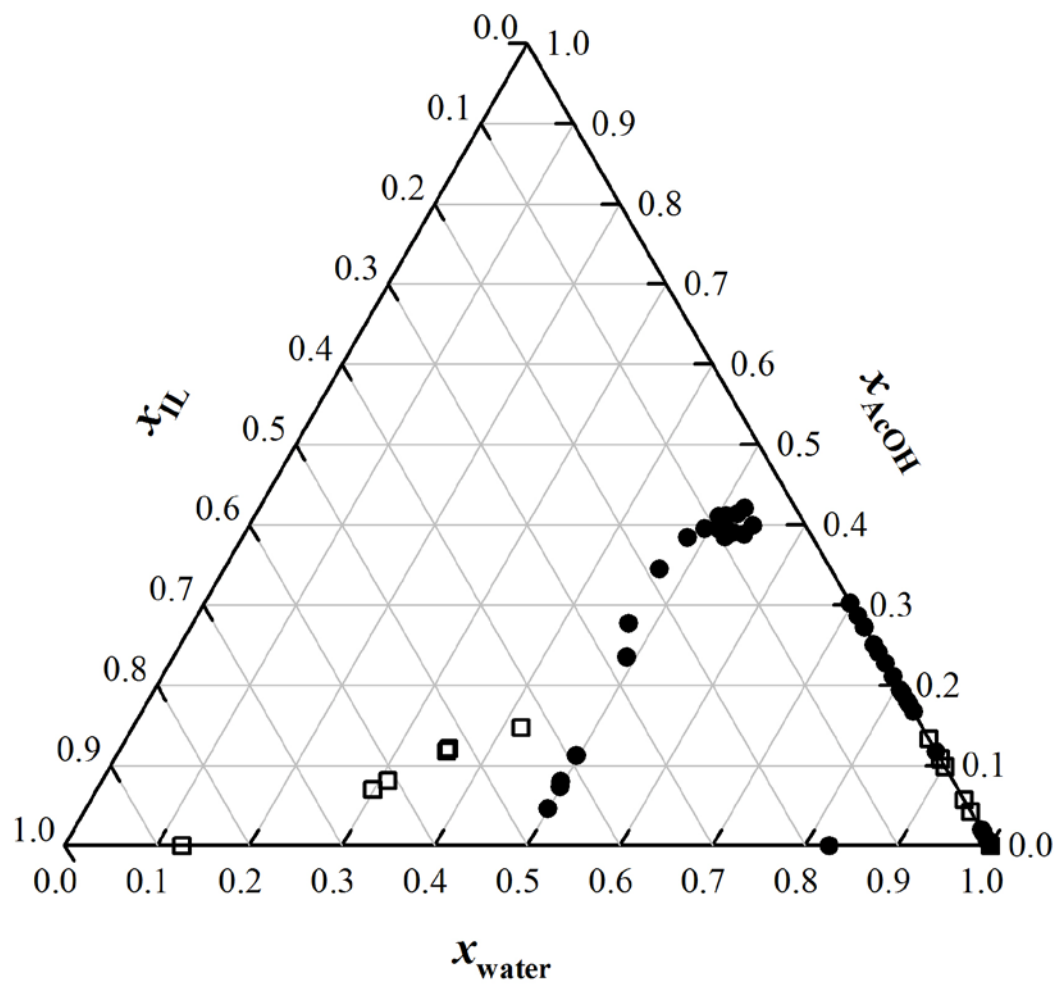


Figure S11. Equilibrium diagram of the ternary system (water + acetic acid + $[C_n\text{mim}][\text{NTf}_2]$) at 293.15 K and at 101 kPa: \diamond , $n = 2$; \bullet , $n = 4$; \triangle , $n = 6$; \blacksquare , $n = 8$; ∇ , $n = 10$.

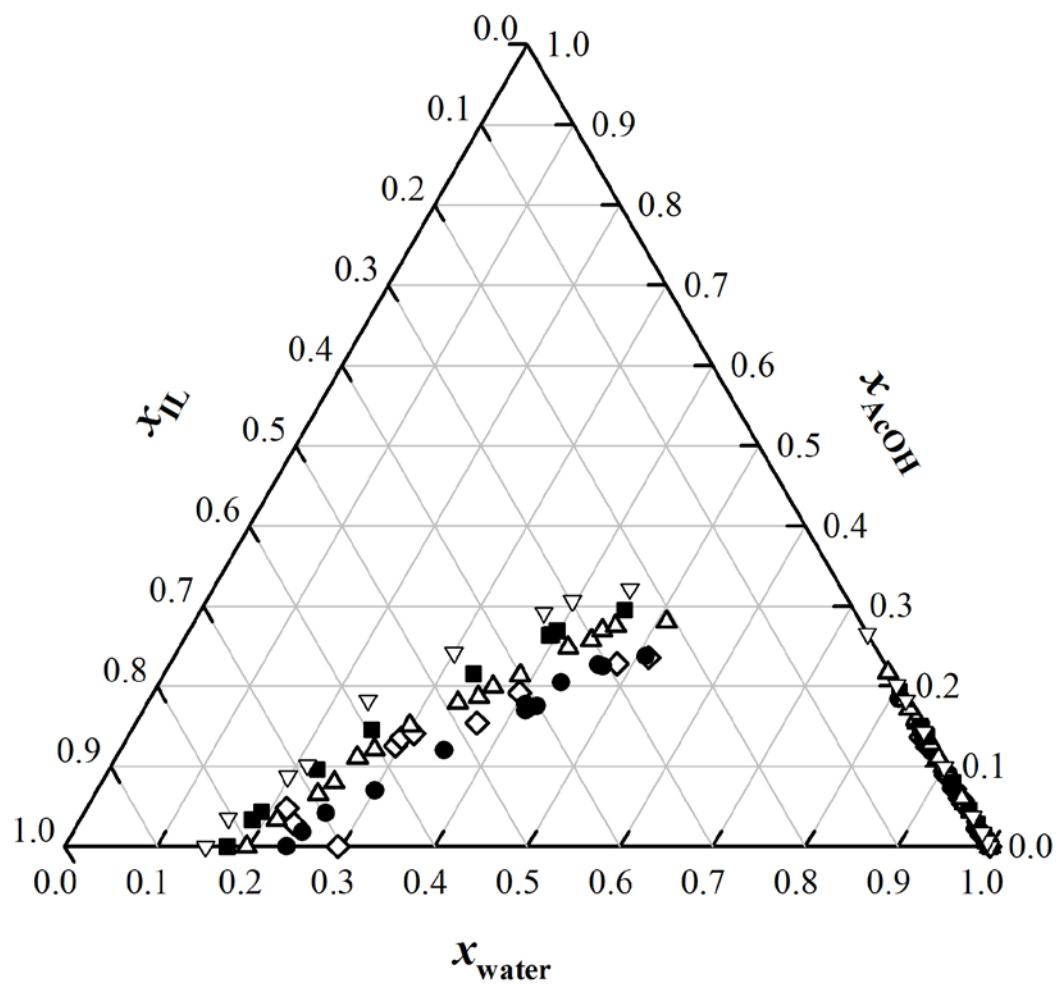


Figure S12. Equilibrium diagram of the ternary system (water + acetic acid + MTBE) at 101 kPa and at: a, 293.15 K; b, 313.15 K; (● and solid lines), experimental data; (○ and dashed lines), predicted using UNIQUAC model with parameters from Miao *et al.*¹⁵

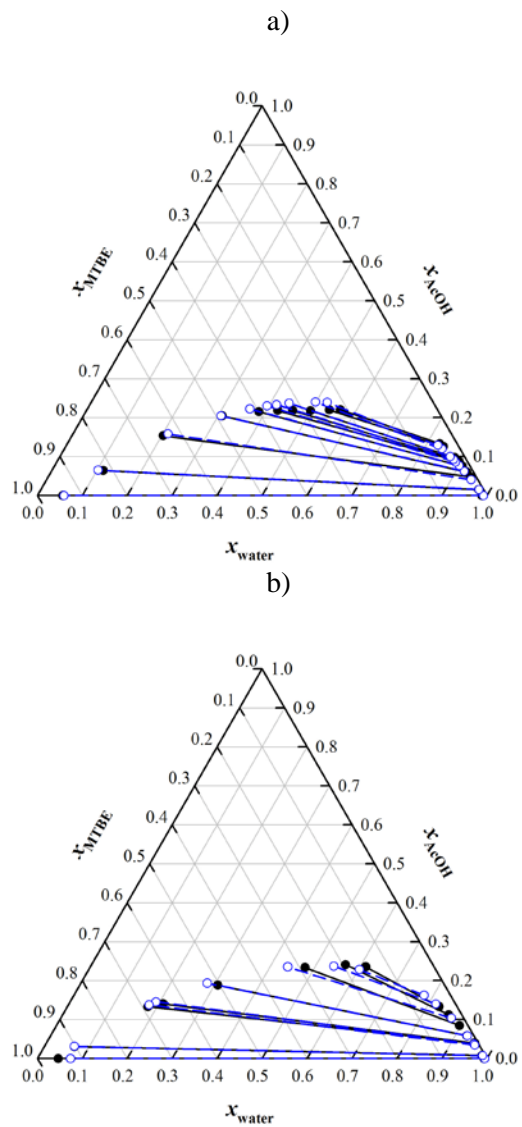


Figure S13. Equilibrium diagram of the ternary system (water + acetic acid + MIBK) at 293.15 K and at 101 kPa: (● and solid lines), experimental data; (○ and dashed lines), correlated using UNIQUAC model.

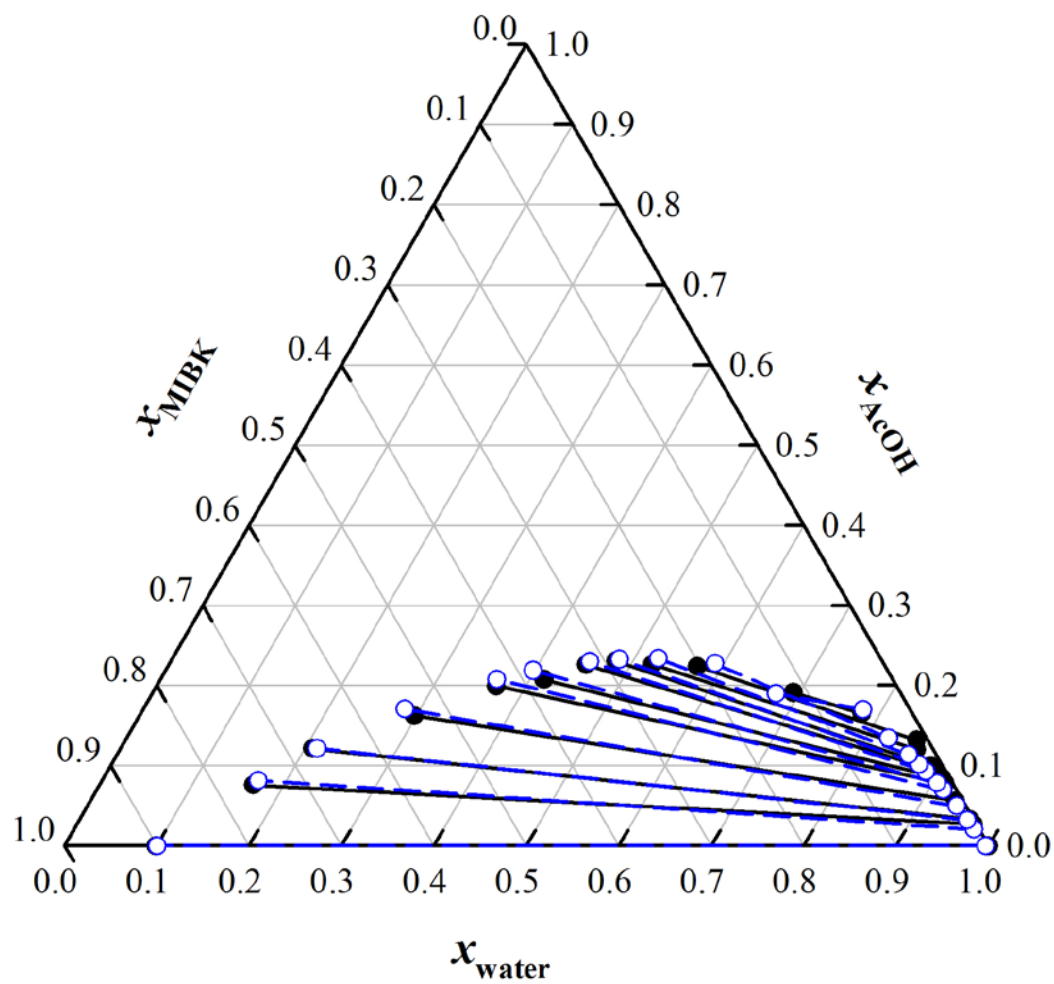


Figure S14. Equilibrium diagram of the ternary system (water + acetic acid + $[P_{666,14}]Cl$) at 293.15 K and at 101 kPa: (● and solid lines), experimental data; (○ and dashed lines), correlated using UNIQUAC model.

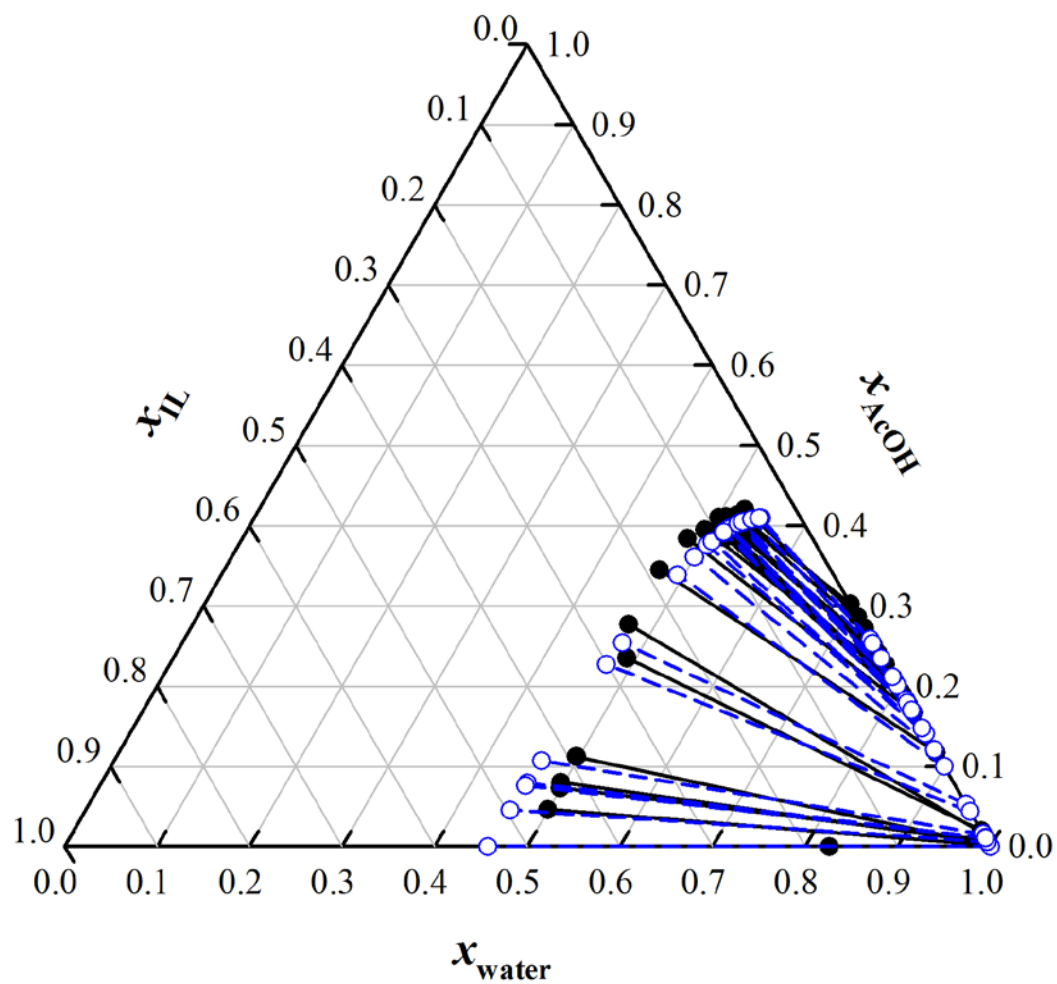


Figure S15. Equilibrium diagram of the ternary system (water + acetic acid + [P_{666,14}][NTf₂]) at 293.15 K and at 101 kPa: (● and solid lines), experimental data; (○ and dashed lines), correlated using UNIQUAC model.

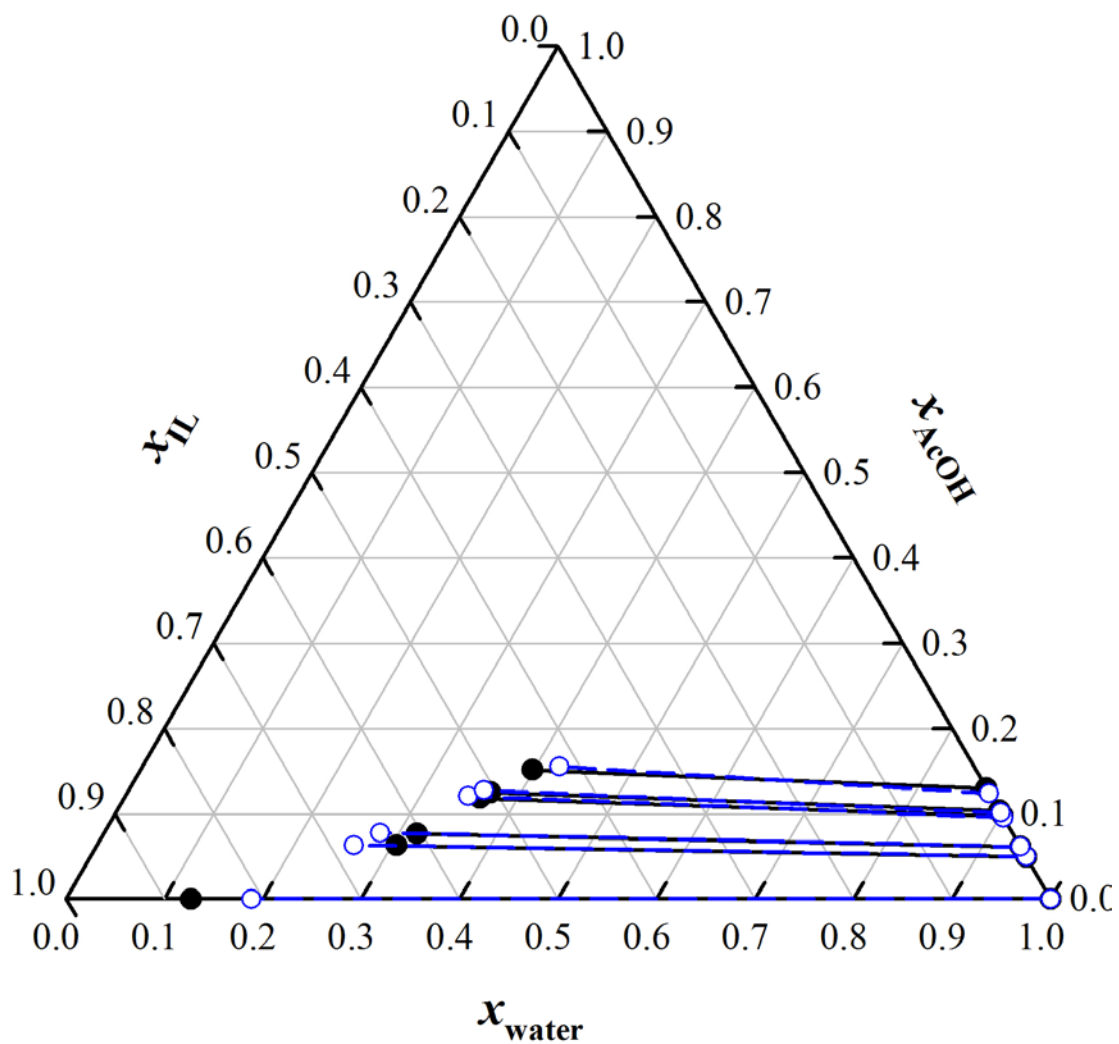


Figure S16. Equilibrium diagram of the ternary system (water + acetic acid + [C₂mim][NTf₂]) at 293.15 K and at 101 kPa: (● and solid lines), experimental data; (○ and dashed lines), correlated using UNIQUAC model.

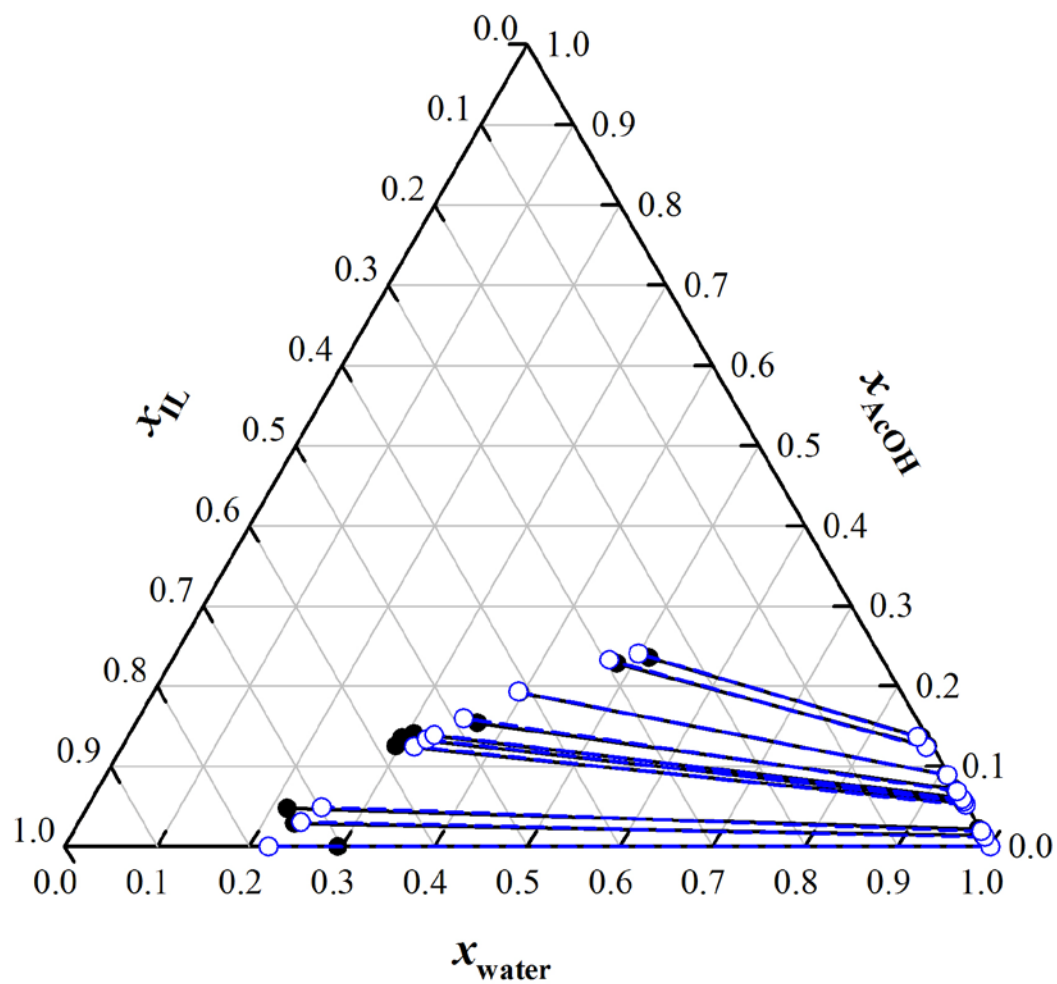


Figure S17. Equilibrium diagram of the ternary system (water + acetic acid + [C₄mim][NTf₂]) at 293.15 K and at 101 kPa: (● and solid lines), experimental data; (○ and dashed lines), correlated using UNIQUAC model.

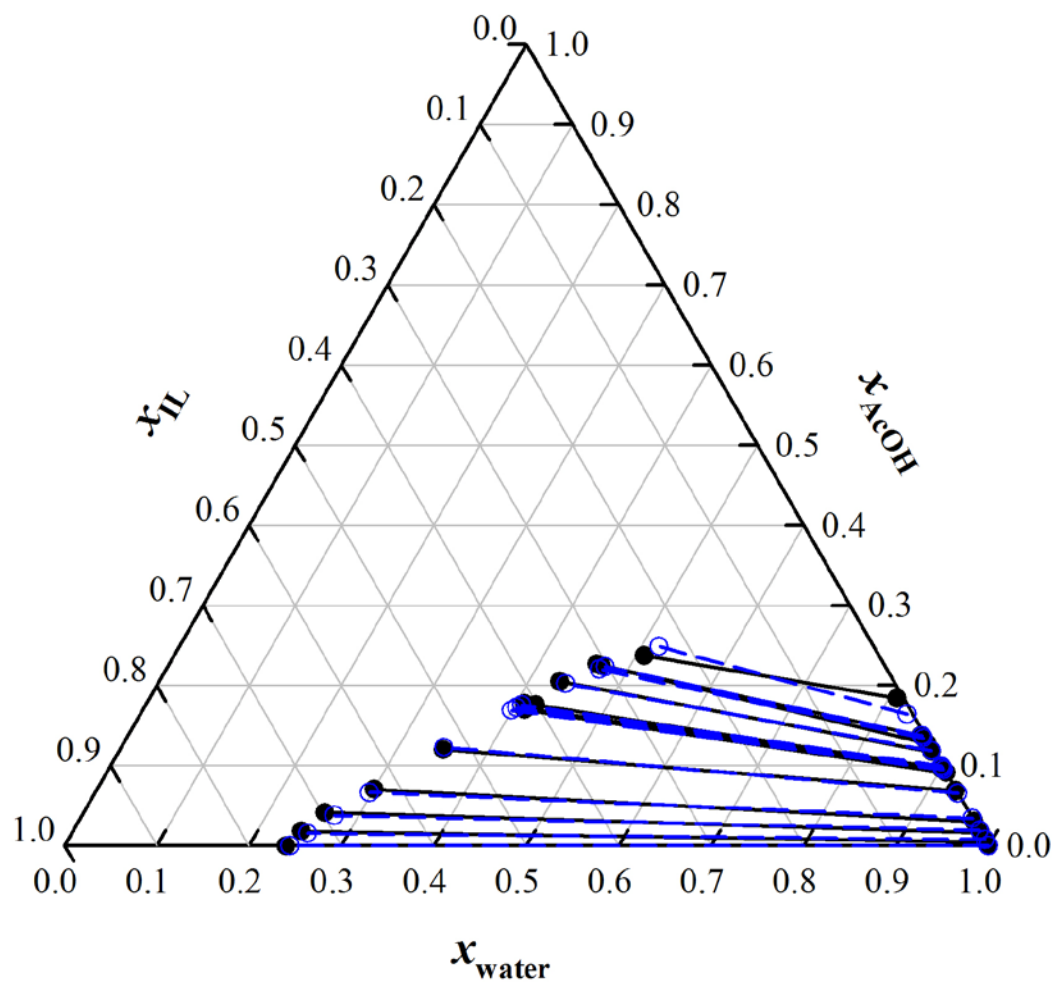


Figure S18. Equilibrium diagram of the ternary system (water + acetic acid + [C₄mim][NTf₂]) at 293.15 K and at 101 kPa: (● and solid lines), experimental data; (○ and dashed lines), correlated using UNIQUAC model.

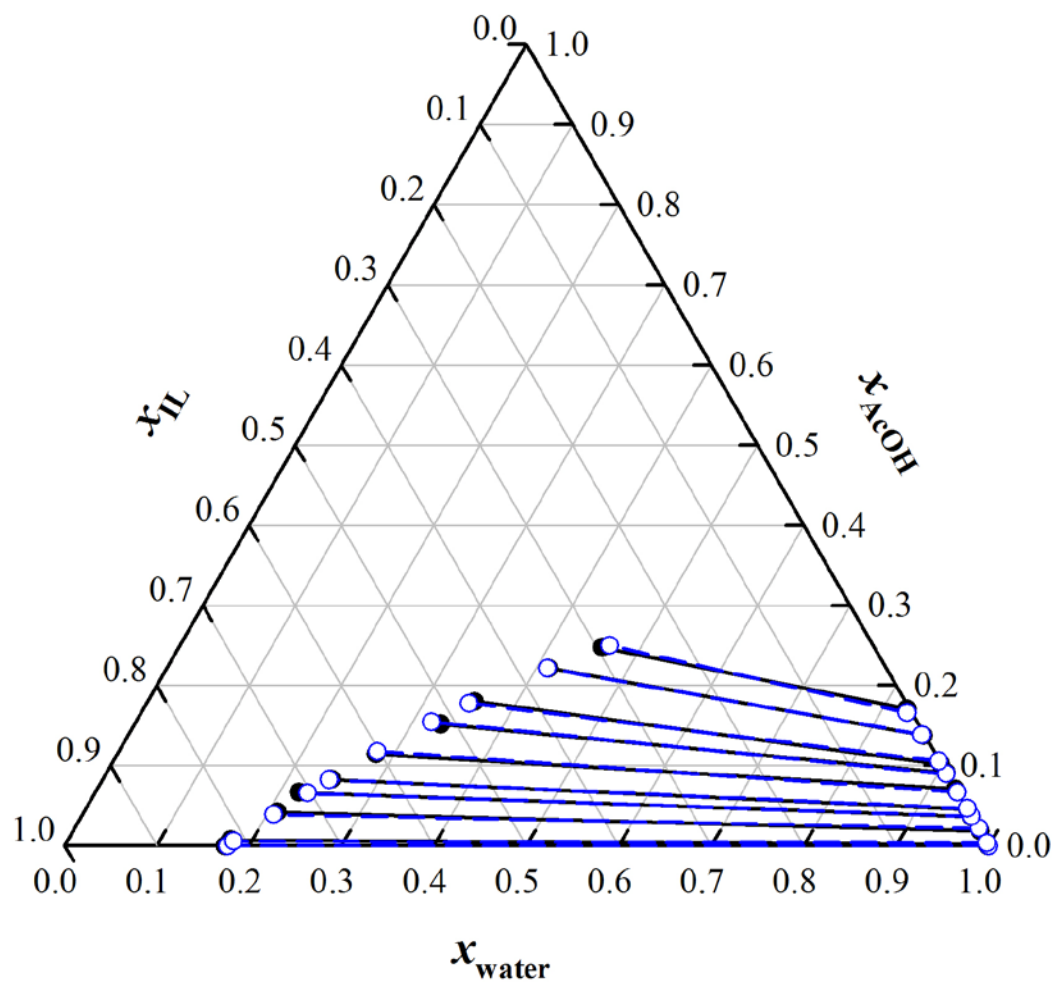


Figure S19. Equilibrium diagram of the ternary system (water + acetic acid + [C₆mim][NTf₂]) at 293.15 K and at 101 kPa: (● and solid lines), experimental data; (○ and dashed lines), correlated using UNIQUAC model.

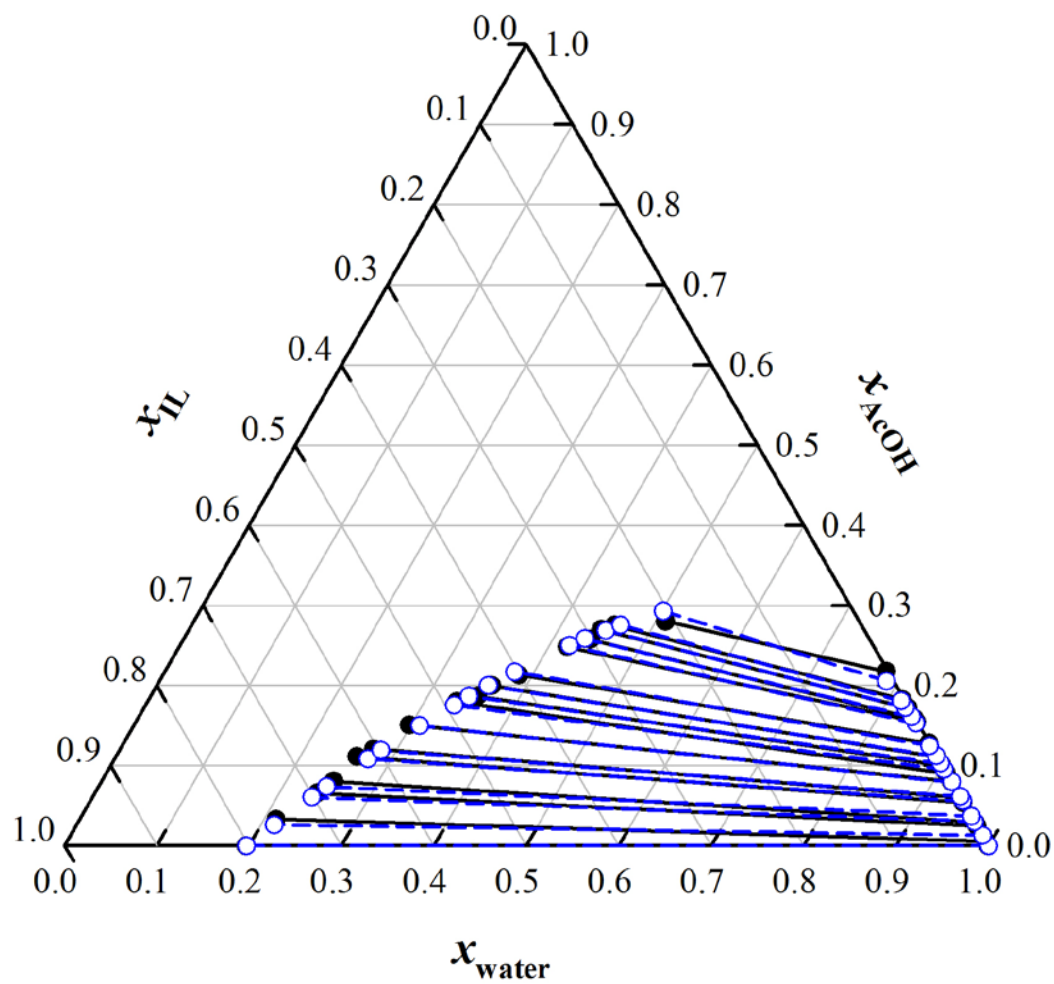


Figure S20. Equilibrium diagram of the ternary system (water + acetic acid + [C₈mim][NTf₂]) at 293.15 K and at 101 kPa: (● and solid lines), experimental data; (○ and dashed lines), correlated using UNIQUAC model.

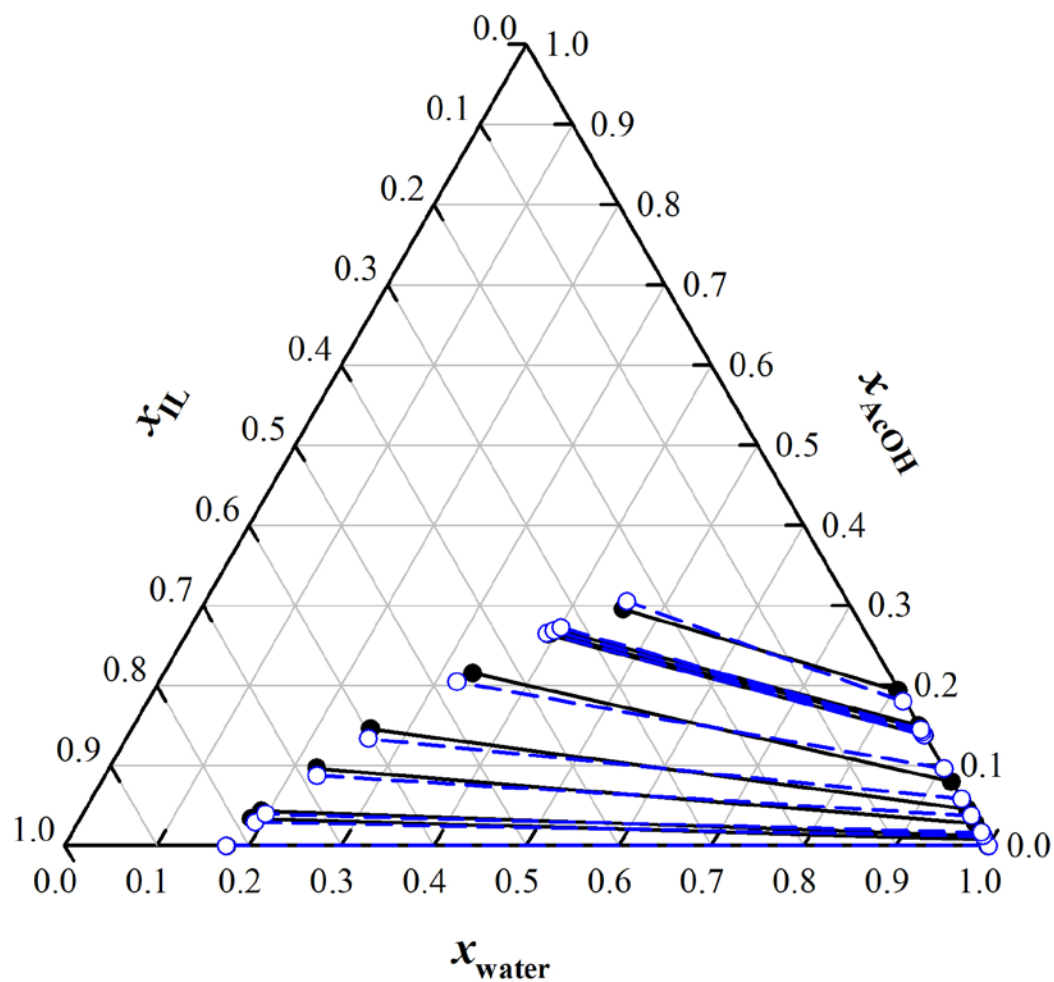


Figure S21. Equilibrium diagram of the ternary system (water + acetic acid + [C₁₀mim][NTf₂]) at 293.15 K and at 101 kPa: (● and solid lines), experimental data; (○ and dashed lines), correlated using UNIQUAC model.

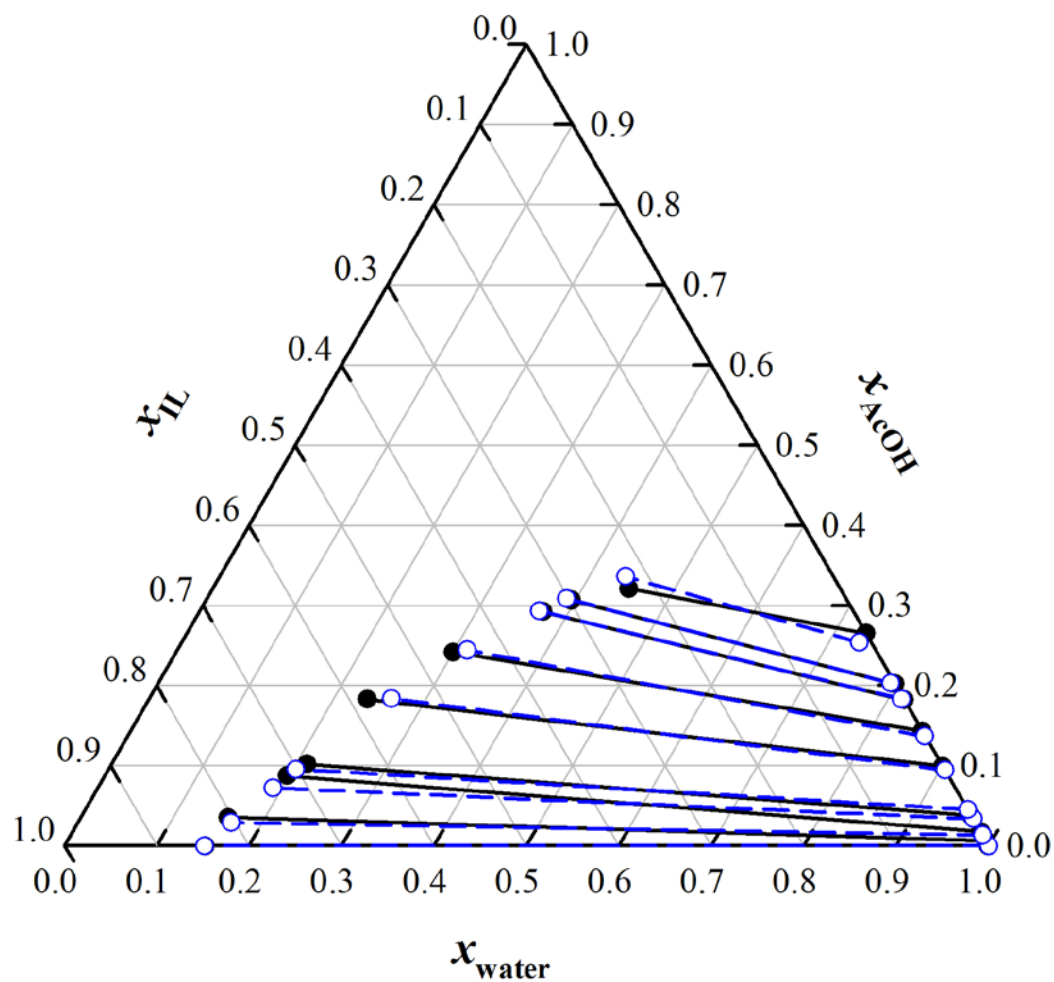


Figure S22. Equilibrium diagram of the ternary system (water + acetic acid + [C₄mpyrr][NTf₂]) at 293.15 K and at 101 kPa: (● and solid lines), experimental data; (○ and dashed lines), correlated using UNIQUAC model.

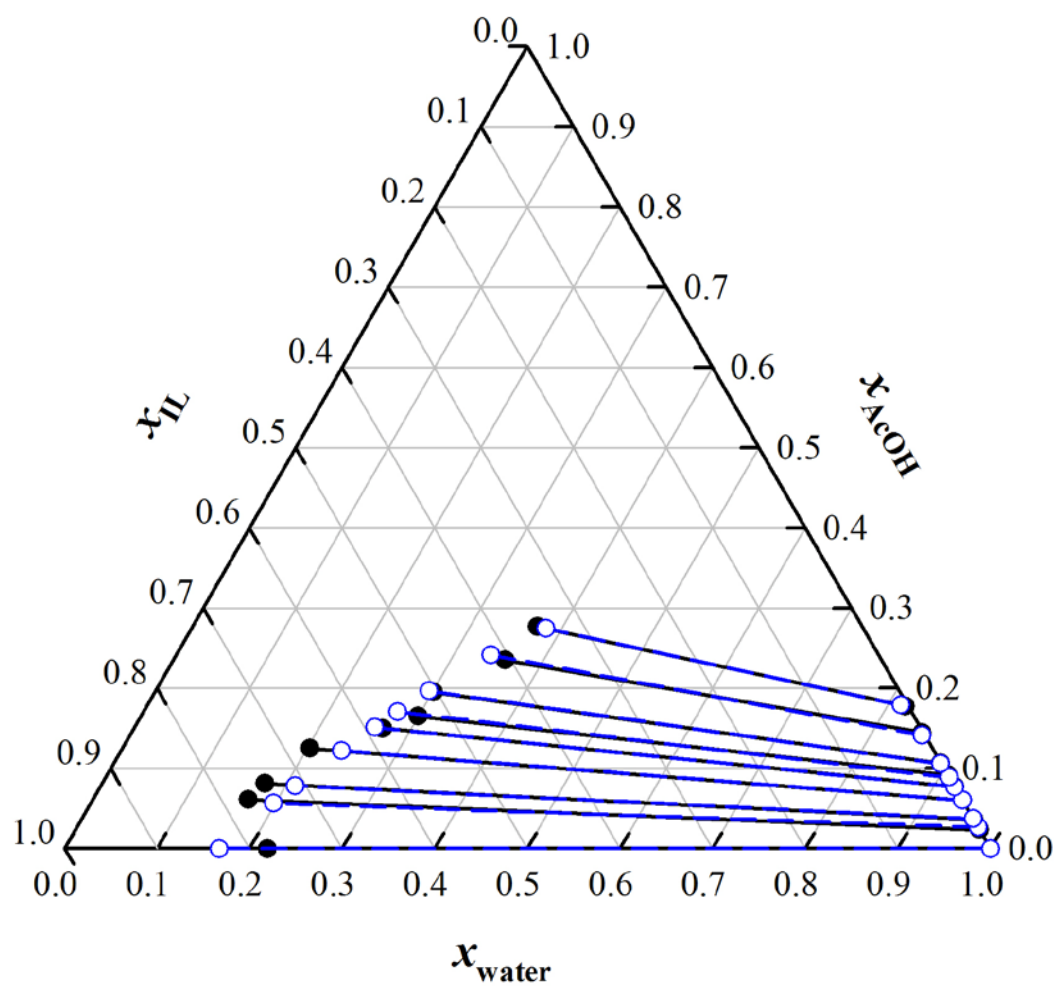


Figure S23. Equilibrium diagram of the ternary system (water + acetic acid + $[N_{1114}][NTf_2]$) at 293.15 K and at 101 kPa: (● and solid lines), experimental data; (○ and dashed lines), correlated using UNIQUAC model.

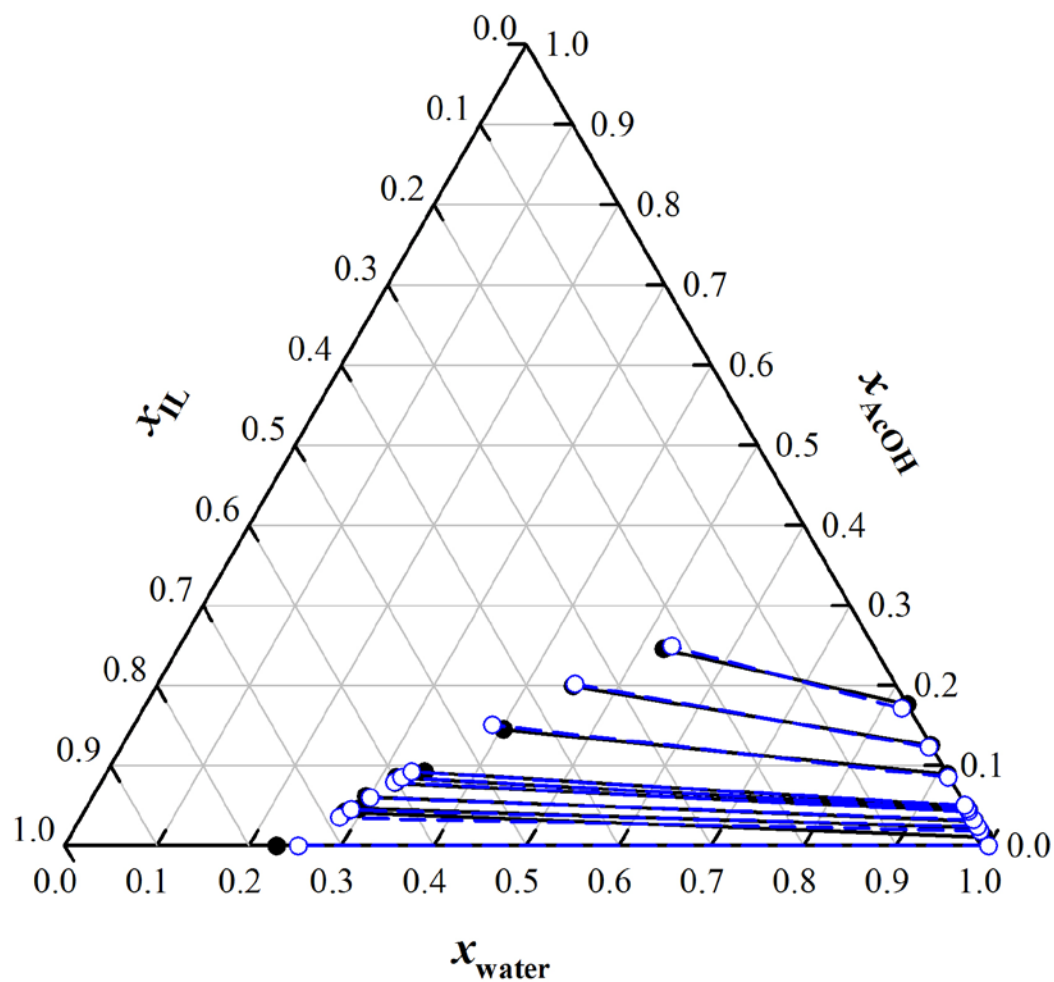
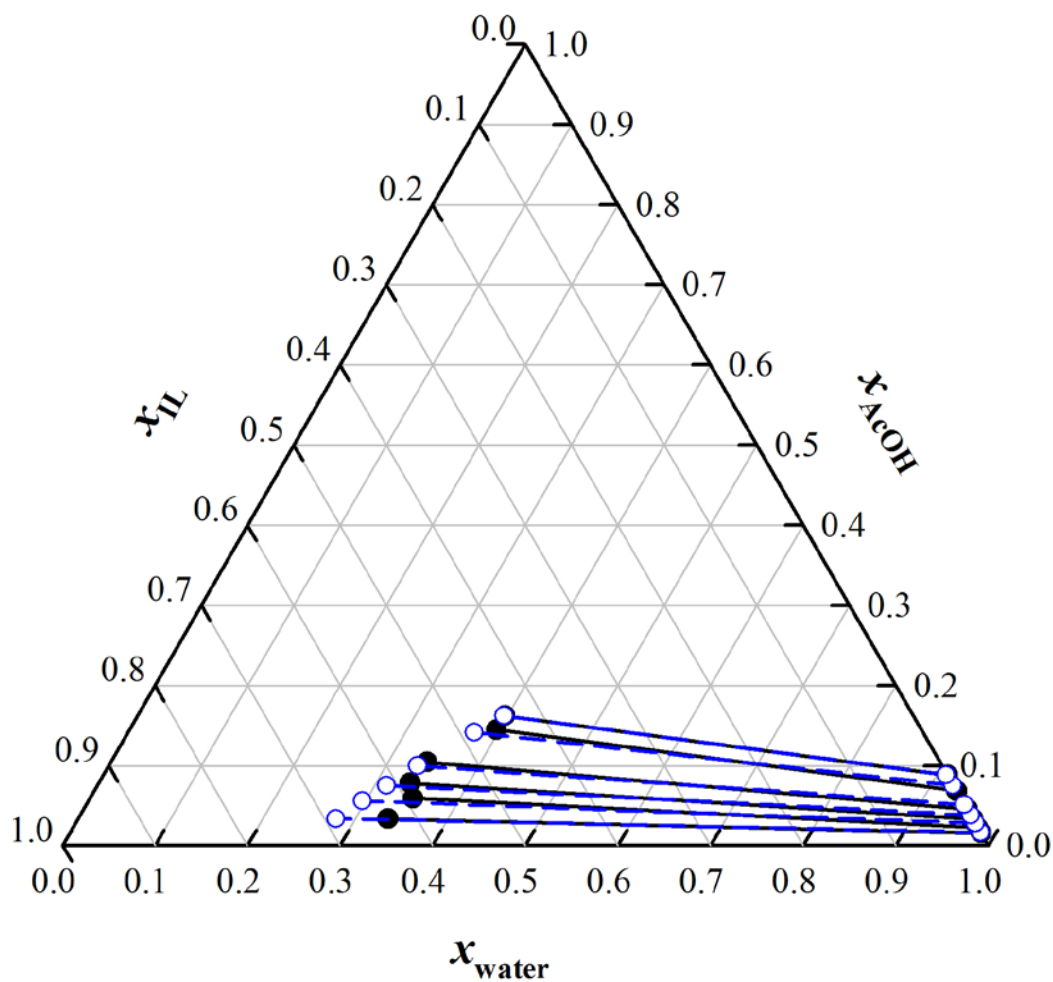


Figure S24. Equilibrium diagram of the ternary system (water + acetic acid + [C₄mim][NTf₂]) at 298.15 K and at 101 kPa: (● and solid lines), experimental data from Bharti and Banerjee;¹⁶ (○ and dashed lines), predicted using UNIQUAC model with parameters reported during this work.



References

- (1) Lago, S.; Rodríguez, H.; Khoshkbarchi, M. K.; Soto, A.; Arce, A. Enhanced Oil Recovery using the Ionic Liquid Trihexyl(Tetradecyl)Phosphonium Chloride: Phase Behaviour and Properties. *RSC Adv.* **2012**, *2*, 9392-9397.
- (2) Lago, S.; Francisco, M.; Arce, A.; Soto, A. Enhanced Oil Recovery with the Ionic Liquid Trihexyl(tetradecyl)phosphonium Chloride: A Phase Equilibria Study at 75 °C. *Energy Fuels* **2013**, *27*, 5806-5810.
- (3) Freire, M. G.; Carvalho, P. J.; Gardas, R. L.; Santos, L. M. N. B. F.; Marrucho, I. M.; Coutinho, J. A. P. Solubility of Water in Tetradecyltrihexylphosphonium-Based Ionic Liquids. *J. Chem. Eng. Data* **2008**, *53*, 2378-2382.
- (4) Neves, C. M. S. S.; Carvalho, P. J.; Freire, M. G.; Coutinho, J. A. P. Thermophysical Properties of Pure and Water-Saturated Tetradecyltrihexylphosphonium-Based Ionic Liquids. *J. Chem. Thermodyn.* **2011**, *43*, 948-957.
- (5) Marták, J.; Schlosser, Š. Extraction of Lactic Acid by Phosphonium Ionic Liquids. *Sep. Purif. Technol.* **2007**, *57*, 483-494.
- (6) <http://www.cyttec.com>, accessed on the 29/10/2016.
- (7) Bonhôte, P.; Dias, A.-P.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. Hydrophobic, Highly Conductive Ambient-Temperature Molten Salts. *Inorg. Chem.* **1996**, *35*, 1168-1178.
- (8) Freire, M. G.; Carvalho, P. J.; Gardas, R. L.; Marrucho, I. M.; Santos, L. M. N. B. F.; Coutinho, J. A. P. Mutual Solubilities of Water and the [C_nmim][Tf₂N] Hydrophobic Ionic Liquids. *J. Phys. Chem. B* **2008**, *112*, 1604-1610.
- (9) Crosthwaite J. M., Aki S. N. V. K., Maginn E. J., Brennecke J. F. Liquid Phase Behavior of Imidazolium-Based Ionic Liquids with Alcohols. *J. Phys. Chem. B* **2004**, *108*, 5113-5119.
- (10) Wang, S.; Jacquemin, J.; Husson, P.; Hardacre, C.; Costa Gomes, M. F. Liquid-Liquid Miscibility and Volumetric Properties of Aqueous Solutions of Ionic Liquids as a Function of Temperature. *J. Chem. Thermodyn.* **2009**, *41*, 1206-1214.
- (11) Jacquemin, J.; Husson, P.; Padua, A. A. H.; Majer, V. Density and Viscosity of Several Pure and Water-Saturated Ionic Liquids. *Green Chem.* **2006**, *8*, 172-180.
- (12) Ha, S. H.; Mai, N. L.; Koo, Y.-M. Butanol Recovery from Aqueous Solution into Ionic Liquids by Liquid-Liquid Extraction. *Process Biochem. (Oxford, U. K.)* **2010**, *45*, 1899-1903.
- (13) Chapeaux, A.; Simoni, L. D.; Stadtherr, M. A.; Brennecke, J. F. Liquid Phase Behavior of Ionic Liquids with Water and 1-Octanol and Modeling of 1-Octanol/Water Partition Coefficients. *J. Chem. Eng. Data* **2007**, *52*, 2462-2467.

-
- (14) Freire, M. G.; Neves, C. M. S. S.; Carvalho, P. J.; Gardas, R. L.; Fernandes, A. M.; Marrucho, I. M.; Santos, L. M. N. B. F.; Coutinho, J. A. P. Mutual Solubilities of Water and Hydrophobic Ionic Liquids. *J. Phys. Chem. B.* **2007**, *111*, 13082-13089.
- (15) Miao, X.; Zhang, H.; Wang, T.; He, M. Liquid–Liquid Equilibria of the Ternary System Water + Acetic Acid + Methyl tert-Butyl Ether. *J. Chem. Eng. Data* **2007**, *52*, 789-793.
- (16) Bharti, A.; Banerjee, T. Enhancement of Bio-Oil Derived Chemicals in Aqueous Phase Using Ionic Liquids: Experimental and COSMO-SAC Predictions using a Modified Hydrogen Bonding Expression. *Fluid Phase Equilib.* **2015**, *400*, 27-37.