

## Supporting Information

# Selection and Characterization of non-ideal Ionic Liquids Mixtures to be used in CO<sub>2</sub> Capture

Mónia A. R. Martins,<sup>1-3</sup> Gyanendra Sharma,<sup>4</sup> Simão P. Pinho,<sup>2,3</sup> Ramesh L. Gardas,<sup>4</sup> João A. P. Coutinho<sup>1</sup> and Pedro J. Carvalho,<sup>1\*</sup>

<sup>1</sup>CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

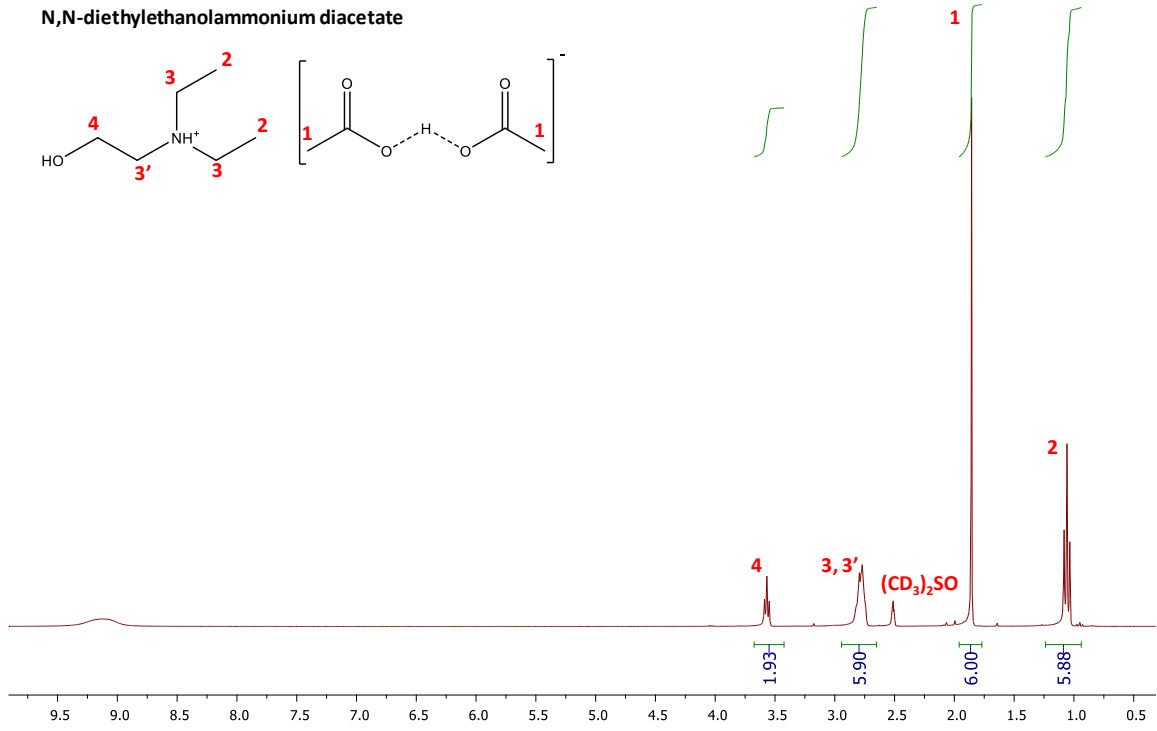
<sup>2</sup>Associate Laboratory LSRE-LCM, Department of Chemical and Biological Technology, Polytechnic Institute of Bragança, 5300-253 Bragança, Portugal

<sup>3</sup>CIMO – Mountain Research Center, Polytechnic Institute of Bragança, 5300-253 Bragança, Portugal

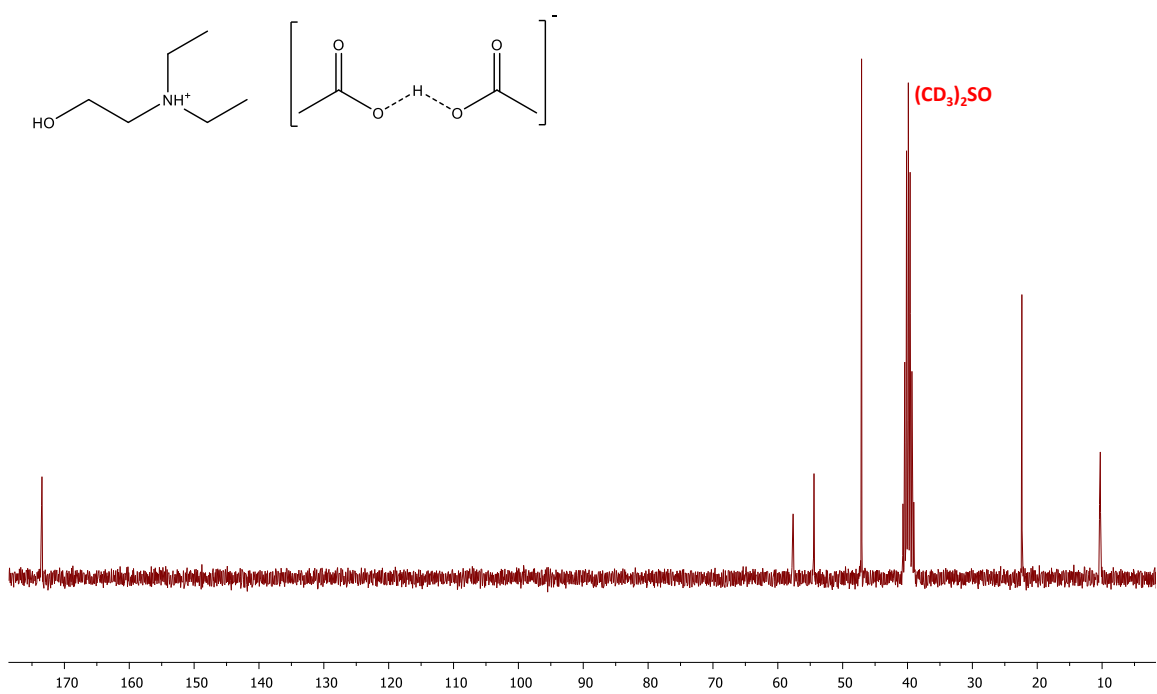
<sup>4</sup>Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India

\*Corresponding author: Pedro J. Carvalho, E-mail address: [quijorge@ua.pt](mailto:quijorge@ua.pt)

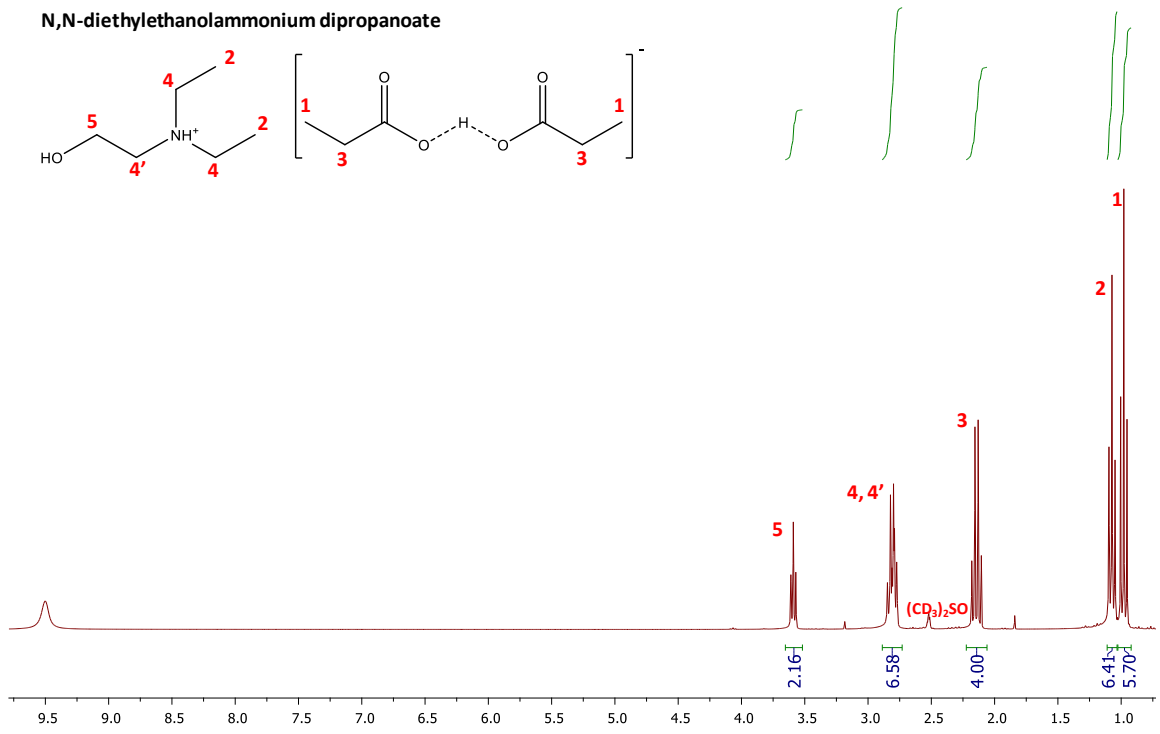
**N,N-diethylethanolammonium diacetate**



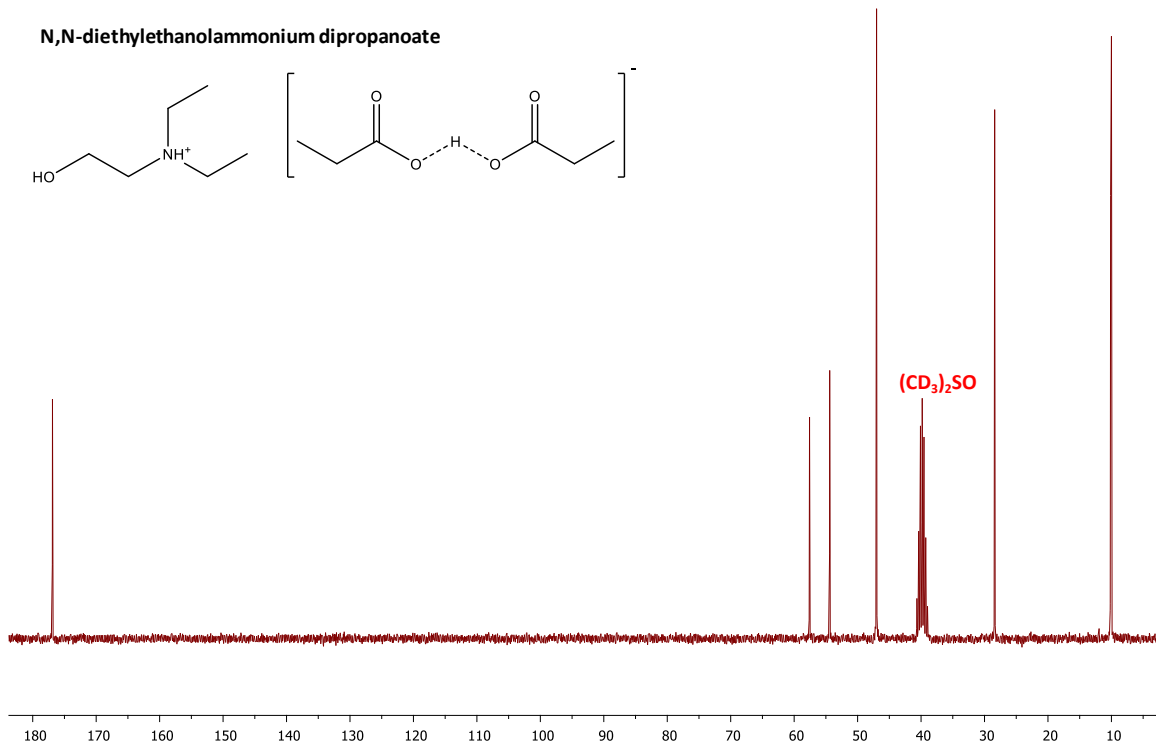
**N,N-diethylethanolammonium diacetate**



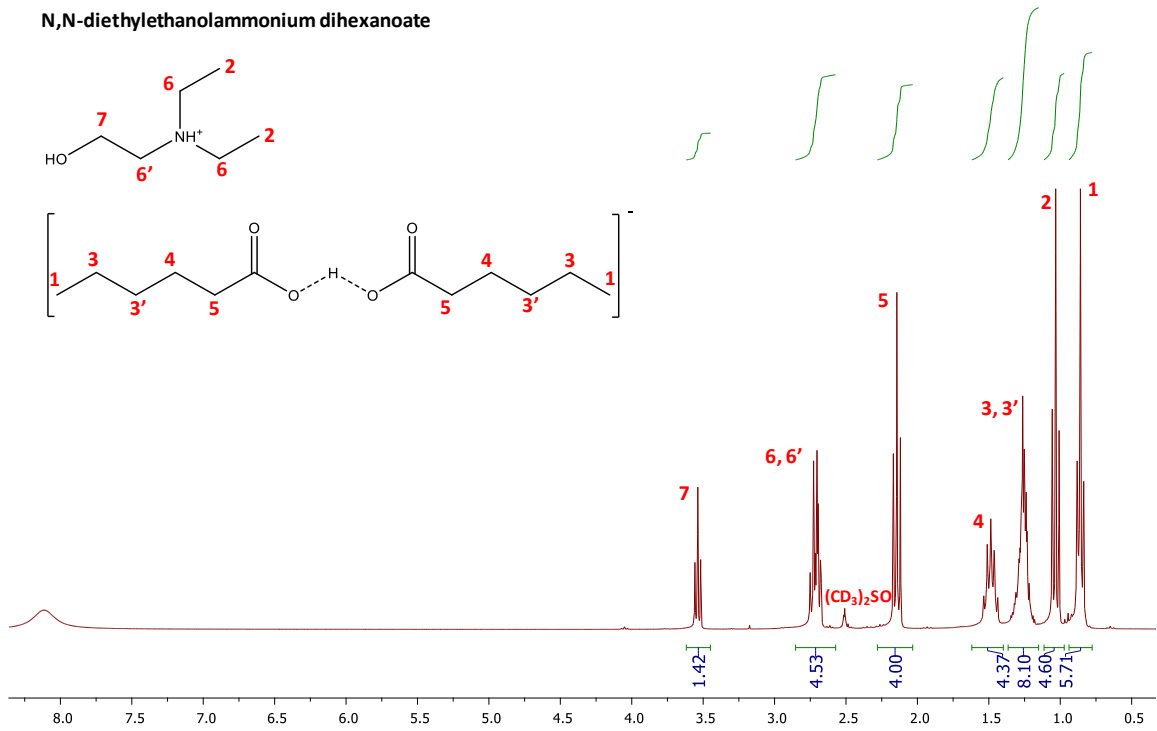
**N,N-diethylethanolammonium dipropoate**



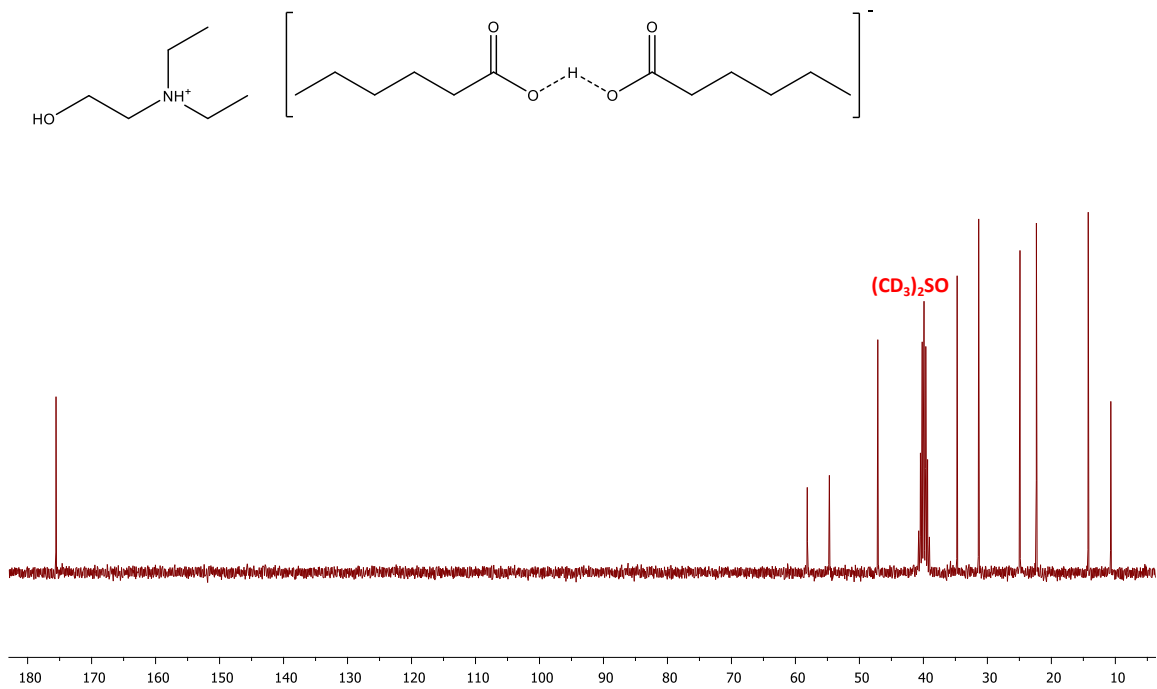
**N,N-diethylethanolammonium dipropoate**



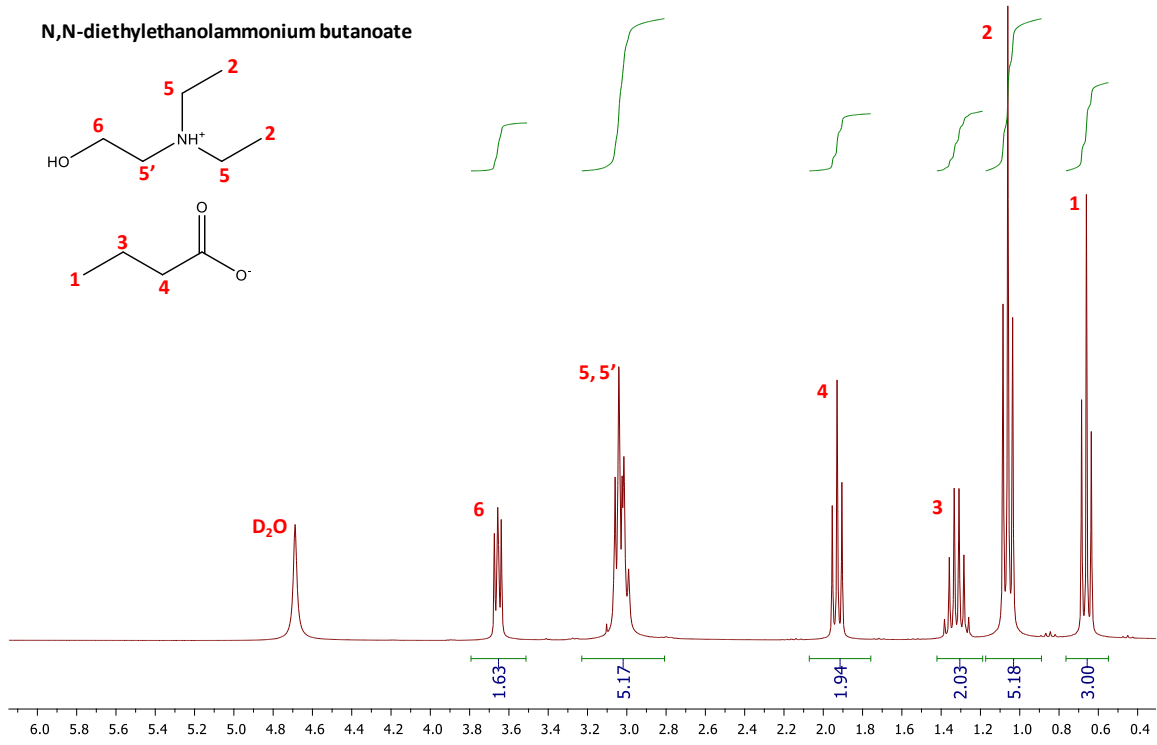
**N,N-diethylethanolammonium dihexanoate**



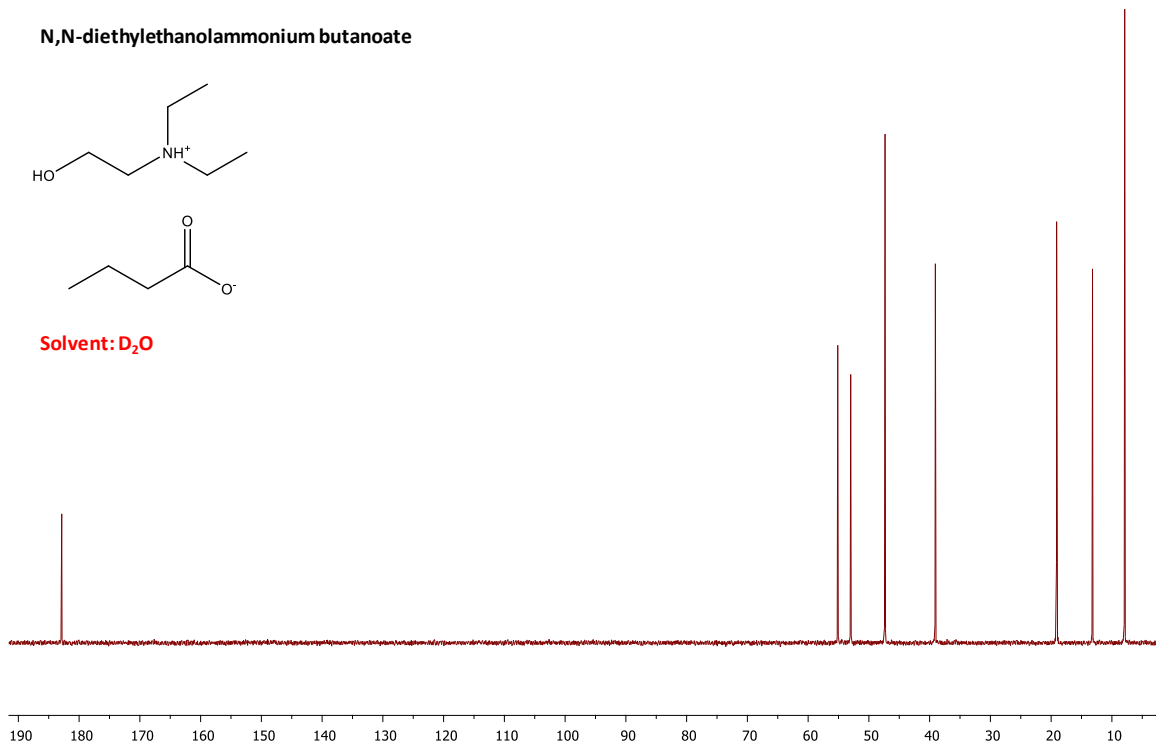
**N,N-diethylethanolammonium dihexanoate**



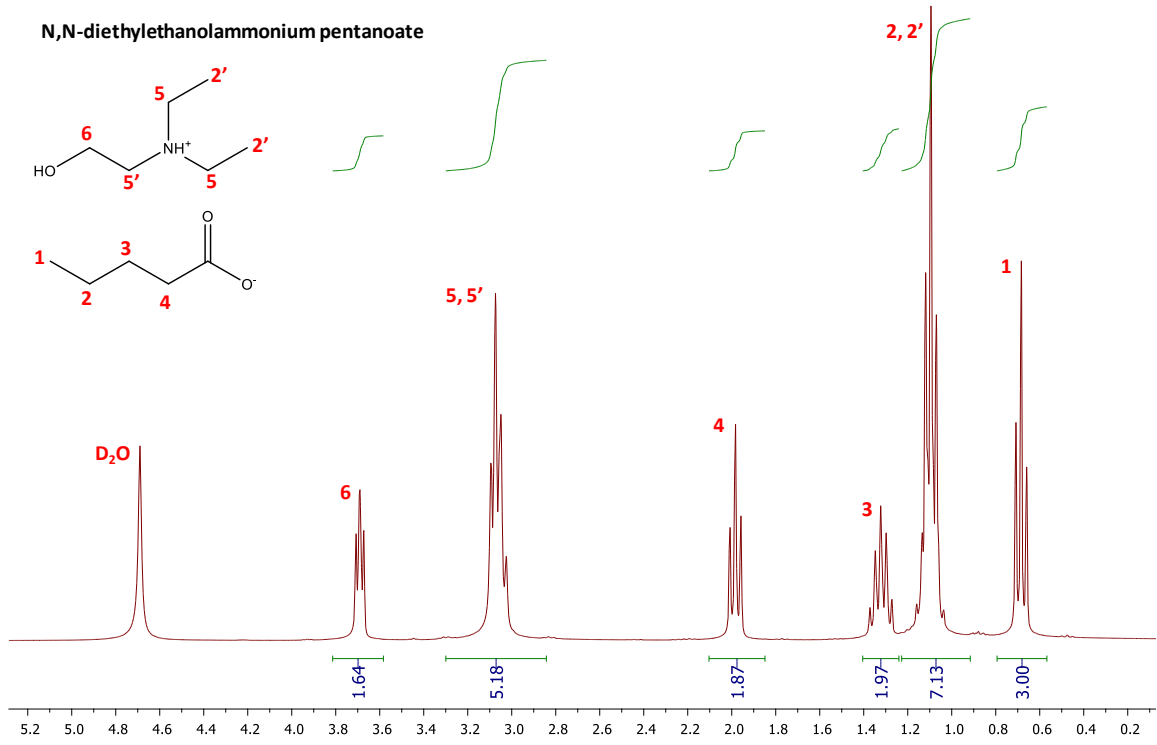
**N,N-diethylethanolammonium butanoate**



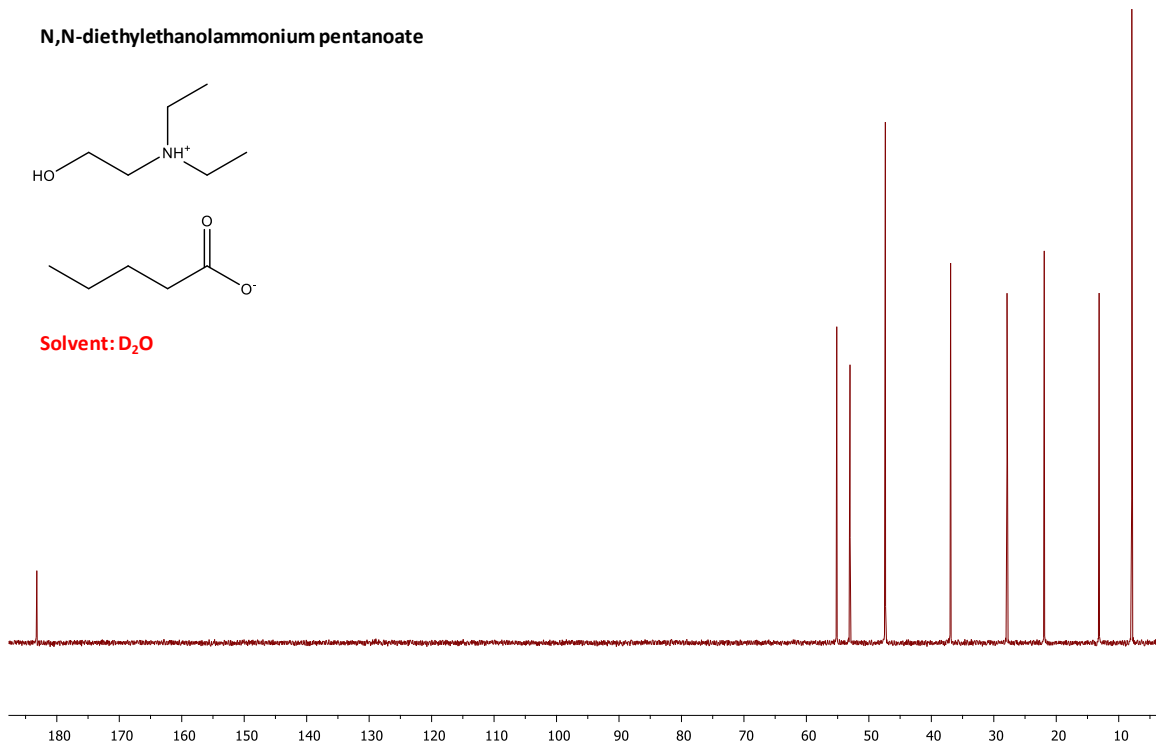
**N,N-diethylethanolammonium butanoate**

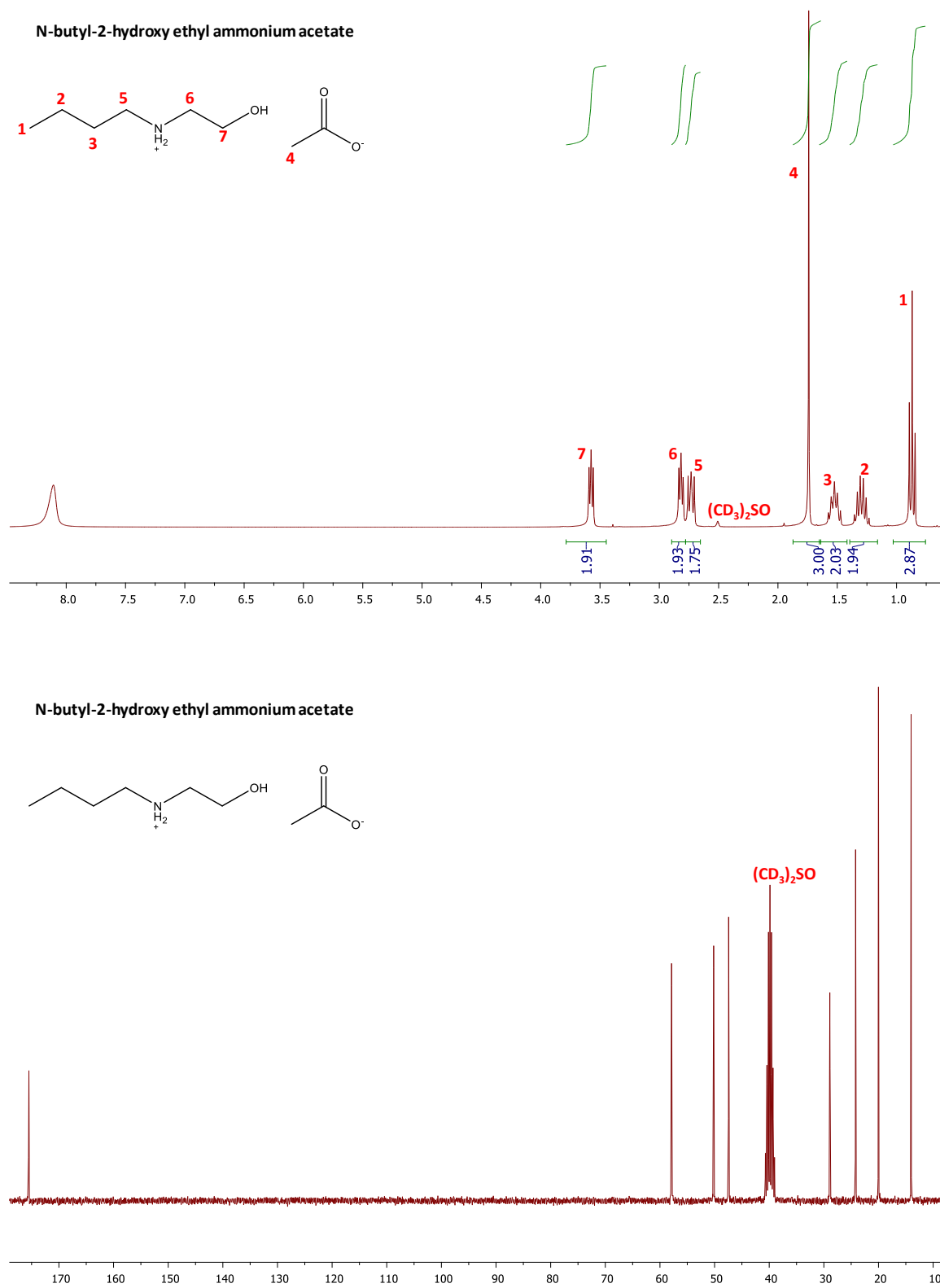


**N,N-diethylethanolammonium pentanoate**



**N,N-diethylethanolammonium pentanoate**





**Figure S1.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of pure protic ionic liquids at room temperature.

**Table S1.** List of cations and anions investigated using COSMO-RS.

Cation Name	Cation Abbreviation	Anion Name	Anion Abbreviation
<i>N,N</i> -dimethylethanolammonium	[DMEA] <sup>+</sup>	Formate	[For] <sup>-</sup>
<i>N,N</i> -diethylethanolammonium	[DEEA] <sup>+</sup>	Acetate	[Ace] <sup>-</sup>
<i>N</i> -butyl-2-hydroxyethylammonium	[BHEA] <sup>+</sup>	Propanoate	[Prop] <sup>-</sup>
1,3-dimethylimidazolium	[C <sub>1</sub> C <sub>1im</sub> ] <sup>+</sup>	Butanoate	[But] <sup>-</sup>
1-ethyl-3-methylimidazolium	[C <sub>2</sub> C <sub>1im</sub> ] <sup>+</sup>	Pentanoate	[Pent] <sup>-</sup>
1-butyl-3-methylimidazolium	[C <sub>4</sub> C <sub>1im</sub> ] <sup>+</sup>	Hexanoate	[Hex] <sup>-</sup>
1-hexyl-3-methylimidazolium	[C <sub>6</sub> C <sub>1im</sub> ] <sup>+</sup>	Dimethylphosphate	[DMP] <sup>-</sup>
1-octyl-3-methylimidazolium	[C <sub>8</sub> C <sub>1im</sub> ] <sup>+</sup>	Tetrafluoroborate	[BF <sub>4</sub> ] <sup>-</sup>
1-decyl-3-methylimidazolium	[C <sub>10</sub> C <sub>1im</sub> ] <sup>+</sup>	Dicyanamide	[DCN] <sup>-</sup>
		Ethyl sulfate	[EtSO <sub>4</sub> ] <sup>-</sup>
		Bis((trifluoromethyl)sulfonyl)amide	[NTf <sub>2</sub> ] <sup>-</sup>
		Hexafluorophosphate	[PF <sub>6</sub> ] <sup>-</sup>

**Table S2.** Excess enthalpies ( $H^E$ ) of the IL-IL mixtures at equimolar composition and at 298.15 K, computed by COSMO-RS.

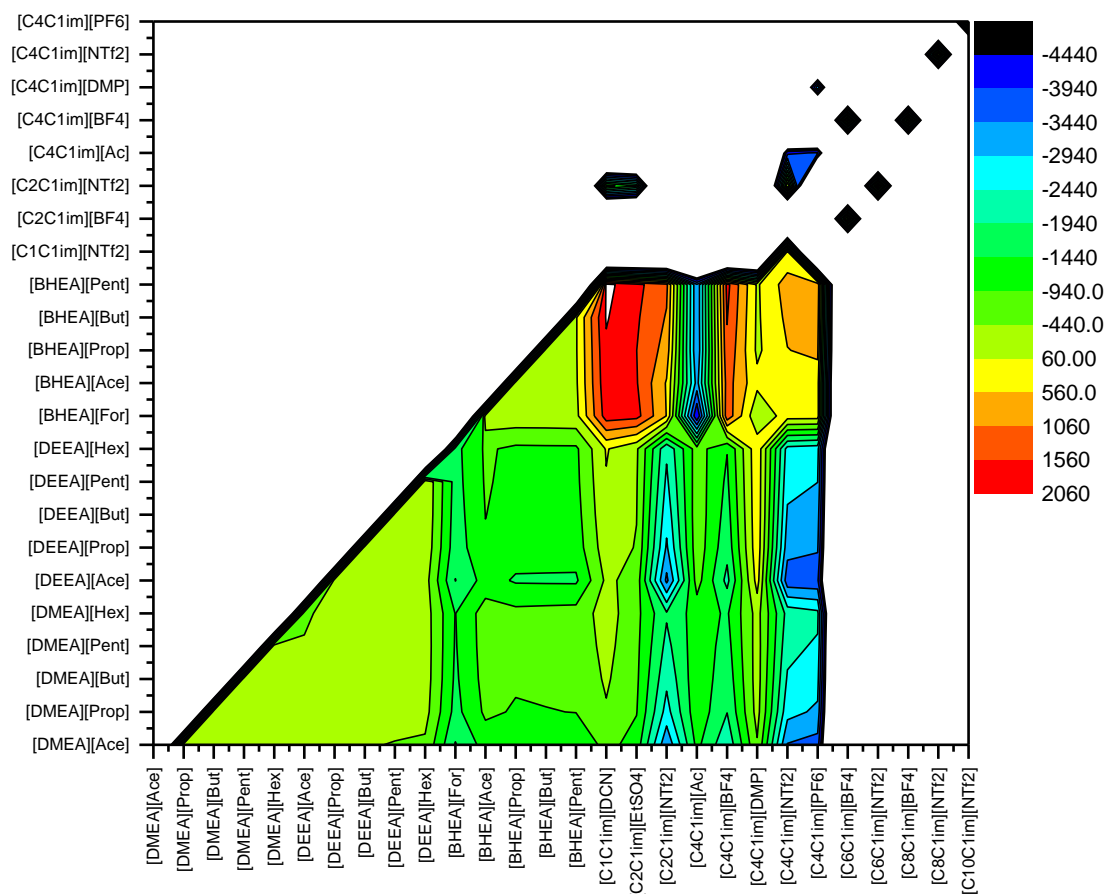
Mixture Abbreviation	$H^E / \text{J}\cdot\text{mol}^{-1}$	Mixture Abbreviation	$H^E / \text{J}\cdot\text{mol}^{-1}$
[BHEA][Pent][C <sub>2</sub> C <sub>1im</sub> ][DCN]	2213.72	[C <sub>4</sub> C <sub>1im</sub> ][NTf <sub>2</sub> ][C <sub>8</sub> C <sub>1im</sub> ][NTf <sub>2</sub> ]	100.10
[BHEA][But][C <sub>2</sub> C <sub>1im</sub> ][DCN]	2099.86	[C <sub>2</sub> C <sub>1im</sub> ][NTf <sub>2</sub> ][C <sub>4</sub> C <sub>1im</sub> ][NTf <sub>2</sub> ]	53.06
[BHEA][Prop][C <sub>2</sub> C <sub>1im</sub> ][DCN]	1985.55	[C <sub>4</sub> C <sub>1im</sub> ][BF <sub>4</sub> ][C <sub>8</sub> C <sub>1im</sub> ][BF <sub>4</sub> ]	32.05
[BHEA][Ace][C <sub>2</sub> C <sub>1im</sub> ][DCN]	1928.55	[DEEA][Pent][C <sub>2</sub> C <sub>1im</sub> ][DCN]	23.77
[BHEA][For][C <sub>2</sub> C <sub>1im</sub> ][DCN]	1805.13	[BHEA][Pent][BHEA][Prop]	7.76
[BHEA][For][C <sub>2</sub> C <sub>1im</sub> ][EtSO <sub>4</sub> ]	1727.45	[BHEA][But][BHEA][Prop]	2.07
[BHEA][Pent][C <sub>4</sub> C <sub>1im</sub> ][BF <sub>4</sub> ]	1714.37	[BHEA][Pent][BHEA][But]	1.78
[BHEA][Pent][C <sub>2</sub> C <sub>1im</sub> ][EtSO <sub>4</sub> ]	1695.33	[C <sub>4</sub> C <sub>1im</sub> ][BF <sub>4</sub> ][C <sub>6</sub> C <sub>1im</sub> ][BF <sub>4</sub> ]	-0.01
[BHEA][But][C <sub>2</sub> C <sub>1im</sub> ][EtSO <sub>4</sub> ]	1627.08	[BHEA][Pent][C <sub>4</sub> C <sub>1im</sub> ][DMP]	-2.07
[BHEA][Ace][C <sub>2</sub> C <sub>1im</sub> ][EtSO <sub>4</sub> ]	1597.23	[DEEA][Hex][DEEA][Pent]	-4.47
[BHEA][But][C <sub>4</sub> C <sub>1im</sub> ][BF <sub>4</sub> ]	1587.24	[DMEA][Hex][DMEA][Pent]	-4.85
[BHEA][Prop][C <sub>2</sub> C <sub>1im</sub> ][EtSO <sub>4</sub> ]	1566.92	[DEEA][Pent][DEEA][But]	-7.67
[BHEA][Prop][C <sub>4</sub> C <sub>1im</sub> ][BF <sub>4</sub> ]	1463.42	[DMEA][Pent][DMEA][But]	-11.03
[BHEA][For][C <sub>4</sub> C <sub>1im</sub> ][BF <sub>4</sub> ]	1404.11	[BHEA][Pent][BHEA][Ace]	-11.32
[BHEA][Ace][C <sub>4</sub> C <sub>1im</sub> ][BF <sub>4</sub> ]	1284.47	[DEEA][But][DEEA][Prop]	-12.34
[BHEA][Pent][C <sub>2</sub> C <sub>1im</sub> ][NTf <sub>2</sub> ]	1169.99	[BHEA][But][C <sub>4</sub> C <sub>1im</sub> ][DMP]	-14.35
[BHEA][But][C <sub>2</sub> C <sub>1im</sub> ][NTf <sub>2</sub> ]	1016.52	[BHEA][But][BHEA][Ace]	-15.96
[BHEA][Pent][C <sub>4</sub> C <sub>1im</sub> ][PF <sub>6</sub> ]	997.97	[BHEA][Prop][BHEA][Ace]	-16.52
[BHEA][Prop][C <sub>2</sub> C <sub>1im</sub> ][NTf <sub>2</sub> ]	857.49	[DMEA][But][DMEA][Prop]	-23.20
[BHEA][But][C <sub>4</sub> C <sub>1im</sub> ][PF <sub>6</sub> ]	831.96	[DEEA][Hex][DEEA][But]	-23.87
[BHEA][Pent][C <sub>4</sub> C <sub>1im</sub> ][NTf <sub>2</sub> ]	795.76	[C <sub>2</sub> C <sub>1im</sub> ][BF <sub>4</sub> ][C <sub>6</sub> C <sub>1im</sub> ][BF <sub>4</sub> ]	-27.49
[BHEA][But][C <sub>4</sub> C <sub>1im</sub> ][NTf <sub>2</sub> ]	672.46	[BHEA][Prop][C <sub>4</sub> C <sub>1im</sub> ][DMP]	-28.89
[BHEA][Prop][C <sub>4</sub> C <sub>1im</sub> ][PF <sub>6</sub> ]	660.74	[DMEA][Hex][DMEA][But]	-30.57
[BHEA][Prop][C <sub>4</sub> C <sub>1im</sub> ][NTf <sub>2</sub> ]	546.81	[DEEA][Pent][DEEA][Prop]	-39.34
[BHEA][For][C <sub>2</sub> C <sub>1im</sub> ][NTf <sub>2</sub> ]	539.51	[DEEA][Prop][DEEA][Ace]	-39.44



[BHEA][Ace][C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	511.35	[DEEA][But][C <sub>2</sub> C <sub>1</sub> im][DCN]	-55.64
[DEEA][Pent][C <sub>4</sub> C <sub>1</sub> im][DMP]	423.27	[DMEA][Pent][DMEA][Prop]	-65.98
[DEEA][Hex][C <sub>4</sub> C <sub>1</sub> im][DMP]	418.54	[DEEA][Hex][DEEA][Prop]	-70.24
[DEEA][But][C <sub>4</sub> C <sub>1</sub> im][DMP]	416.27	[DMEA][Prop][DMEA][Ace]	-79.84
[DEEA][Prop][C <sub>4</sub> C <sub>1</sub> im][DMP]	385.29	[BHEA][Pent][BHEA][For]	-83.44
[BHEA][For][C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	314.23	[BHEA][But][BHEA][For]	-100.06
[BHEA][Ace][C <sub>4</sub> C <sub>1</sub> im][PF <sub>6</sub> ]	308.69	[DEEA][But][DEEA][Ace]	-100.37
[BHEA][For][C <sub>4</sub> C <sub>1</sub> im][PF <sub>6</sub> ]	304.24	[DMEA][Hex][DMEA][Prop]	-106.59
[DEEA][Ace][C <sub>4</sub> C <sub>1</sub> im][DMP]	257.93	[BHEA][Prop][BHEA][For]	-107.40
[BHEA][Ace][C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	229.69	[BHEA][Ace][BHEA][For]	-112.04
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ][C <sub>10</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	197.33	[DEEA][Prop][C <sub>2</sub> C <sub>1</sub> im][DCN]	-146.11
[BHEA][Ace][C <sub>4</sub> C <sub>1</sub> im][DMP]	187.77	[DEEA][Pent][DEEA][Ace]	-167.64
[C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ][C <sub>6</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	162.31	[DEEA][Hex][DMEA][Pent]	-180.47
[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ][C <sub>1</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	133.61	[DEEA][Pent][DMEA][But]	-186.83
[DEEA][Hex][C <sub>2</sub> C <sub>1</sub> im][DCN]	100.24	[DEEA][But][DMEA][But]	-187.16
[DEEA][Pent][DMEA][Pent]	-189.29	[DEEA][Hex][DMEA][Ace]	-531.24
[DEEA][Hex][DMEA][But]	-191.02	[DEEA][But][C <sub>4</sub> C <sub>1</sub> im][Ac]	-622.08
[DEEA][Prop][DMEA][Prop]	-191.78	[DEEA][Prop][C <sub>4</sub> C <sub>1</sub> im][Ac]	-628.36
[DEEA][Hex][DMEA][Hex]	-192.38	[DEEA][Ace][C <sub>2</sub> C <sub>1</sub> im][EtSO <sub>4</sub> ]	-631.49
[DEEA][Prop][DMEA][But]	-201.28	[DEEA][Pent][C <sub>4</sub> C <sub>1</sub> im][Ac]	-656.12
[DMEA][But][DMEA][Ace]	-201.33	[DEEA][Hex][C <sub>4</sub> C <sub>1</sub> im][Ac]	-694.95
[DMEA][Hex][C <sub>2</sub> C <sub>1</sub> im][DCN]	-203.55	[BHEA][Ace][DMEA][Hex]	-700.07
[DEEA][But][DMEA][Pent]	-207.61	[BHEA][Ace][DMEA][Pent]	-716.30
[DEEA][But][DMEA][Prop]	-209.89	[DEEA][Ace][C <sub>4</sub> C <sub>1</sub> im][Ac]	-734.79
[DEEA][Pent][DMEA][Hex]	-210.59	[BHEA][Pent][DMEA][Hex]	-742.06
[DMEA][But][C <sub>4</sub> C <sub>1</sub> im][DMP]	-220.45	[C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ][C <sub>2</sub> C <sub>1</sub> im][DCN]	-742.48
[DMEA][Pent][C <sub>4</sub> C <sub>1</sub> im][DMP]	-226.02	[BHEA][Ace][DMEA][But]	-755.82
[DEEA][Hex][DEEA][Ace]	-231.79	[BHEA][But][DMEA][Hex]	-766.89
[DEEA][Pent][DMEA][Prop]	-233.46	[DMEA][Ace][C <sub>2</sub> C <sub>1</sub> im][DCN]	-766.95
[DEEA][Ace][DMEA][Prop]	-236.10	[BHEA][Pent][DMEA][Pent]	-767.39
[DEEA][But][DMEA][Hex]	-241.92	[DMEA][Hex][C <sub>2</sub> C <sub>1</sub> im][EtSO <sub>4</sub> ]	-793.67
[DEEA][Prop][DMEA][Pent]	-245.64	[BHEA][But][DMEA][Pent]	-793.74
[DEEA][Ace][DMEA][Ace]	-245.92	[BHEA][Prop][DMEA][Hex]	-797.11
[DMEA][Hex][C <sub>4</sub> C <sub>1</sub> im][DMP]	-250.49	[DMEA][Pent][C <sub>2</sub> C <sub>1</sub> im][EtSO <sub>4</sub> ]	-814.86
[DEEA][Hex][DMEA][Prop]	-254.86	[BHEA][Pent][DMEA][But]	-821.18
[DMEA][Prop][C <sub>4</sub> C <sub>1</sub> im][DMP]	-260.46	[BHEA][Prop][DMEA][Pent]	-825.09
[DMEA][Pent][C <sub>2</sub> C <sub>1</sub> im][DCN]	-283.11	[BHEA][Ace][DMEA][Prop]	-843.64
[DEEA][Prop][DMEA][Hex]	-297.16	[DMEA][But][C <sub>2</sub> C <sub>1</sub> im][EtSO <sub>4</sub> ]	-847.54
[DEEA][Prop][DMEA][Ace]	-308.42	[BHEA][But][DMEA][But]	-848.25
[DEEA][Ace][DMEA][But]	-311.28	[BHEA][Ace][DEEA][Hex]	-868.26
[DMEA][Pent][DMEA][Ace]	-318.48	[BHEA][Prop][DMEA][But]	-879.55
[DEEA][Ace][C <sub>2</sub> C <sub>1</sub> im][DCN]	-336.62	[BHEA][Ace][DEEA][Pent]	-893.27
[DEEA][Hex][C <sub>2</sub> C <sub>1</sub> im][EtSO <sub>4</sub> ]	-353.13	[DMEA][Prop][C <sub>2</sub> C <sub>1</sub> im][EtSO <sub>4</sub> ]	-913.20
[DMEA][But][C <sub>2</sub> C <sub>1</sub> im][DCN]	-371.74	[BHEA][Pent][DMEA][Prop]	-930.10

[BHEA][For][C <sub>4</sub> C <sub>1</sub> im][DMP]	-381.29	[BHEA][Ace][DEEA][But]	-932.44
[DEEA][Pent][C <sub>2</sub> C <sub>1</sub> im][EtSO <sub>4</sub> ]	-386.11	[BHEA][But][DMEA][Prop]	-957.12
[DEEA][But][DMEA][Ace]	-392.21	[BHEA][Prop][DMEA][Prop]	-986.87
[DEEA][Ace][DMEA][Pent]	-408.09	[BHEA][Ace][DEEA][Prop]	-991.15
[DMEA][Hex][DMEA][Ace]	-414.73	[BHEA][Pent][DEEA][Hex]	-1026.21
[DEEA][But][C <sub>2</sub> C <sub>1</sub> im][EtSO <sub>4</sub> ]	-424.29	[BHEA][But][DEEA][Hex]	-1034.75
[DEEA][Pent][DMEA][Ace]	-468.24	[BHEA][Prop][DEEA][Hex]	-1048.18
[DEEA][Prop][C <sub>2</sub> C <sub>1</sub> im][EtSO <sub>4</sub> ]	-475.38	[BHEA][Pent][DEEA][Pent]	-1063.94
[DMEA][Prop][C <sub>2</sub> C <sub>1</sub> im][DCN]	-489.34	[BHEA][But][DEEA][Pent]	-1072.23
[DMEA][Ace][C <sub>4</sub> C <sub>1</sub> im][DMP]	-490.82	[BHEA][Prop][DEEA][Pent]	-1084.90
[DEEA][Ace][DMEA][Hex]	-501.22	[DMEA][But][C <sub>4</sub> C <sub>1</sub> im][Ac]	-1086.16
[DMEA][Prop][C <sub>4</sub> C <sub>1</sub> im][Ac]	-1095.05	[DMEA][Pent][C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	-2083.30
[BHEA][Pent][DEEA][But]	-1120.45	[DMEA][Hex][C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	-2121.51
[BHEA][But][DEEA][But]	-1127.59	[DMEA][Pent][C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	-2291.74
[BHEA][Prop][DEEA][But]	-1138.28	[DMEA][Hex][C <sub>4</sub> C <sub>1</sub> im][PF <sub>6</sub> ]	-2315.09
[DMEA][Pent][C <sub>4</sub> C <sub>1</sub> im][Ac]	-1140.42	[DMEA][But][C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	-2324.82
[DMEA][Ace][C <sub>2</sub> C <sub>1</sub> im][EtSO <sub>4</sub> ]	-1156.48	[DMEA][Ace][C <sub>4</sub> C <sub>1</sub> im][BF <sub>4</sub> ]	-2334.70
[BHEA][Pent][DEEA][Prop]	-1202.09	[DEEA][Hex][C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	-2351.25
[DMEA][Hex][C <sub>4</sub> C <sub>1</sub> im][Ac]	-1204.31	[DMEA][But][C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	-2498.37
[BHEA][But][DEEA][Prop]	-1207.25	[DMEA][Pent][C <sub>4</sub> C <sub>1</sub> im][PF <sub>6</sub> ]	-2514.22
[BHEA][Prop][DEEA][Prop]	-1214.55	[DEEA][Pent][C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	-2542.86
[BHEA][Ace][DMEA][Ace]	-1224.95	[DMEA][Prop][C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	-2635.38
[BHEA][Ace][DEEA][Ace]	-1228.41	[DEEA][Hex][C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	-2639.79
[DMEA][Ace][C <sub>4</sub> C <sub>1</sub> im][Ac]	-1298.34	[DMEA][But][C <sub>4</sub> C <sub>1</sub> im][PF <sub>6</sub> ]	-2745.47
[BHEA][Pent][DMEA][Ace]	-1400.56	[DEEA][Hex][C <sub>4</sub> C <sub>1</sub> im][PF <sub>6</sub> ]	-2756.20
[BHEA][But][DMEA][Ace]	-1412.64	[DEEA][But][C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	-2759.08
[DEEA][Hex][C <sub>4</sub> C <sub>1</sub> im][BF <sub>4</sub> ]	-1420.95	[DMEA][Prop][C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	-2770.97
[BHEA][Prop][DMEA][Ace]	-1422.89	[DEEA][Pent][C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	-2807.42
[C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ][C <sub>2</sub> C <sub>1</sub> im][EtSO <sub>4</sub> ]	-1425.67	[DEEA][Pent][C <sub>4</sub> C <sub>1</sub> im][PF <sub>6</sub> ]	-2936.92
[BHEA][For][DMEA][Hex]	-1453.11	[C <sub>4</sub> C <sub>1</sub> im][PF <sub>6</sub> ][C <sub>4</sub> C <sub>1</sub> im][DMP]	-2948.05
[BHEA][For][DMEA][Pent]	-1478.44	[DEEA][But][C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	-2998.75
[BHEA][Prop][DEEA][Ace]	-1498.07	[DEEA][Prop][C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	-3014.56
[DMEA][Hex][C <sub>4</sub> C <sub>1</sub> im][BF <sub>4</sub> ]	-1505.96	[DMEA][Prop][C <sub>4</sub> C <sub>1</sub> im][PF <sub>6</sub> ]	-3035.71
[BHEA][But][DEEA][Ace]	-1508.33	[DEEA][But][C <sub>4</sub> C <sub>1</sub> im][PF <sub>6</sub> ]	-3136.26
[BHEA][Pent][DEEA][Ace]	-1517.37	[BHEA][Ace][C <sub>4</sub> C <sub>1</sub> im][Ac]	-3138.11
[BHEA][For][DMEA][But]	-1523.98	[DEEA][Prop][C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	-3227.90
[DEEA][Pent][C <sub>4</sub> C <sub>1</sub> im][BF <sub>4</sub> ]	-1529.10	[DMEA][Ace][C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	-3348.63
[BHEA][For][DEEA][Hex]	-1592.56	[DEEA][Prop][C <sub>4</sub> C <sub>1</sub> im][PF <sub>6</sub> ]	-3366.64
[BHEA][For][DMEA][Prop]	-1606.80	[BHEA][Prop][C <sub>4</sub> C <sub>1</sub> im][Ac]	-3385.57
[DMEA][Pent][C <sub>4</sub> C <sub>1</sub> im][BF <sub>4</sub> ]	-1619.44	[BHEA][But][C <sub>4</sub> C <sub>1</sub> im][Ac]	-3386.02
[BHEA][For][DEEA][Pent]	-1624.33	[BHEA][Pent][C <sub>4</sub> C <sub>1</sub> im][Ac]	-3401.56
[DEEA][But][C <sub>4</sub> C <sub>1</sub> im][BF <sub>4</sub> ]	-1647.28	[DMEA][Ace][C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	-3470.00
[BHEA][For][DEEA][But]	-1667.16	[DEEA][Ace][C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	-3567.83
[BHEA][For][DEEA][Prop]	-1720.15	[DMEA][Ace][C <sub>4</sub> C <sub>1</sub> im][PF <sub>6</sub> ]	-3656.15

[DMEA][But][C <sub>4</sub> C <sub>1</sub> im][BF <sub>4</sub> ]	-1752.30	[DEEA][Ace][C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	-3775.69
[DEEA][Prop][C <sub>4</sub> C <sub>1</sub> im][BF <sub>4</sub> ]	-1784.45	[DEEA][Ace][C <sub>4</sub> C <sub>1</sub> im][PF <sub>6</sub> ]	-3837.10
[DMEA][Hex][C <sub>2</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	-1880.55	[C <sub>4</sub> C <sub>1</sub> im][PF <sub>6</sub> ][C <sub>4</sub> C <sub>1</sub> im][Ac]	-3867.17
[DMEA][Prop][C <sub>4</sub> C <sub>1</sub> im][BF <sub>4</sub> ]	-1926.89	[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ][C <sub>4</sub> C <sub>1</sub> im][Ac]	-4098.74
[BHEA][For][DEEA][Ace]	-1951.71	[BHEA][For][C <sub>4</sub> C <sub>1</sub> im][Ac]	-4431.80
[BHEA][For][DMEA][Ace]	-1973.54		
[DEEA][Ace][C <sub>4</sub> C <sub>1</sub> im][BF <sub>4</sub> ]	-2080.79		

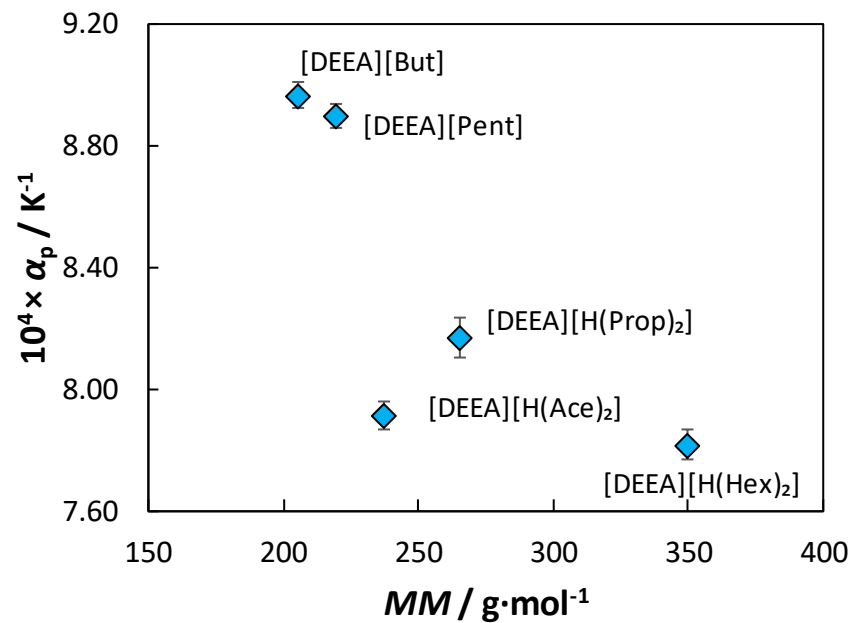


**Figure S2.** Excess enthalpy ( $H^E$ ) of the equimolar IL-IL binary mixtures computed by COSMO-RS at  $T = 298.15$  K.

**Table S3.** Densities ( $\rho$  / g·cm<sup>-3</sup>), viscosities ( $\eta$  / mPa·s) and water content (ppm) of the pure ionic liquids selected for characterization, at different temperatures.<sup>a</sup>

	[C <sub>4</sub> C <sub>1</sub> im][DMP]		[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]		[DEEA][H(Ace) <sub>2</sub> ]		[DEEA][H(Prop) <sub>2</sub> ]		[DEEA][H(Hex) <sub>2</sub> ]		[DEEA][But]		[DEEA][Pent]		[BHEA][Ace]	
Water Content	169		279		-		301		857		792		812		517	
T / K	$\rho$	$\eta$	$\rho$	$\eta$	$\rho$	$\eta$	$\rho$	$\eta$	$\rho$	$\eta$	$\rho$	$\eta$	$\rho$	$\eta$	$\rho$	$\eta$
278.15	1.1741	3502.80	1.4560	145.55	1.0684	339.51	1.0335	243.96	0.9750	178.96	0.9963	188.98	0.9814	156.60	1.0286	6138.10
283.15	1.1704	2141.70	1.4513	108.96	1.0643	226.97	1.0296	168.98	0.9714	132.55	0.9919	133.86	0.9771	113.06	1.0252	3633.80
288.15	1.1668	1361.10	1.4465	83.44	1.0604	156.12	1.0257	120.66	0.9679	100.10	0.9877	96.88	0.9730	83.22	1.0217	2229.70
293.15	1.1634	895.42	1.4417	65.11	1.0567	110.44	1.0218	88.32	0.9643	76.90	0.9834	71.57	0.9689	62.45	1.0183	1412.30
298.15	1.1601	608.88	1.4370	51.73	1.0526	80.19	1.0179	66.16	0.9608	60.01	0.9792	53.96	0.9647	47.75	1.0147	921.14
303.15	1.1570	425.97	1.4322	41.80	1.0486	59.63	1.0140	50.60	0.9572	47.52	0.9750	41.42	0.9606	37.12	1.0112	616.90
308.15	1.1537	305.80	1.4274	34.30	1.0446	45.32	1.0100	39.40	0.9536	38.14	0.9708	32.34	0.9565	29.31	1.0075	423.27
313.15	1.1501	224.87	1.4227	28.55	1.0406	35.12	1.0061	31.21	0.9500	31.00	0.9665	25.64	0.9523	23.48	1.0039	296.96
318.15	1.1471	168.93	1.4179	24.05	1.0366	27.71	1.0021	25.10	0.9464	25.48	0.9623	20.63	0.9482	19.07	1.0004	212.68
323.15	1.1436	129.38	1.4132	20.50	1.0326	22.22	0.9984	20.46	0.9427	21.16	0.9581	16.82	0.9441	15.68	0.9971	155.26
328.15	1.1403	100.91	1.4084	17.64	1.0285	18.08	0.9943	16.89	0.9391	17.75	0.9538	13.87	0.9399	13.03	0.9934	115.31
333.15	1.1374	79.94	1.4037	15.33	1.0245	14.90	0.9903	14.08	0.9354	15.02	0.9496	11.56	0.9357	10.94	0.9898	87.04
338.15	1.1342	64.25	1.3990	13.43	1.0204	12.45	0.9862	11.89	0.9317	12.81	0.9453	9.73	0.9315	9.27	0.9861	66.73
343.15	1.1307	52.35	1.3943	11.85	1.0163	10.49	0.9820	10.12	0.9280	11.01	0.9410	8.27	0.9273	7.91	0.9824	51.88
348.15	1.1275	43.18	1.3896	10.53	1.0121	8.93	0.9778	8.68	0.9243	9.52	0.9367	7.08	0.9231	6.81	0.9787	40.87
353.15	1.1243	36.02	1.3849	9.41	1.0079	7.67	0.9734	7.50	0.9205	8.28	0.9323	6.11	0.9189	5.90	0.9748	32.60
358.15	1.1211	30.38	1.3803	8.46	1.0037	6.65	0.9691	6.52	0.9167	7.24	0.9279	5.31	0.9146	5.15	0.9710	26.29
363.15	1.1180	25.86	1.3756	7.65	0.9994	5.80	0.9647	5.70	0.9128	6.36	0.9235	4.65	0.9102	4.52	0.9671	21.43
368.15	1.1148	22.22	1.3709	6.95	0.9951	5.09	0.9603	5.01	0.9089	5.61	0.9190	4.09	0.9059	3.99	0.9632	17.63
373.15	1.1117	19.25	1.3663	6.34	0.9907	4.50	0.9558	4.41	0.9049	4.96	0.9145	3.61	0.9014	3.53	0.9593	14.64

<sup>a</sup>Standard uncertainties,  $u$ , are  $u(T) = 0.02$  K,  $u(\rho) = 0.0005$  g·cm<sup>-3</sup>,  $u_r(\eta) = 0.35\%$  and  $u_r(\rho) = 0.05$ .



**Figure S3.** Graphic representation of the thermal expansion coefficient as a function of the molar mass of the protic IL.

**Table S4.** Densities and water content (ppm) of the mixtures of ionic liquids at different temperatures and compositions.<sup>a</sup>

$T / K$	$\rho_{\text{mixture}} / \text{g}\cdot\text{cm}^{-3}$
---------	---

[DEEA][H(Ace) <sub>2</sub> ](1)+[C <sub>4</sub> C <sub>1</sub> im][DMP](2)									
<b>x<sub>1</sub></b>	0.8567	0.7493	0.6343	0.5275	0.4263	0.3316			0.0748
<b>x<sub>2</sub></b>	0.1433	0.2507	0.3657	0.4725	0.5737	0.6684			0.9252
<b>Water content</b>	226	218	210	203	196	190			174
278.15	1.0811	1.0929	1.1022	1.1107	1.1185	1.1271			1.1625
283.15	1.0770	1.0891	1.0982	1.1067	1.1145	1.1231			1.1588
288.15	1.0730	1.0852	1.0942	1.1026	1.1105	1.1192			1.1552
293.15	1.0691	1.0814	1.0902	1.0986	1.1065	1.1153			1.1518
298.15	1.0650	1.0775	1.0863	1.0946	1.1025	1.1114			1.1483
303.15	1.0610	1.0736	1.0824	1.0907	1.0986	1.1076			1.1449
308.15	1.0569	1.0697	1.0785	1.0867	1.0947	1.1038			1.1415
313.15	1.0529	1.0658	1.0745	1.0828	1.0907	1.1001			1.1383
318.15	1.0488	1.0618	1.0706	1.0788	1.0868	1.0964			1.1349
323.15	1.0448	1.0578	1.0666	1.0748	1.0830	1.0926			1.1313
328.15	1.0407	1.0538	1.0625	1.0708	1.0792	1.0888			1.1279
333.15	1.0366	1.0498	1.0585	1.0667	1.0753	1.0851			1.1246
338.15	1.0325	1.0457	1.0544	1.0627	1.0713	1.0813			1.1213
343.15	1.0284	1.0416	1.0503	1.0586	1.0674	1.0776			1.1182
348.15	1.0243	1.0376	1.0462	1.0546	1.0635	1.0738			1.1146
353.15	1.0201	1.0334	1.0421	1.0505	1.0595	1.0701			1.1113
358.15	1.0159	1.0293	1.0380	1.0464	1.0556	1.0663			1.1081
363.15	1.0116	1.0251	1.0338	1.0424	1.0517	1.0626			1.1048
368.15	1.0074	1.0209	1.0297	1.0383	1.0478	1.0589			1.1015
373.15	1.0030	1.0167	1.0255	1.0343	1.0439	1.0552			1.0982
[DEEA][H(Prop) <sub>2</sub> ](1)+[C <sub>4</sub> C <sub>1</sub> im][DMP](2)									
<b>x<sub>1</sub></b>	0.8667	0.7416	0.6252	0.4953	0.4183	0.3281	0.2364	0.1549	0.0800
<b>x<sub>2</sub></b>	0.1333	0.2584	0.3748	0.5047	0.5817	0.6719	0.7636	0.8451	0.9200

<b>Water content</b>	284	267	252	235	225	213	201	190	180
278.15	1.0474	1.0614	1.0764	1.0891	1.0984	1.1106	1.1254	1.1398	1.1567
283.15	1.0430	1.0572	1.0722	1.0849	1.0941	1.1064	1.1215	1.1358	1.1528
288.15	1.0389	1.0530	1.0680	1.0808	1.0902	1.1025	1.1176	1.1321	1.1492
293.15	1.0347	1.0489	1.0640	1.0767	1.0861	1.0988	1.1139	1.1283	1.1458
298.15	1.0306	1.0448	1.0598	1.0726	1.0821	1.0949	1.1102	1.1245	1.1424
303.15	1.0265	1.0406	1.0558	1.0686	1.0781	1.0911	1.1066	1.1208	1.1389
308.15	1.0223	1.0365	1.0517	1.0646	1.0742	1.0871	1.1031	1.1170	1.1355
313.15	1.0182	1.0324	1.0476	1.0605	1.0702	1.0833	1.0993	1.1133	1.1324
318.15	1.0140	1.0283	1.0435	1.0565	1.0663	1.0795	1.0959	1.1097	1.1287
323.15	1.0099	1.0241	1.0395	1.0525	1.0624	1.0757	1.0920	1.1061	1.1253
328.15	1.0057	1.0200	1.0354	1.0485	1.0585	1.0720	1.0887	1.1025	1.1220
333.15	1.0016	1.0158	1.0313	1.0446	1.0546	1.0683	1.0851	1.0994	1.1186
338.15	0.9974	1.0117	1.0273	1.0406	1.0508	1.0648	1.0816	1.0956	1.1156
343.15	0.9932	1.0075	1.0232	1.0367	1.0471	1.0611	1.0781	1.0921	1.1120
348.15	0.9890	1.0034	1.0191	1.0329	1.0431	1.0574	1.0746	1.0886	1.1087
353.15	0.9848	0.9992	1.0151	1.0289	1.0393	1.0537	1.0708	1.0852	1.1054
358.15	0.9805	0.9950	1.0110	1.0248	1.0357	1.0501	1.0673	1.0818	1.1022
363.15	0.9762	0.9907	1.0071	1.0209	1.0317	1.0464	1.0638	1.0785	1.0989
368.15	0.9718	0.9865	1.0028	1.0169	1.0281	1.0426	1.0604	1.0751	1.0957
373.15	0.9674	0.9822	0.9987	1.0130	1.0240	1.0391	1.0571	1.0717	1.0924
[DEEA][H(Hex) <sub>2</sub> ](1)+[C <sub>4</sub> C <sub>1</sub> im][DMP](2)									
<b>x<sub>1</sub></b>	0.8535	0.7258	0.6088	0.4995	0.3966	0.3088	0.2213	0.1429	0.0684
<b>x<sub>2</sub></b>	0.1465	0.2742	0.3912	0.5005	0.6034	0.6912	0.7787	0.8571	0.9316
<b>Water content</b>	778	704	632	561	489	425	357	294	230
278.15	0.9931	1.0108	1.0279	1.0454	1.0633	1.0823	1.1037	1.1261	1.1503
283.15	0.9896	1.0071	1.0242	1.0416	1.0594	1.0784	1.1000	1.1225	1.1468
288.15	0.9860	1.0034	1.0204	1.0378	1.0556	1.0746	1.0962	1.1189	1.1433

293.15	0.9824	0.9997	1.0167	1.0340	1.0518	1.0709	1.0926	1.1152	1.1398
298.15	0.9788	0.9963	1.0129	1.0303	1.0481	1.0672	1.0890	1.1116	1.1363
303.15	0.9751	0.9926	1.0092	1.0265	1.0443	1.0635	1.0854	1.1081	1.1328
308.15	0.9715	0.9889	1.0054	1.0227	1.0405	1.0598	1.0818	1.1047	1.1294
313.15	0.9678	0.9852	1.0016	1.0189	1.0367	1.0562	1.0783	1.1012	1.1260
318.15	0.9641	0.9814	0.9981	1.0152	1.0329	1.0525	1.0747	1.0978	1.1227
323.15	0.9606	0.9777	0.9943	1.0114	1.0291	1.0489	1.0712	1.0944	1.1194
328.15	0.9569	0.9739	0.9904	1.0076	1.0253	1.0452	1.0677	1.0909	1.1160
333.15	0.9532	0.9701	0.9866	1.0038	1.0215	1.0415	1.0641	1.0875	1.1127
338.15	0.9494	0.9664	0.9828	1.0000	1.0177	1.0379	1.0606	1.0841	1.1094
343.15	0.9457	0.9626	0.9789	0.9965	1.0139	1.0343	1.0571	1.0807	1.1060
348.15	0.9419	0.9587	0.9751	0.9926	1.0102	1.0307	1.0536	1.0773	1.1027
353.15	0.9381	0.9549	0.9712	0.9888	1.0064	1.0270	1.0501	1.0739	1.0993
358.15	0.9343	0.9511	0.9673	0.9850	1.0027	1.0234	1.0466	1.0705	1.0960
363.15	0.9304	0.9472	0.9635	0.9812	0.9991	1.0198	1.0431	1.0671	1.0927
368.15	0.9265	0.9433	0.9596	0.9774	0.9954	1.0162	1.0396	1.0637	1.0893
373.15	0.9226	0.9394	0.9557	0.9736	0.9931	1.0126	1.0362	1.0604	1.0860

[DEEA][But](1)+[C<sub>4</sub>C<sub>1</sub>im][DMP](2)

<b>x<sub>1</sub></b>	0.8788	0.8006	0.6613	0.6001	0.4980	0.3985	0.3026	0.1989	0.1023
<b>x<sub>2</sub></b>	0.1212	0.1994	0.3387	0.3999	0.5020	0.6015	0.6974	0.8011	0.8977

<b>Water content</b>	698	641	544	504	440	381	326	270	220
----------------------	-----	-----	-----	-----	-----	-----	-----	-----	-----

278.15	1.0151	1.0270	1.0482	1.0574	1.0746	1.0920	1.1106	1.1319	1.1525
283.15	1.0107	1.0227	1.0439	1.0530	1.0704	1.0880	1.1068	1.1281	1.1487
288.15	1.0065	1.0185	1.0397	1.0491	1.0664	1.0841	1.1029	1.1245	1.1452
293.15	1.0023	1.0143	1.0357	1.0449	1.0625	1.0805	1.0993	1.1211	1.1419
298.15	0.9981	1.0101	1.0316	1.0409	1.0586	1.0765	1.0956	1.1174	1.1385
303.15	0.9939	1.0060	1.0275	1.0370	1.0547	1.0727	1.0920	1.1141	1.1351
308.15	0.9897	1.0018	1.0234	1.0331	1.0508	1.0689	1.0886	1.1106	1.1317



313.15	0.9855	0.9977	1.0194	1.0292	1.0469	1.0652	1.0848	1.1070	1.1280
318.15	0.9813	0.9935	1.0154	1.0253	1.0431	1.0615	1.0812	1.1035	1.1247
323.15	0.9772	0.9894	1.0114	1.0214	1.0393	1.0578	1.0779	1.1001	1.1213
328.15	0.9730	0.9852	1.0074	1.0174	1.0355	1.0541	1.0744	1.0967	1.1179
333.15	0.9688	0.9811	1.0033	1.0134	1.0317	1.0506	1.0708	1.0933	1.1146
338.15	0.9646	0.9769	0.9993	1.0095	1.0279	1.0468	1.0674	1.0901	1.1112
343.15	0.9604	0.9728	0.9954	1.0056	1.0241	1.0434	1.0636	1.0865	1.1079
348.15	0.9562	0.9686	0.9914	1.0017	1.0206	1.0396	1.0604	1.0832	1.1046
353.15	0.9520	0.9644	0.9875	0.9977	1.0166	1.0362	1.0567	1.0798	1.1014
358.15	0.9477	0.9602	0.9833	0.9938	1.0129	1.0326	1.0535	1.0765	1.0981
363.15	0.9434	0.9560	0.9793	0.9899	1.0091	1.0291	1.0501	1.0734	1.0948
368.15	0.9391	0.9518	0.9753	0.9860	1.0056	1.0255	1.0464	1.0698	1.0916
373.15	0.9347	0.9476	0.9714	0.9821	1.0018	1.0219	1.0432	1.0665	1.0883
[DEEA][Pent](1)+[C <sub>4</sub> C <sub>1</sub> im][DMP](2)									
<b>x<sub>1</sub></b>	0.8868	0.7978	0.6984	0.5989	0.4973	0.4003	0.3029	0.1952	0.1018
<b>x<sub>2</sub></b>	0.1132	0.2022	0.3016	0.4011	0.5027	0.5997	0.6971	0.8048	0.8982
<b>Water content</b>	726	662	592	525	459	399	340	277	225
278.15	0.9999	1.0142	1.0313	1.0468	1.0643	1.0820	1.1040	1.1275	1.1501
283.15	0.9956	1.0100	1.0271	1.0426	1.0602	1.0778	1.1001	1.1237	1.1463
288.15	0.9914	1.0059	1.0230	1.0386	1.0562	1.0738	1.0966	1.1202	1.1428
293.15	0.9873	1.0018	1.0189	1.0346	1.0523	1.0699	1.0928	1.1167	1.1396
298.15	0.9832	0.9977	1.0149	1.0306	1.0484	1.0661	1.0892	1.1131	1.1362
303.15	0.9791	0.9937	1.0109	1.0267	1.0445	1.0623	1.0855	1.1097	1.1327
308.15	0.9750	0.9896	1.0068	1.0228	1.0407	1.0587	1.0820	1.1062	1.1292
313.15	0.9709	0.9856	1.0028	1.0188	1.0368	1.0554	1.0784	1.1030	1.1258
318.15	0.9668	0.9815	0.9988	1.0149	1.0330	1.0517	1.0749	1.0995	1.1226
323.15	0.9627	0.9774	0.9948	1.0110	1.0292	1.0486	1.0716	1.0958	1.1190
328.15	0.9586	0.9734	0.9908	1.0071	1.0254	1.0453	1.0681	1.0927	1.1157

333.15	0.9545	0.9693	0.9868	1.0033	1.0217	1.0420	1.0646	1.0893	1.1126
338.15	0.9504	0.9653	0.9829	0.9994	1.0182	1.0387	1.0611	1.0859	1.1090
343.15	0.9463	0.9612	0.9789	0.9956	1.0143	1.0350	1.0576	1.0825	1.1057
348.15	0.9421	0.9571	0.9749	0.9917	1.0106	1.0317	1.0542	1.0789	1.1024
353.15	0.9380	0.9530	0.9709	0.9878	1.0069	1.0282	1.0505	1.0756	1.0992
358.15	0.9338	0.9489	0.9669	0.9840	1.0032	1.0246	1.0473	1.0722	1.0959
363.15	0.9296	0.9448	0.9629	0.9801	0.9996	1.0211	1.0436	1.0689	1.0929
368.15	0.9254	0.9407	0.9589	0.9762	0.9961	1.0173	1.0405	1.0656	1.0894
373.15	0.9211	0.9365	0.9548	0.9724	0.9924	1.0138	1.0368	1.0623	1.0862
[BHEA][Ace](1)+[C <sub>4</sub> C <sub>1</sub> im][DMP](2)									
$x_1$	0.8913	0.8011	0.7065	0.6316	0.4989	0.4067	0.2979	0.1720	0.1014
$x_2$	0.1087	0.1989	0.2935	0.3684	0.5011	0.5933	0.7021	0.8280	0.8986
<b>Water content</b>	463	423	384	355	309	279	246	212	194
283.15	1.0423	1.0560	1.0701	1.0819	1.1016	1.1142	1.1301	1.1480	1.1576
288.15	1.0388	1.0524	1.0664	1.0782	1.0979	1.1105	1.1264	1.1444	1.1541
293.15	1.0353	1.0488	1.0627	1.0744	1.0941	1.1067	1.1227	1.1408	1.1506
298.15	1.0316	1.0450	1.0589	1.0706	1.0903	1.1030	1.1189	1.1372	1.1470
303.15	1.0279	1.0413	1.0552	1.0669	1.0866	1.0993	1.1152	1.1336	1.1435
308.15	1.0243	1.0376	1.0515	1.0632	1.0829	1.0956	1.1116	1.1301	1.1400
313.15	1.0206	1.0339	1.0478	1.0595	1.0792	1.0919	1.1080	1.1266	1.1366
318.15	1.0170	1.0302	1.0441	1.0558	1.0755	1.0883	1.1045	1.1232	1.1332
323.15	1.0133	1.0265	1.0405	1.0521	1.0718	1.0847	1.1009	1.1197	1.1299
328.15	1.0096	1.0228	1.0367	1.0484	1.0681	1.0810	1.0974	1.1163	1.1266
333.15	1.0059	1.0190	1.0330	1.0446	1.0644	1.0774	1.0938	1.1128	1.1232
338.15	1.0021	1.0152	1.0291	1.0408	1.0606	1.0737	1.0902	1.1094	1.1198
343.15	0.9986	1.0114	1.0253	1.0370	1.0569	1.0700	1.0867	1.1059	1.1165
348.15	0.9948	1.0075	1.0214	1.0331	1.0531	1.0663	1.0831	1.1025	1.1131
353.15	0.9909	1.0036	1.0175	1.0293	1.0493	1.0626	1.0795	1.0990	1.1098
358.15	0.9870	0.9997	1.0136	1.0254	1.0455	1.0589	1.0759	1.0956	1.1064

363.15	0.9831	0.9961	1.0097	1.0215	1.0417	1.0552	1.0723	1.0922	1.1030
368.15	0.9791	0.9921	1.0058	1.0176	1.0379	1.0515	1.0687	1.0888	1.0997
373.15	0.9752	0.9882	1.0019	1.0137	1.0341	1.0478	1.0652	1.0854	1.0964
[BHEA][Ace](1)+[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ](2)									
<b>x<sub>1</sub></b>	0.9010	0.8008	0.6987	0.6018	0.4998	0.4230	0.3002	0.2257	0.1012
<b>x<sub>2</sub></b>	0.0990	0.1992	0.3013	0.3982	0.5002	0.5770	0.6998	0.7743	0.8988
<b>Water content</b>	468	429	397	372	350	335	316	305	290
283.15	1.0919	1.1511	1.2046	1.2490	1.2917	1.3208	1.3628	1.3872	
288.15	1.0883	1.1473	1.2005	1.2447	1.2872	1.3163	1.3588	1.3826	
293.15	1.0847	1.1435	1.1964	1.2405	1.2829	1.3119	1.3547	1.3780	
298.15	1.0810	1.1395	1.1922	1.2363	1.2786	1.3075	1.3504	1.3734	
303.15	1.0772	1.1355	1.1882	1.2321	1.2743	1.3031	1.3459	1.3688	
308.15	1.0734	1.1316	1.1841	1.2279	1.2700	1.2987	1.3414	1.3642	1.3990
313.15	1.0697	1.1277	1.1801	1.2238	1.2657	1.2943	1.3369	1.3595	1.3950
318.15	1.0660	1.1239	1.1761	1.2196	1.2614	1.2899	1.3323	1.3549	1.3907
323.15	1.0622	1.1200	1.1720	1.2154	1.2570	1.2855	1.3277	1.3503	1.3861
328.15	1.0585	1.1161	1.1679	1.2112	1.2526	1.2810	1.3232	1.3456	1.3815
333.15	1.0547	1.1121	1.1638	1.2069	1.2482	1.2765	1.3186	1.3410	1.3768
338.15	1.0509	1.1081	1.1596	1.2025	1.2438	1.2721	1.3139	1.3363	1.3721
343.15	1.0470	1.1041	1.1554	1.1982	1.2394	1.2676	1.3093	1.3316	1.3674
348.15	1.0431	1.1000	1.1512	1.1940	1.2349	1.2630	1.3047	1.3270	1.3627
353.15	1.0391	1.0959	1.1469	1.1896	1.2304	1.2585	1.3001	1.3223	1.3580
358.15	1.0352	1.0918	1.1427	1.1853	1.2259	1.2539	1.2954	1.3176	1.3533
363.15	1.0311	1.0876	1.1384	1.1809	1.2214	1.2494	1.2908	1.3129	1.3486
368.15	1.0271	1.0834	1.1340	1.1764	1.2169	1.2448	1.2861	1.3083	1.3439
373.15	1.0230	1.0792	1.1297	1.1720	1.2124	1.2402	1.2815	1.3036	1.3393

<sup>a</sup>Standard uncertainties,  $u$ , are:  $u(T) = 0.02$  K,  $u_r(x) = 0.002$ ,  $u(\rho) = 0.0005$  g·cm<sup>-3</sup> and  $u_r(\rho) = 0.05$ .

**Table S5.** Redlich–Kister expansion parameters for the correlation of the excess molar volumes along with the corresponding standard deviation.

	$a_1$	$a_2$	$a_3$	$a_4$	$b_1$	$b_2$	$b_3$	$b_4$	$\sigma$
[DEEA][H(Ace) <sub>2</sub> ]+[C <sub>4</sub> C <sub>1</sub> im][DMP]	-9.941	-7.664	8.572	1.423	0.061	-0.017	-0.023	0.046	0.03
[DEEA][H(Prop) <sub>2</sub> ]+[C <sub>4</sub> C <sub>1</sub> im][DMP]	-8.281	-16.655	0.085	0.076	0.063	0.017	0.013	0.046	0.18
[DEEA][H(Hex) <sub>2</sub> ]+[C <sub>4</sub> C <sub>1</sub> im][DMP]	-11.184	-9.529	15.106	10.288	0.067	-0.004	-0.057	0.001	0.08
[DEEA][But]+[C <sub>4</sub> C <sub>1</sub> im][DMP]	7.704	-0.552	1.820	0.540	0.017	0.000	-0.022	0.001	0.07
[DEEA][Pent]+[C <sub>4</sub> C <sub>1</sub> im][DMP]	10.545	-1.576	2.018	0.366	0.007	-0.003	-0.026	0.011	0.14
[BHEA][Ace]+[C <sub>4</sub> C <sub>1</sub> im][DMP]	-10.223	0.531	-0.731	0.893	0.052	0.001	-0.001	0.002	0.05
[BHEA][Ace]+[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]	-1.844	1.226	0.528	1.100	0.007	-0.009	-0.003	-0.006	0.05

**Table S6.** Viscosities and water content (ppm) of the ionic liquids mixtures at different temperatures and compositions.<sup>a</sup>

<i>T</i> / K	$\eta_{\text{mixture}} / \text{mPa}\cdot\text{s}$								
	[DEEA][H(Ace) <sub>2</sub> ](1)+[C <sub>4</sub> C <sub>1</sub> im][DMP](2)								
<i>x</i> <sub>1</sub>	0.8567	0.7493	0.6343	0.5275	0.4263	0.3316		0.0748	
<i>x</i> <sub>2</sub>	0.1433	0.2507	0.3657	0.4725	0.5737	0.6684		0.9252	
<b>Water content</b>	226	218	210	203	196	190		174	
278.15	310.05	314.40	329.15	334.59	362.69	453.16		2020.40	
283.15	210.05	220.04	229.00	234.66	254.32	314.65		1280.50	
288.15	146.33	157.87	164.02	168.31	183.68	224.35		839.67	
293.15	104.72	116.28	120.63	124.02	135.25	164.33		568.03	
298.15	76.88	87.95	91.10	93.67	102.22	123.73		396.00	
303.15	57.76	67.90	70.26	72.40	79.01	95.17		283.61	
308.15	44.33	53.39	55.21	57.04	62.24	74.59		207.98	
313.15	34.65	41.14	42.60	44.19	48.55	58.30		155.81	
318.15	27.56	34.54	35.71	36.97	40.43	48.01		119.09	
323.15	22.27	28.27	29.17	30.28	33.11	39.18		92.68	
328.15	18.26	23.34	24.08	25.04	27.40	32.29		73.28	
333.15	15.16	17.41	18.02	18.82	20.72	24.59		58.80	
338.15	12.72	16.24	16.79	17.53	19.20	22.48		47.83	
343.15	10.79	13.68	14.16	14.82	16.24	18.97		39.38	
348.15	9.24	11.59	12.02	12.60	13.83	16.13		32.81	
353.15	7.98	9.16	9.54	10.04	11.07	12.97		27.63	
358.15	6.94	8.46	8.82	9.30	10.22	11.89		23.49	
363.15	6.09	7.29	7.63	8.06	8.87	10.32		20.16	
368.15	5.37	6.33	6.64	7.03	7.75	9.01		17.45	
373.15	4.76	5.43	5.71	6.06	6.70	7.79		15.23	
	[DEEA][H(Prop) <sub>2</sub> ](1)+[C <sub>4</sub> C <sub>1</sub> im][DMP](2)								
<i>x</i> <sub>1</sub>	0.8667	0.7416	0.6252	0.4953	0.4183	0.3281	0.2364	0.1549	0.0800
<i>x</i> <sub>2</sub>	0.1333	0.2584	0.3748	0.5047	0.5817	0.6719	0.7636	0.8451	0.9200

<b>Water content</b>	284	267	252	235	225	213	201	190	180
278.15	184.23	208.24	241.42	293.55	328.86	428.43	655.09	1099.10	1955.90
283.15	131.05	147.73	170.95	205.57	230.27	296.91	445.60	725.57	1248.10
288.15	95.27	107.15	123.78	147.54	165.25	211.12	311.40	493.75	821.85
293.15	70.84	79.52	91.72	108.59	121.50	153.95	223.34	345.69	558.77
298.15	53.78	60.29	69.46	81.76	91.39	114.90	164.20	248.60	391.03
303.15	41.64	46.61	53.65	62.83	70.18	87.58	123.43	183.16	280.90
308.15	32.83	36.68	42.19	49.19	54.90	68.05	94.67	137.86	206.64
313.15	26.32	29.33	33.72	39.17	43.67	53.80	73.94	105.84	155.27
318.15	21.38	23.81	27.36	31.69	35.28	43.21	58.71	82.71	118.96
323.15	17.60	19.58	22.51	25.98	28.91	35.21	47.32	65.70	92.73
328.15	14.65	16.29	18.74	21.58	23.98	29.06	38.66	52.95	73.49
333.15	12.33	13.70	15.77	18.11	20.13	24.27	31.98	43.24	59.07
338.15	10.47	11.64	13.40	15.33	17.07	20.49	26.76	35.76	48.11
343.15	8.98	9.98	11.50	13.09	14.60	17.47	22.63	29.90	39.67
348.15	7.75	8.63	9.95	11.29	12.61	15.03	19.32	25.27	33.08
353.15	6.75	7.52	8.67	9.81	10.98	13.04	16.64	21.56	27.89
358.15	5.91	6.59	7.61	8.59	9.63	11.40	14.45	18.56	23.73
363.15	5.21	5.82	6.72	7.58	8.50	10.04	12.65	16.10	20.39
368.15	4.62	5.16	5.98	6.73	7.55	8.90	11.15	14.09	17.66
373.15	4.11	4.60	5.34	6.01	6.75	7.94	9.89	12.40	15.41
[DEEA][H(Hex) <sub>2</sub> ](1)+[C <sub>4</sub> C <sub>1</sub> im][DMP](2)									
<b>x<sub>1</sub></b>	0.8535	0.7258	0.6088	0.4995	0.3966	0.3088	0.2213	0.1429	0.0684
<b>x<sub>2</sub></b>	0.1465	0.2742	0.3912	0.5005	0.6034	0.6912	0.7787	0.8571	0.9316
<b>Water content</b>	778	704	632	561	489	425	357	294	230
278.15	217.25	255.88	295.27	342.99	412.45	529.09	768.35	1198.10	2020.50
283.15	159.02	185.26	211.57	242.54	288.73	365.41	519.83	787.13	1279.60
288.15	118.90	137.17	155.10	176.09	207.69	259.67	362.38	534.71	840.65
293.15	90.52	103.51	116.04	130.67	152.86	189.06	259.32	373.78	570.10
298.15	70.07	79.51	88.48	98.94	114.92	140.77	190.07	268.20	398.06

303.15	55.10	62.08	68.65	76.32	88.10	106.98	142.39	197.06	285.36
308.15	43.94	49.21	54.11	59.86	68.74	82.82	108.77	147.88	209.38
313.15	35.51	39.55	43.28	47.69	54.51	65.21	84.60	113.17	156.96
318.15	29.04	32.20	35.09	38.54	43.87	52.14	66.90	88.15	119.97
323.15	24.02	26.52	28.81	31.55	35.80	42.29	53.69	69.79	93.34
328.15	20.07	22.08	23.92	26.14	29.57	34.74	43.70	56.08	73.82
333.15	16.93	18.56	20.08	21.89	24.70	28.88	36.01	45.69	59.25
338.15	14.40	15.76	17.01	18.53	20.85	24.28	30.03	37.68	48.21
343.15	12.35	13.48	14.54	15.82	17.77	20.61	25.30	31.44	39.73
348.15	10.67	11.63	12.53	13.63	15.28	17.66	21.54	26.52	33.12
353.15	9.27	10.11	10.89	11.83	13.25	15.27	18.50	22.58	27.90
358.15	8.11	8.84	9.52	10.34	11.58	13.30	16.02	19.41	23.74
363.15	7.13	7.77	8.38	9.10	10.19	11.67	13.98	16.82	20.39
368.15	6.30	6.87	7.42	8.06	9.02	10.31	12.30	14.68	17.66
373.15	5.59	6.11	6.60	7.18	8.04	9.17	10.88	12.91	15.41
[DEEA][But](1)+[C <sub>4</sub> C <sub>1</sub> im][DMP](2)									
<b>x<sub>1</sub></b>	0.8788	0.8006	0.6613	0.6001	0.4980	0.3985	0.3026	0.1989	0.1023
<b>x<sub>2</sub></b>	0.1212	0.1994	0.3387	0.3999	0.5020	0.6015	0.6974	0.8011	0.8977
<b>Water content</b>	698	641	544	504	440	381	326	270	220
278.15	191.00	196.81	231.03	255.24	322.40	445.02	670.57	1152.20	2057.90
283.15	136.48	140.95	165.40	182.33	228.53	311.50	459.05	764.34	1309.90
288.15	99.62	103.18	121.09	133.24	165.89	223.44	322.92	522.44	863.95
293.15	74.21	77.11	90.51	99.45	123.08	163.92	232.99	366.71	587.08
298.15	56.38	58.76	69.02	75.76	93.26	122.92	172.08	264.27	410.74
303.15	43.60	45.58	53.58	58.76	72.00	93.97	129.77	194.79	294.91
308.15	34.28	35.94	42.29	46.34	56.55	73.21	99.76	146.67	216.64
313.15	27.36	28.77	33.88	37.10	45.11	57.98	78.02	112.55	162.66
318.15	22.14	23.35	27.53	30.12	36.50	46.61	61.99	87.89	124.40
323.15	18.14	19.20	22.66	24.77	29.93	37.99	49.98	69.72	96.88
328.15	15.04	15.97	18.87	20.62	24.84	31.37	40.85	56.15	76.70

333.15	12.60	13.42	15.88	17.35	20.85	26.18	33.80	45.81	61.58
338.15	10.66	11.39	13.49	14.74	17.68	22.09	28.27	37.83	50.11
343.15	9.09	9.74	11.56	12.63	15.13	18.82	23.89	31.59	41.29
348.15	7.82	8.41	9.99	10.92	13.05	16.18	20.38	26.65	34.41
353.15	6.78	7.30	8.69	9.51	11.35	14.02	17.55	22.70	28.99
358.15	5.92	6.39	7.62	8.33	9.95	12.24	15.22	19.51	24.65
363.15	5.20	5.63	6.72	7.36	8.77	10.76	13.30	16.90	21.15
368.15	4.60	4.99	5.97	6.53	7.78	9.52	11.71	14.76	18.30
373.15	4.08	4.45	5.33	5.84	6.95	8.47	10.37	12.97	15.96
[DEEA][Pent](1)+[C <sub>4</sub> C <sub>1</sub> im][DMP](2)									
$x_1$	0.8868	0.7978	0.6984	0.5989	0.4973	0.4003	0.3029	0.1952	0.1018
$x_2$	0.1132	0.2022	0.3016	0.4011	0.5027	0.5997	0.6971	0.8048	0.8982
<b>Water content</b>	726	662	592	525	459	399	340	277	225
278.15	171.40	190.64	216.76	250.78	318.20	439.88	676.01	1185.70	2088.20
283.15	123.89	137.61	156.20	180.34	226.83	309.00	464.01	785.53	1327.50
288.15	91.43	101.46	114.99	132.55	165.47	222.46	327.11	536.33	874.13
293.15	68.79	76.33	86.36	99.40	123.28	163.75	236.34	376.31	594.30
298.15	52.75	58.54	66.12	76.04	93.78	123.25	174.78	271.22	415.55
303.15	41.15	45.65	51.52	59.21	72.66	94.57	131.99	199.87	298.45
308.15	32.59	36.17	40.78	46.85	57.24	73.84	101.57	150.44	219.31
313.15	26.19	29.07	32.76	37.62	45.77	58.57	79.49	115.41	164.69
318.15	21.33	23.66	26.67	30.62	37.12	47.13	63.20	90.07	126.01
323.15	17.59	19.50	21.99	25.23	30.50	38.46	50.96	71.43	98.11
328.15	14.66	16.26	18.34	21.04	25.35	31.79	41.66	57.48	77.67
333.15	12.34	13.70	15.45	17.73	21.30	26.54	34.47	46.87	62.36
338.15	10.49	11.64	13.14	15.08	18.07	22.42	28.83	38.69	50.75
343.15	8.99	9.98	11.27	12.94	15.48	19.11	24.35	32.29	41.81
348.15	7.76	8.63	9.74	11.19	13.36	16.43	20.77	27.23	34.84
353.15	6.75	7.51	8.48	9.76	11.63	14.23	17.87	23.18	29.34
358.15	5.91	6.58	7.44	8.56	10.19	12.43	15.50	19.90	24.95



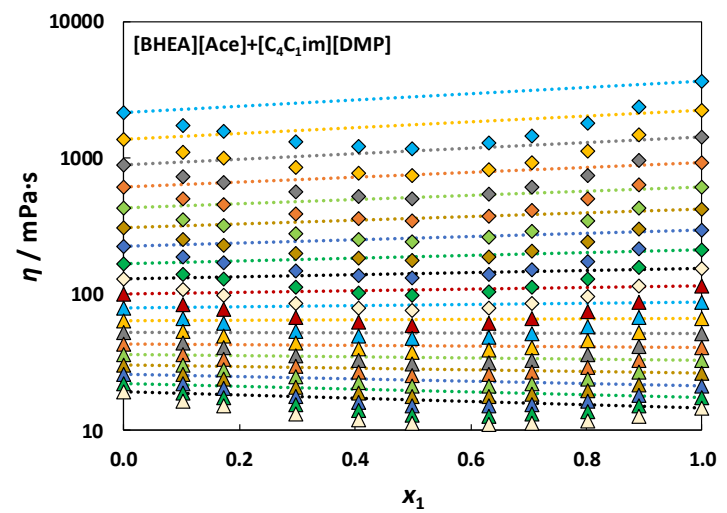
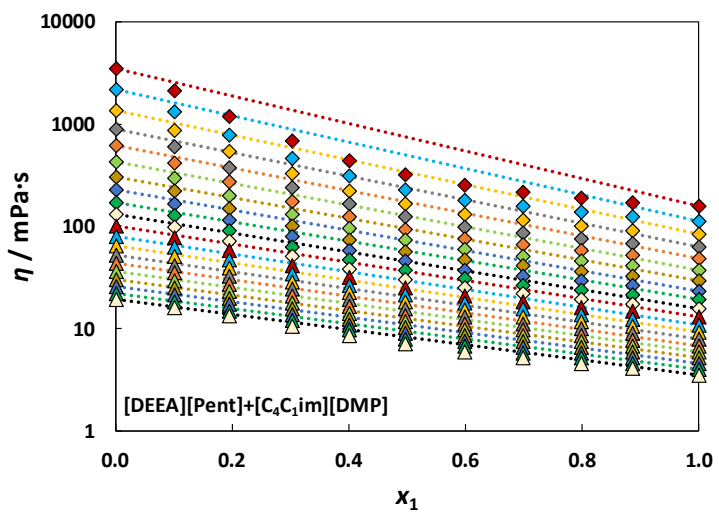
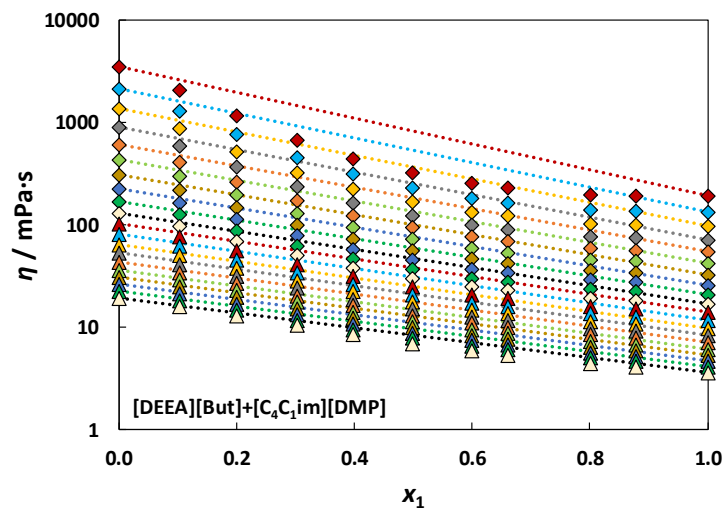
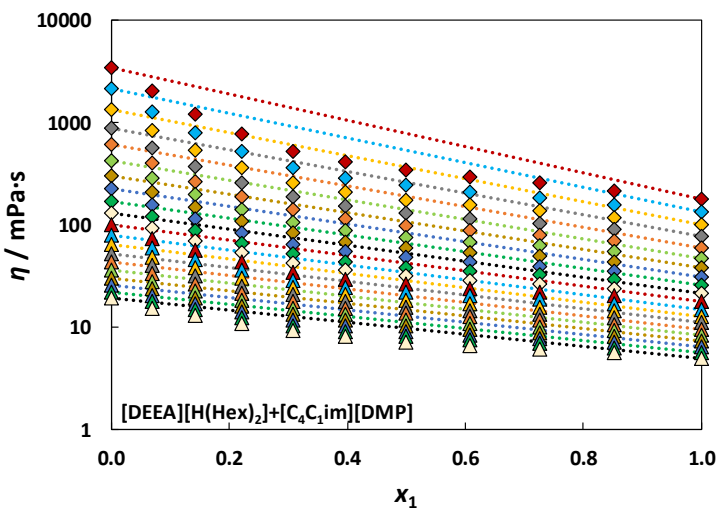
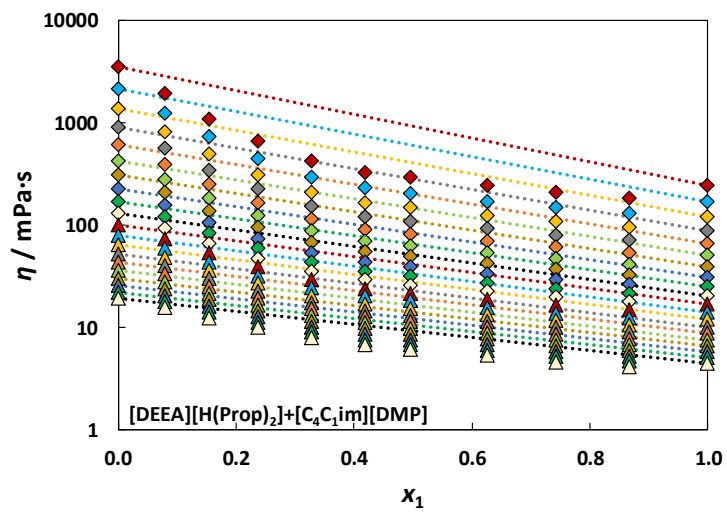
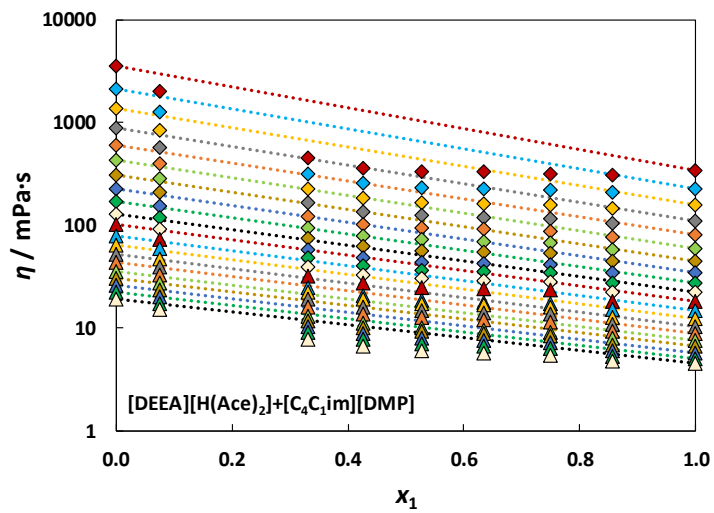
363.15	5.20	5.81	6.56	7.56	8.99	10.92	13.54	17.23	21.41
368.15	4.61	5.15	5.83	6.72	7.98	9.66	11.92	15.03	18.52
373.15	4.10	4.59	5.20	6.00	7.12	8.60	10.55	13.21	16.15
[BHEA][Ace](1)+[C <sub>4</sub> C <sub>1</sub> im][DMP](2)									
<b>x<sub>1</sub></b>	0.8913	0.8011	0.7065	0.6316	0.4989	0.4067	0.2979	0.1720	0.1014
<b>x<sub>2</sub></b>	0.1087	0.1989	0.2935	0.3684	0.5011	0.5933	0.7021	0.8280	0.8986
<b>Water content</b>	463	423	384	355	309	279	246	212	194
283.15	2359.90	1793.10	1456.80	1287.50	1160.80	1207.90	1327.60	1555.40	1724.90
288.15	1474.60	1134.80	930.21	825.28	751.15	780.79	855.27	996.92	1102.60
293.15	952.02	741.48	613.79	548.15	502.51	522.07	570.64	662.30	730.45
298.15	632.53	498.65	416.82	374.80	346.30	359.52	392.45	453.85	499.31
303.15	431.25	344.12	290.56	263.10	244.79	254.29	277.35	319.82	351.11
308.15	301.02	243.20	207.41	189.09	177.17	184.24	200.89	231.06	253.19
313.15	214.84	175.66	151.31	138.86	131.07	136.47	148.74	170.81	186.80
318.15	156.46	129.45	112.63	104.03	98.92	103.14	112.43	128.90	140.74
323.15	116.10	97.18	85.38	79.37	76.03	79.40	86.59	99.13	108.08
328.15	87.66	74.22	65.85	61.57	59.42	62.17	67.84	77.57	84.47
333.15	67.26	57.58	51.57	48.50	47.16	49.43	53.98	61.68	67.08
338.15	52.38	45.33	40.98	38.75	37.96	39.88	43.58	49.76	54.05
343.15	41.36	36.18	33.00	31.37	30.96	32.60	35.65	40.69	44.14
348.15	33.08	29.24	26.90	25.71	25.56	26.96	29.51	33.69	36.50
353.15	26.78	23.90	22.18	21.31	21.33	22.56	24.71	28.22	30.53
358.15	21.91	19.75	18.48	17.86	17.99	19.07	20.91	23.88	25.80
363.15	18.11	16.48	15.55	15.10	15.31	16.27	17.86	20.40	22.02
368.15	15.12	13.89	13.21	12.89	13.15	14.01	15.40	17.58	18.97
373.15	12.72	11.80	11.30	11.09	11.38	12.15	13.38	15.28	16.47
[BHEA][Ace](1)+[C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ](2)									
<b>x<sub>1</sub></b>	0.9010	0.8008	0.6987	0.6018	0.4998	0.4230	0.3002	0.2257	0.1012
<b>x<sub>2</sub></b>	0.0990	0.1992	0.3013	0.3982	0.5002	0.5770	0.6998	0.7743	0.8988
<b>Water content</b>	468	429	397	372	350	335	316	305	290

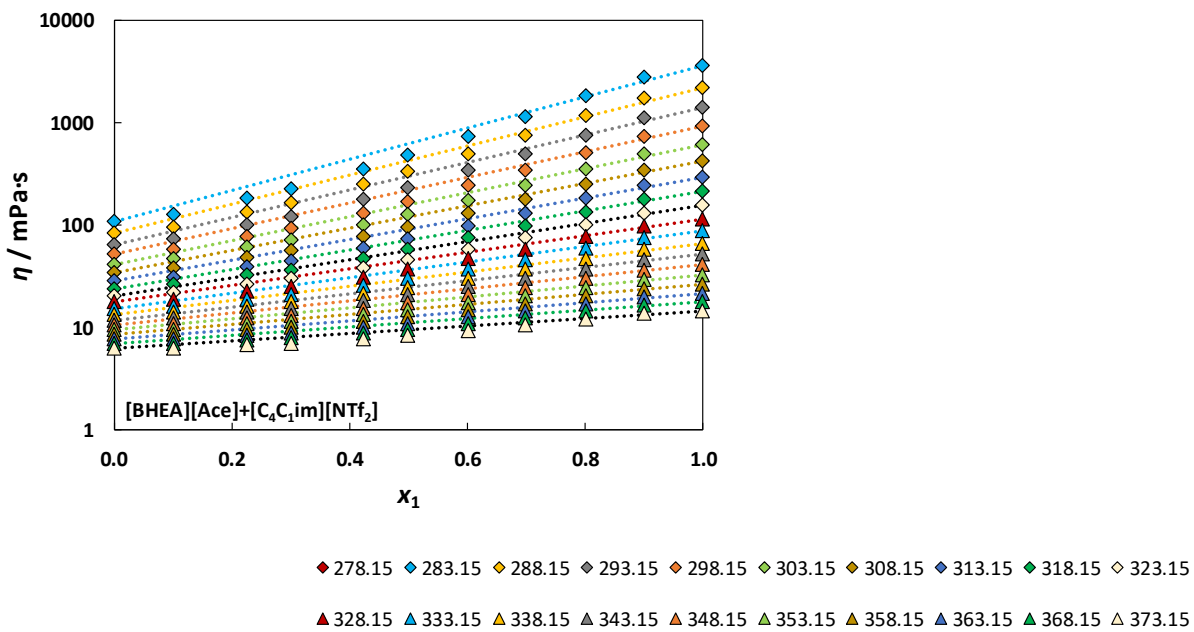
283.15	2806.30	1849.70	1144.50	744.86	481.26	353.37	226.67	183.09	127.37
288.15	1734.80	1169.70	745.32	498.75	331.48	248.27	164.23	134.73	96.23
293.15	1109.30	764.85	500.68	343.74	234.66	179.13	121.91	101.49	74.29
298.15	731.02	514.86	345.74	243.13	170.15	132.24	92.44	78.02	58.45
303.15	495.00	355.73	244.73	176.02	126.13	99.69	71.45	61.09	46.77
308.15	343.49	251.68	177.16	130.15	95.34	76.57	56.19	48.63	38.01
313.15	243.79	181.97	130.89	98.11	73.38	59.83	44.89	39.30	31.32
318.15	176.63	134.20	98.54	75.27	57.42	47.48	36.38	32.20	26.13
323.15	130.41	100.81	75.47	58.70	45.61	38.23	29.87	26.72	22.05
328.15	97.99	77.01	58.73	46.47	36.74	31.18	24.83	22.42	18.81
333.15	74.82	59.75	46.37	37.29	29.98	25.75	20.86	19.00	16.19
338.15	58.01	47.02	37.11	30.30	24.74	21.49	17.70	16.27	14.06
343.15	45.60	37.51	30.07	24.92	20.65	18.12	15.16	14.05	12.31
348.15	36.31	30.28	24.65	20.70	17.40	15.42	13.09	12.23	10.85
353.15	29.26	24.73	20.42	17.37	14.79	13.24	11.40	10.72	9.63
358.15	23.84	20.41	17.08	14.71	12.68	11.46	9.99	9.47	8.60
363.15	19.63	17.00	14.42	12.57	10.96	9.98	8.82	8.41	7.73
368.15	16.31	14.29	12.27	10.81	9.54	8.76	7.83	7.51	6.98
373.15	13.67	12.11	10.52	9.37	8.35	7.73	6.99	6.75	6.33

<sup>a</sup>Standard uncertainties,  $u$ , are:  $u(T) = 0.02$  K,  $u_r(x) = 0.002$ ,  $u_r(\eta) = 0.35\%$  and  $u_r(\rho) = 0.05$ .

**Table S7.** Grunberg and Nissan parameters,  $G_{12}$ .

	[DEEA][H(Ace) <sub>2</sub> ] + [C <sub>4</sub> C <sub>1</sub> im][DMP]	[DEEA][H(Prop) <sub>2</sub> ] + [C <sub>4</sub> C <sub>1</sub> im][DMP]	[DEEA][H(Hex) <sub>2</sub> ] + [C <sub>4</sub> C <sub>1</sub> im][DMP]	[DEEA][But] + [C <sub>4</sub> C <sub>1</sub> im][DMP]	[DEEA][Pent] + [C <sub>4</sub> C <sub>1</sub> im][DMP]	[BHEA][Ace] + [C <sub>4</sub> C <sub>1</sub> im][DMP]	[BHEA][Ace] + [C <sub>4</sub> C <sub>1</sub> im][NTf <sub>2</sub> ]
278.15	-4.48	-5.14	-4.01	-3.61	-3.23		
283.15	-4.12	-4.80	-3.76	-3.32	-2.97	-3.51	-1.07
288.15	-3.80	-4.50	-3.53	-3.03	-2.73	-3.36	-1.05
293.15	-3.50	-4.23	-3.32	-2.77	-2.49	-3.22	-1.02
298.15	-3.22	-3.98	-3.13	-2.57	-2.26	-3.08	-0.99
303.15	-2.95	-3.75	-2.95	-2.38	-2.05	-2.96	-0.96
308.15	-2.70	-3.54	-2.79	-2.20	-1.86	-2.83	-0.93
313.15	-2.60	-3.34	-2.64	-2.04	-1.68	-2.71	-0.91
318.15	-2.27	-3.16	-2.50	-1.88	-1.53	-2.60	-0.88
323.15	-2.10	-2.99	-2.37	-1.72	-1.42	-2.49	-0.85
328.15	-1.95	-2.83	-2.25	-1.60	-1.31	-2.39	-0.82
333.15	-2.25	-2.64	-2.14	-1.48	-1.21	-2.28	-0.79
338.15	-1.74	-2.48	-2.03	-1.37	-1.12	-2.18	-0.76
343.15	-1.66	-2.34	-1.93	-1.28	-1.03	-2.08	-0.73
348.15	-1.60	-2.20	-1.83	-1.18	-0.95	-1.99	-0.70
353.15	-1.85	-2.11	-1.74	-1.09	-0.85	-1.90	-0.68
358.15	-1.53	-2.02	-1.65	-0.99	-0.76	-1.81	-0.65
363.15	-1.51	-1.94	-1.57	-0.91	-0.68	-1.72	-0.62
368.15	-1.50	-1.85	-1.48	-0.82	-0.60	-1.64	-0.60
373.15	-1.56	-1.76	-1.40	-0.74	-0.53	-1.56	-0.57





**Figure S4.** Viscosity versus mole fraction of the protic IL for the investigated systems at different temperatures. Symbols represent experimental values and the solid curves represent the Grunberg and Nissan ideal ( $G_{12} = 0$ ) predictions.