

*Supporting Information*

**The polarity effect upon the methane solubility  
in ionic liquids: A contribution for the design of  
ionic liquids for enhanced CO<sub>2</sub>/CH<sub>4</sub> and  
H<sub>2</sub>S/CH<sub>4</sub> selectivities**

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**Table S1.** Bubble point data of the system CH<sub>4</sub> (1) + [THTDP][NTf<sub>2</sub>] (2).

$x_1$	$T/K$	$p/MPa$	$x_1$	$T/K$	$p/MPa$	$x_1$	$T/K$	$p/MPa$	$x_1$	$T/K$	$p/MPa$	$x_1$	$T/K$	$p/MPa$
0.123	293.00	1.264	0.209	293.09	2.384	0.297	293.12	4.229	0.398	293.23	7.428	0.503	293.28	12.005
0.123	303.15	1.426	0.209	303.23	2.632	0.297	303.39	4.564	0.398	303.07	7.978	0.503	303.21	12.742
0.123	313.43	1.640	0.209	313.42	2.879	0.297	313.44	4.905	0.398	313.24	8.436	0.503	313.06	13.421
0.123	323.56	1.781	0.209	323.18	3.127	0.297	323.29	5.225	0.398	323.24	8.927	0.503	323.32	14.052
0.123	333.31	1.943	0.209	333.26	3.345	0.297	333.24	5.550	0.398	333.26	9.357	0.503	333.29	14.625
0.123	343.11	2.115	0.209	343.08	3.557	0.297	343.10	5.870	0.398	343.39	9.787	0.503	343.22	15.205
0.123	353.11	2.261	0.209	353.14	3.777	0.297	353.17	6.185	0.398	353.26	10.165	0.503	353.09	15.735
0.123	363.30	2.417	0.209	363.09	4.032	0.297	363.20	6.390	0.398	363.43	10.536	0.503	363.23	16.263
$x_1$	$T/K$	$p/MPa$	$x_1$	$T/K$	$p/MPa$	$x_1$	$T/K$	$p/MPa$	$x_1$	$T/K$	$p/MPa$	$x_1$	$T/K$	$p/MPa$
0.606	293.33	21.051	0.664	293.07	29.481	0.712	293.29	40.393	0.755	293.06	54.028	0.786	293.13	64.054
0.606	303.12	21.795	0.664	303.37	30.205	0.712	303.21	40.498	0.755	303.21	53.467	0.786	303.26	63.608
0.606	313.08	22.407	0.664	313.42	30.778	0.712	313.22	40.732	0.755	313.14	53.286	0.786	313.42	62.834
0.606	323.30	23.085	0.664	323.46	31.328	0.712	323.10	40.905	0.755	323.25	53.110	0.786	323.44	61.974
0.606	333.20	23.696	0.664	333.46	31.843	0.712	333.17	41.175	0.755	333.24	52.783	0.786	333.28	61.285
0.606	343.13	24.275	0.664	343.25	32.266	0.712	343.28	41.270	0.755	343.18	52.558	0.786	343.20	60.375
0.606	353.34	24.835	0.664	353.30	32.934	0.712	353.23	41.545	0.755	353.24	52.664	0.786	353.44	59.839
0.606	363.26	25.245	0.664	363.26	33.429	0.712	363.52	41.762	0.755	363.34	52.485	0.786	363.22	59.473
												0.853	363.73	99.379

**Table S2.** Bubble point data of the system CH<sub>4</sub> (1) + [C<sub>4</sub>mim][NTf<sub>2</sub>] (2).

$x_1$	$T/K$	$p/MPa$	$x_1$	$T/K$	$p/MPa$	$x_1$	$T/K$	$p/MPa$	$x_1$	$T/K$	$p/MPa$
0.041	293.48	1.165	0.114	293.62	4.967	0.167	292.97	8.955	0.213	292.86	13.312
0.041	313.73	1.567	0.114	313.71	5.586	0.167	313.55	9.904	0.213	313.62	14.601
0.041	332.65	1.722	0.114	333.47	6.092	0.167	333.36	10.759	0.213	333.70	15.663
0.041	353.43	2.067	0.114	353.15	6.658	0.167	353.38	11.310	0.213	353.38	16.597
$x_1$	$T/K$	$p/MPa$	$x_1$	$T/K$	$p/MPa$	$x_1$	$T/K$	$p/MPa$	$x_1$	$T/K$	$p/MPa$
0.263	293.36	20.565	0.302	293.31	29.327	0.362	293.31	51.267	0.400	293.31	71.340
0.263	313.51	21.520	0.302	313.38	29.610	0.362	313.43	49.180	0.400	313.38	66.847
0.263	333.64	22.480	0.302	333.40	29.897	0.362	333.50	46.879	0.400	333.06	63.275
0.263	353.81	23.160	0.302	352.76	30.720	0.362	353.41	45.183	0.400	353.30	60.550

**Table S3.** Bubble point data of the system CH<sub>4</sub> (1) + 2mHEAPr (2).

<i>x</i> <sub>1</sub>	<i>T</i> /K	<i>p</i> /MPa	<i>x</i> <sub>1</sub>	<i>T</i> /K	<i>p</i> /MPa	<i>x</i> <sub>1</sub>	<i>T</i> /K	<i>p</i> /MPa
0.030	293.00	3.963	0.047	293.46	7.087	0.074	293.20	13.525
0.030	303.47	4.166	0.047	303.60	7.290	0.074	303.21	13.562
0.030	313.33	4.316	0.047	313.24	7.450	0.074	313.26	13.630
0.030	323.30	4.484	0.047	323.23	7.619	0.074	323.34	13.664
0.030	333.18	4.650	0.047	333.18	7.790	0.074	333.25	13.717
0.030	343.26	4.783	0.047	343.19	7.920	0.074	343.34	13.728
0.030	353.22	4.941	0.047	353.40	8.075	0.074	353.43	13.745
0.030	363.17	5.037	0.047	363.17	8.176	0.074	363.41	13.782
<i>x</i> <sub>1</sub>	<i>T</i> /K	<i>p</i> /MPa	<i>x</i> <sub>1</sub>	<i>T</i> /K	<i>p</i> /MPa			
0.101	293.39	29.090	0.132	323.15	46.675			
0.101	303.06	27.110	0.132	333.38	44.588			
0.101	313.26	26.545	0.132	343.17	41.999			
0.101	323.11	26.006	0.132	353.30	39.817			
0.101	333.20	25.174	0.132	363.37	37.821			
0.101	343.32	24.494						
0.101	353.43	23.998						
0.101	363.48	23.465						

**Table S4.** Bubble point data of the system CH<sub>4</sub> (1) + [C<sub>4</sub>mim][[CH<sub>3</sub>SO<sub>3</sub>] (2).

$x_1$	$T/\text{K}$	$p/\text{MPa}$	$x_1$	$T/\text{K}$	$p/\text{MPa}$	$x_1$	$T/\text{K}$	$p/\text{MPa}$
0.062	353.30	14.358	0.097	353.75	29.520	0.141	353.65	49.850
0.062	363.40	14.480	0.097	363.95	29.656	0.141	363.27	48.180

**Table S5.** Carbon dioxide / methane selectivities as function of temperature for the studied ILs.

T /K	CO <sub>2</sub> /CH <sub>4</sub> Selectivities						
	[THTDP][NTf <sub>2</sub> ]	[C <sub>4</sub> mim][NTf <sub>2</sub> ]	2mHEAPr	[C <sub>4</sub> mim][CH <sub>3</sub> SO <sub>3</sub> ]	[C6mim][NTf <sub>2</sub> ] <sup>1</sup>	[C <sub>4</sub> mim][CH <sub>3</sub> SO <sub>4</sub> ] <sup>2</sup>	[C1mim][CH <sub>3</sub> SO <sub>4</sub> ] <sup>1</sup>
293.15	6.36	20.98	91.37				
303.15	6.17	19.34 <sup>a</sup>	81.50		9.51	35.00 <sup>a</sup>	67.30a
313.15	6.16	18.50	70.88		8.14	20.83	
323.15	5.72		62.84				
333.15	5.30	13.96	55.93			19.54	
343.15	4.93		49.58		5.31		
353.15	4.54	12.75	44.67	46.74	4.84		
363.15	4.40		39.53	45.17			

<sup>a</sup> Interpolated

## References

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