Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Thermophysical Properties of Imidazolium Tricyanomethanide Ionic Liquids: Experiments and Molecular Simulation

Lawien F. Zubeir[a,], Marisa A.A. Rocha[a,b], Niki Vergadou[c], Wilko M.A. Weggemans[a],* Loukas

D. Peristeras[c], *Peter S. Schulz[d], Ioannis G. Economou[c,e], Maaike C. Kroon[a,f]*

[a] Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Den Dolech 2, 5612 AZ Eindhoven, The Netherlands.

[b] University of Bremen, Engineering Thermodynamics, Badgasteiner Str. 1, D-28359 Bremen, Germany.

[c] Molecular Thermodynamics and Modelling of Materials Laboratory, Institute of Nanoscience and Nanotechnology, National Center of Scientific Research (NCSR) "Demokritos", GR-15310 Aghia Paraskevi Attikis, Greece.

[d] Department of Chemical and Biological Engineering, Institute of Chemical Reaction Engineering, University of Erlangen-Nuremberg, Egerlandstrasse 3, D-91058 Erlangen, Germany.

[e] Texas A&M University at Qatar, Chemical Engineering Program, Education City, PO Box 23874, Doha, Qatar.

[f] The Petroleum Institute, Department of Chemical Engineering, P.O. Box 2533, Abu Dhabi, United Arab Emirates.

*Corresponding author: lawienf.zubeir@gmail.com

TABLES

Table S1: Experimental results of density, ρ, at 0.1 MPa for the [$C_n$mim][TCM] ionic liquid series as a function of temperature *T*

T/K	ρ/kg·m^{-3}				
	[C_2mim][TCM]	[C_4mim][TCM][1]	[C_6mim][TCM]	[C_7mim][TCM]	[C_8mim][TCM]
288.15	1088.9		1027.3	1016.1	1007.2
293.15	1085.4		1023.9	1012.8	1004.0
298.15	1081.8	1046.2	1020.6	1009.6	1000.8
303.15	1078.2	1042.9	1017.3	1006.4	997.9
308.15	1074.7	1039.5	1014.1	1003.1	994.7
313.15	1071.2	1036.1	1010.8	999.9	991.5
318.15	1067.7	1032.8	1007.6	997.0	988.3
323.15	1064.2	1029.5	1004.4	993.8	985.2
328.15	1060.7	1026.3	1001.2	990.7	982.0
333.15	1057.3	1023.0	998.3	987.5	978.9
338.15	1053.9	1019.8	995.1	984.4	975.8
343.15	1050.5	1016.5	991.9	981.3	972.7
348.15	1047.1	1013.3	988.8	978.2	969.6
353.15	1043.7	1010.2	985.6	975.1	966.5
358.15	1040.4	1007.0	982.5	972.0	963.4
363.15	1037.1	1003.9	979.5	969.0	960.4
Water mass fraction	$114\cdot10^{-6}$	$30\cdot10^{-6}$	$128\cdot10^{-6}$	$43.6\cdot10^{-6}$	$80.4\cdot10^{-6}$

Table S2: Fitting parameters of eq.(5) and molar volume at 298.15 K and 0.1 MPa

IL	*a*/kg·m^{-3}	*b*/10^{-1} kg·m^{-3}·K^{-1}	*c*/10^{-4} kg·m^{-3}·K^{-2}	V_m(*T*=298.15 K)/10^{-4} m^3·mol^{-1}
[C_2mim][TCM]	1328.0	−9.3968	3.8165	1.86
[C_4mim][TCM]	1285.7	−9.2758	4.1758	2.19
[C_6mim][TCM]	1249.0	−8.7582	3.6835	2.52
[C_7mim][TCM]	1220.1	−7.7267	2.2386	2.69
[C_8mim][TCM]	1199.1	−6.9806	1.1169	2.85

Table S3: Experimental data for dynamic viscosities, η, at 0.1 MPa for the [$C_n$mim][TCM] ionic liquid series as a function of temperature T

T/K	η/mPa·s				
	[C_2mim][TCM]	[C_4mim][TCM][1]	[C_6mim][TCM]	[C_7mim][TCM]	[C_8mim][TCM]
288.15	20.615		70.301	83.457	101.740
293.15	17.153		53.640	63.143	76.261
298.15	14.481	27.840	41.952	48.917	58.595
303.15	12.394	22.798	33.411	38.701	45.928
308.15	10.734	18.972	27.151	31.208	36.731
313.15	9.3915	16.009	22.424	25.586	29.886
318.15	8.2927	13.675	18.803	21.298	24.695
323.15	7.3820	11.810	15.957	17.966	20.687
328.15	6.6175	10.297	13.704	15.328	17.554
333.15	5.9717	9.0572	11.900	13.224	15.055
338.15	5.4223	8.0292	10.428	11.514	13.040
343.15	4.9492	7.1680	9.2108	10.119	11.398
348.15	4.5393	6.4431	8.1971	8.9603	10.044
353.15	4.1801	5.8300	7.3388	7.9906	8.9281
358.15	3.8697	5.3047	6.6200	7.1674	7.9725
363.15	3.5917	4.8519	6.0035	6.4710	7.1703
Water mass fraction	$114 \cdot 10^{-6}$	$30 \cdot 10^{-6}$	$128 \cdot 10^{-6}$	$43.6 \cdot 10^{-6}$	$80.4 \cdot 10^{-6}$

Table S4: Fitted parameters of the VFT equation (6) to viscosity data for the studied ILs and the derived energy barrier at 298.15 K

IL	A_η/mPa·s	B_η/K	C_η/K	$E(T=298.15\ \mathrm{K})$/kJ·mol^{-1}
[C_2mim][TCM]	0.229 ± 0.003	533.1 ± 4.5	169.6 ± 0.6	23.9 ± 0.6
[C_4mim][TCM]	0.193 ± 0.001	595.9 ± 2.0	178.2 ± 0.2	30.6 ± 0.3
[C_6mim][TCM]	0.210 ± 0.001	594.0 ± 1.8	186.0 ± 0.2	34.9 ± 0.4
[C_7mim][TCM]	0.186 ± 0.001	635.9 ± 1.1	184.0 ± 0.1	36.1 ± 0.2
[C_8mim][TCM]	0.178 ± 0.001	663.7 ± 2.1	183.7 ± 0.2	37.4 ± 0.4

Table S5: Experimentally determined data for the surface tension, γ, for the [$C_n$mim][TCM] ionic liquid series as a function of temperature T

[C_2mim][TCM]		[C_4mim][TCM][1]		[C_6mim][TCM]		[C_7mim][TCM]		[C_8mim][TCM]	
T/K	γ/mN·m^{-1}	T/K	γ/mN·m^{-1}	T/K	γ/mN·m^{-1}	T/K	γ/mN·m^{-1}	T/K	γ/mN·m^{-1}
298.14	43.82 ± 0.13	298.32	47.04 ± 0.14	298.60	41.92 ± 0.13	299.17	39.64 ± 0.16	297.65	35.64 ± 0.14
308.05	42.29 ± 0.11	307.12	46.29 ± 0.07	308.45	41.24 ± 0.12	307.27	39.22 ± 0.11	307.08	35.05 ± 0.11
318.49	41.08 ± 0.12	318.81	45.14 ± 0.14	320.28	40.17 ± 0.14	316.54	38.55 ± 0.11	318.84	34.18 ± 0.11
327.95	39.89 ± 0.13	328.45	44.30 ± 0.12	331.24	39.35 ± 0.18	326.41	37.87 ± 0.12	329.57	33.57 ± 0.13
339.09	38.88 ± 0.12	341.33	43.30 ± 0.10	339.38	38.57 ± 0.44	337.36	37.15 ± 0.13	340.06	33.04 ± 0.16
					Water mass fraction				
Initial	$1.8\cdot10^{-3}$		$7.3\cdot10^{-4}$		$7.0\cdot10^{-4}$		$1.2\cdot10^{-3}$		$2.7\cdot10^{-3}$
Final	$6.2\cdot10^{-3}$		$5.2\cdot10^{-3}$		$5.0\cdot10^{-3}$		$5.2\cdot10^{-3}$		$5.2\cdot10^{-3}$

$u(T)$ = 0.01 K and the uncertainty limits represent the 95% (k = 2) confidence level.

Table S6: Surface tension, γ, of standard solvents. Experimental values measured here and literature data

Water				Toluene				Diisodecyl phthalate			
Experimental		Vargafik *et al.*[2]		Experimental		Kahl *et al.*[3]		Experimental		Caetano *et al.*[4]	
T/K	γ/mN·m^{-1}	T/K	γ/mN·m^{-1}	T/K	γ/mN·m^{-1}	T/K	γ/mN·m^{-1}	T/K	γ/mN·m^{-1}	T/K	γ/mN·m^{-1}
298.19	71.46 ± 0.06	298.15	71.99 ± 0.36	298.95	27.97 ± 0.08	297.82	27.76 ± 0.1	290.61	29.82 ± 0.14	288.15	30.5 ± 0.15
308.12	70.03 ± 0.08	303.15	71.2 ± 0.36	309.28	26.71 ± 0.10	302.83	27.17 ± 0.1	294.07	29.49 ± 0.16	293.15	30.2 ± 0.15
316.74	68.41 ± 0.07	308.15	70.41 ± 0.35	317.88	25.72 ± 0.07	307.86	26.6 ± 0.1	298.33	29.20 ± 0.16	298.15	29.7 ± 0.15
326.99	66.38 ± 0.11	313.15	69.6 ± 0.35	329.20	24.34 ± 0.06	312.87	26.03 ± 0.06	302.96	28.92 ± 0.12	303.15	29.4 ± 0.15
		318.15	68.78 ± 0.34	286.99	29.12 ± 0.06	317.86	25.46 ± 0.08	307.85	28.51 ± 0.12	308.15	29.1 ±0.15
		323.15	67.94 ± 0.34	304.50	27.19 ± 0.09	327.88	24.29 ± 0.08				
				323.86	24.92 ± 0.07						
AARD (%)			0.84				0.85				1.84

$u(T)$ = 0.01 K and the uncertainty limits represent the 95% (k = 2) confidence level.

Table S7: The surface enthalpy, H^A, and the surface entropy, S^A, of the [$C_n$mim][TCM] ILs

IL	H^A/mN·m^{-1}	S^A/mN·m^{-1}·K^{-1}
[C_2mim][TCM]	72.5 ± 2.1	0.088 ± 0.007
[C_4mim][TCM][1]	73.3 ± 1.4	0.088 ± 0.005
[C_6mim][TCM]	66.5 ± 1.4	0.082 ± 0.004
[C_7mim][TCM]	59.6 ± 1.0	0.066 ± 0.003
[C_8mim][TCM]	54.1 ± 1.6	0.062 ± 0.005

Uncertainty limits represent the 95% (k = 2) confidence level

Table S8: Surface enthalpies, H^A, and entropies, S^A, of a selected group of organic solvents[5]

Organic solvent	H^A/mN·m^{-1}	S^A/mN·m^{-1}·K^{-1}
Hexane	48.38	0.1023
Heptane	48.87	0.0980
Cyclohexane	60.06	0.1188
Toluene	63.36	0.1189
Ethylbenzene	61.38	0.1094
Iodobenzene	72.20	0.1123
Quinoline	74.29	0.1063
Furfural	82.64	0.1327
Cyclohexanone	71.60	0.1242
Hexanol	50.98	0.0900
Piperidine	63.30	0.1153
Cyclopentanone	65.60	0.1100

Table S9: Electrical conductivity, κ, of [$C_n$mim][TCM] as a function of temperature T

[C_2mim][TCM]		[C_4mim][TCM][1]		[C_6mim][TCM]		[C_8mim][TCM]	
T/K	κ/mS·cm^{-1}	T/K	κ/mS·cm^{-1}	T/K	κ/mS·cm^{-1}	T/K	κ/mS·cm^{-1}
293.15	23.70	293.25	10.27	293.15	5.09	293.15	2.85
300.05	30.20	300.35	13.03	300.65	6.89	300.55	3.85
309.85	34.00	309.75	16.30	310.15	9.19	310.15	5.25
316.35	37.70	316.25	18.40	316.45	11.28	316.45	6.44
324.35	42.70	325.55	22.00	324.55	13.43	325.55	8.27
333.85	47.60	333.15	25.70	333.65	16.45	334.15	10.28
341.65	52.60	341.65	28.80	341.15	18.02	341.95	11.90
348.65	57.00	347.95	31.70	347.75	21.20	349.15	13.50
360.65	62.50	360.25	36.10	360.45	24.80	360.65	16.32
367.65	66.20	367.65	39.60	369.15	27.70	368.65	17.25
Water mass fraction							
	$1.05\cdot10^{-3}$		$1.1\cdot10^{-3}$		$6.0\cdot10^{-4}$		$5.0\cdot10^{-4}$

Table S10: VFT parameters of electrical conductivity, κ, for [Cnmim][TCM] ILs

IL	κ_0/mS·cm^{-1}	B/K	T_0/K	R^2
[C_2mim][TCM]	251.86	233.57	192.71	0.998
[C_4mim][TCM]	233.85	308.82	194.09	0.999
[C_6mim][TCM]	179.16	299.03	209.02	0.999
[C_8mim][TCM]	103.75	259.54	222.25	0.998

Table S11: Estimation of the cations and the anion effective radius in [$C_n$mim][TCM] ILs

Ion	Radius/Å
[C_2mim]$^+$	3.26
[C_4mim]$^+$	3.54
[C_6mim]$^+$	3.77
[C_8mim]$^+$	4.01
[TCM]$^-$	2.84

The effective ion sizes were extracted from the ion volume as calculated on minimized isolated ion structures under the assumption of a spherical ion shape. The atomic van der Waals radii considered for the ionic volume calculation correspond to the ones of the force field in use for the molecular simulations[6] augmented by 0.1 Å.

Table S12: Deviation, Δ*W*, of the [TCM]--based ILs from the reference KCl line

IL	*T* / K	Δ*W*	Δ*W* (Adjusted)
[C_2mim][TCM]	298.15	0.13	-0.05
	318.15	0.21	0.03
	338.15	0.28	0.10
	363.15	0.35	0.17
[C_4mim][TCM]	298.15	0.13	-0.06
	318.15	0.23	0.03
	338.15	0.31	0.11
	363.15	0.38	0.18
[C_6mim][TCM]	298.15	0.18	-0.03
	318.15	0.26	0.05
	338.15	0.32	0.11
	363.15	0.39	0.18
[C_8mim][TCM]	298.15	0.25	0.03
	318.15	0.31	0.09
	338.15	0.38	0.16
	363.15	0.46	0.24

Table S13: Self-diffusion coefficients, D_{self}, of the cations [Cnmim]+(n = 2, 4, 6, 8) and the [TCM]- anion as a function of temperature *T*

Experimental			Molecular simulation							
Cation	*T*/K	D_{self}/10^{-11}m^2 s^{-1}	D_{self} / 10^{-11}m^2 s^{-1}							
			T/K	[C_2mim]$^+$	[TCM]$^-$	[C_4mim]$^+$	[TCM]$^-$	[C_6mim]$^+$	[TCM]$^-$	[C_8mim]$^+$	[TCM]$^-$
[C_2mim]$^+$	293.15	7.30 ± 0.17	300	6.1	5.3	3.6	3.7	2.0	2.3	1.1	1.7
	298.15	8.64 ± 0.25	315	10.8	10.3	7.2	7.4	3.9	4.5	3.1	4.0
	303.15	9.91 ± 0.53	330	15	15.2	10.7	13	7.1	8.0	4.8	7.3
	313.15	13.3 ± 0.70	345	24.1	24.3	16.8	18.8	11.6	13.9	9.1	12
	323.15	18.8 ± 1.3	366	36	34.4	27.6	28.9	19.7	24.3	14.7	20.2
[C_4mim]$^+$	298.15	3.95									
[C_6mim]$^+$	298.15	2.73									
[C_8mim]$^+$	298.15	1.72									

FIGURES

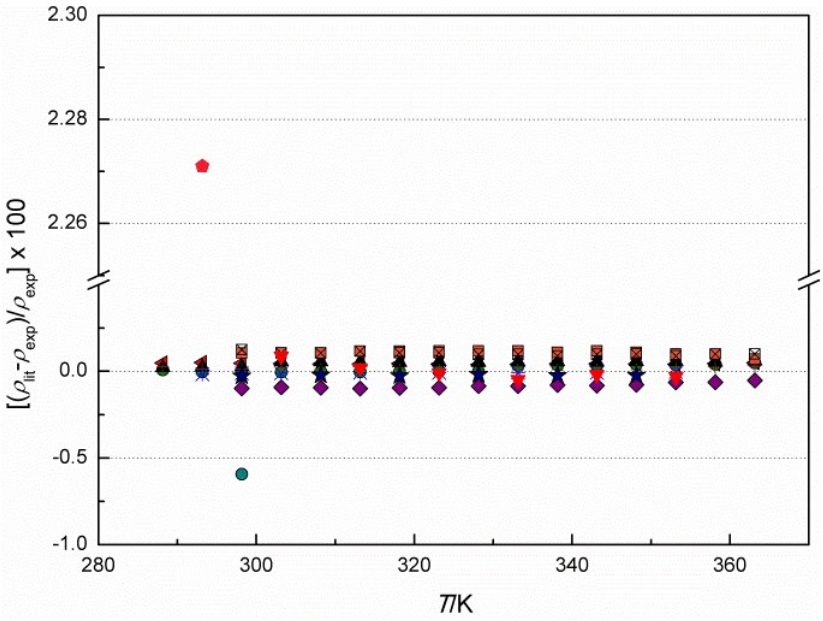

Figure S1: Relative deviations between the experimentally measured densities in this work and literature data. Koller *et al.*[2].: ♦ - [C_2mim][TCM]; ◴- [C_4mim][TCM][1]; ⌀ - [C_6mim][TCM];◘ - [C_8mim][TCM]. Carvalho *et al.*[3]: ■ - [C_4mim][TCM]. Larriba *et al.*[4]: ⊂ - [C_2mim][TCM]. Yoshida *et al.*[5]:◴ - [C_2mim][TCM]. Neves *et al.*[6]: ⌭ - [C_2mim][TCM]; ❄ - [C_4mim][TCM]. Mahurin *et al.*[7]: ⌀ - [C_2mim][TCM]. Gardas *et al.*[8]:❑ - [C_4mim][TCM]. Królikowski *et al.*[9]:⇔- [C_2mim][TCM].

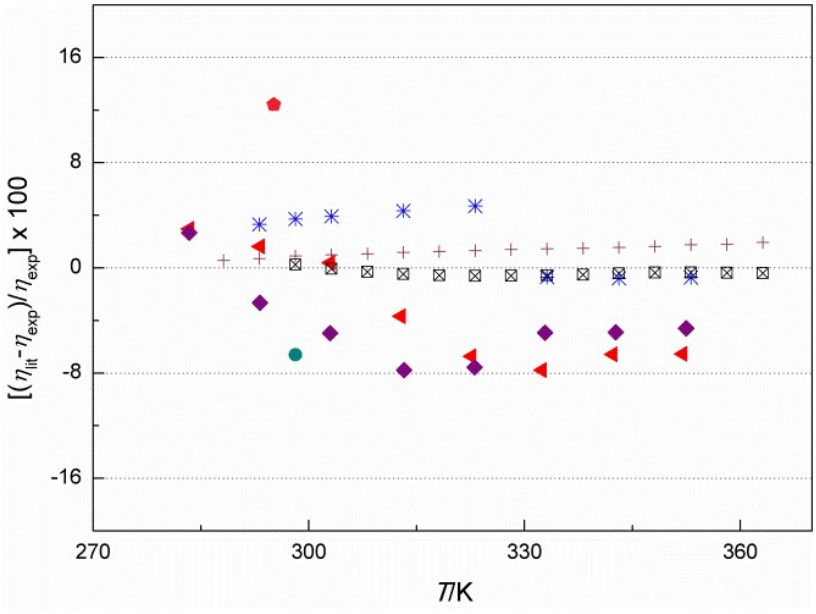

Figure S2: Relative deviations between the experimentally measured viscosities in this work and literature data. Bi *et al.*[10]: ♦ - [C_2mim][TCM]; ◴- [C_4mim][TCM]; Larriba *et al.*[4]: ⊂ - [C_2mim][TCM]. Yoshida*et al.*[5]:◴ - [C_2mim][TCM]. Neves *et al.*[6]: ⌭ - [C_2mim][TCM]; ❄ - [C_4mim][TCM]. Mahurin *et al.*[7]: ⌀ - [C_2mim][TCM].

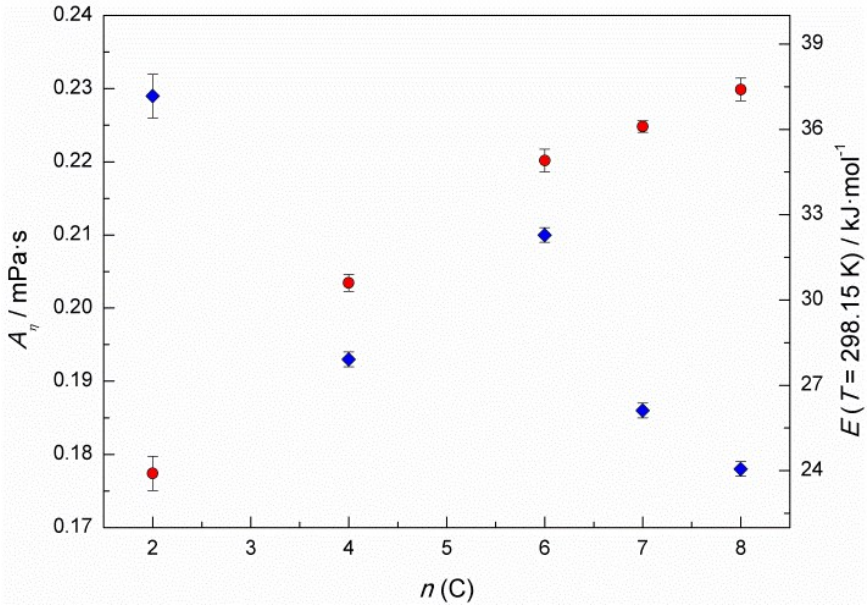

Figure S3: Pre-exponential coefficient of the VFT equation (6) (A_η/ mPa·s), and energy barrier (E / kJ·mol^{-1}) eq. (7) at T = 298.15 K as function of the number of carbon atoms in the alkyl chains of the cation, n(C). ○ -E / kJ·mol^{-1} and◴ -A_η/ mPa·s. Both plots show the parameters of [C$_n$mim][TCM] ILs.

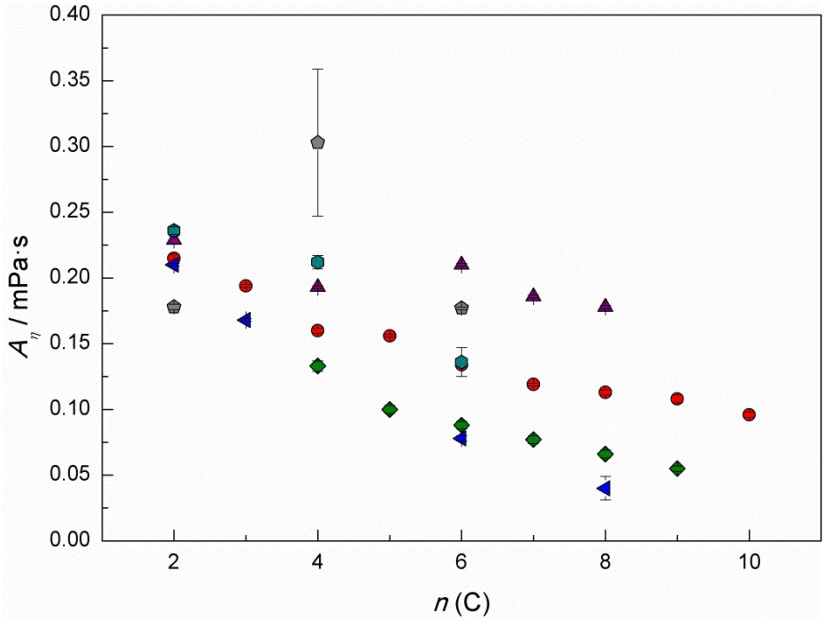

Figure S4: Pre-exponential coefficient of the VFT equation (6) (A_η / mPa·s) as function of the number of carbon atoms in the alkyl side chains of the cation, n(C). This work: □- [C$_n$mim][TCM] (n = 2, 4, 6 - 8). Literature:○ - [C$_n$mim][Tf$_2$N] (n = 2 - 10)[7,8]; ◴ - [C$_n$mim][PF$_6$] (n = 4 - 9)[9]; ③ - [C$_n$mim][BF$_4$] (n = 2, 3, 6, 8)[10,11]; ◷ - [C$_n$mim][TCB] (n = 2, 4, 6, 8, 10)[12,13]; ◇ - [C$_n$mim][DCA] (n = 2, 4, 6)[13,14].

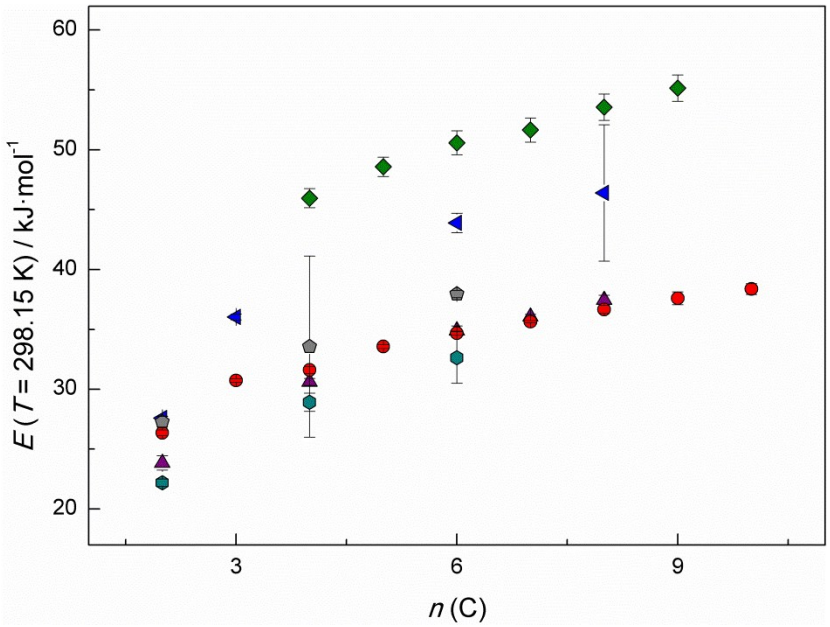

Figure S5: Energy barrier (E / kJ·mol^{-1}) eq. (7) at T = 298.15 K as function of the number of carbon atoms in the alkyl side chains of the cation, n(C). ◘- [$C_n$mim][TCM] (n = 2, 4, 6 - 8). Literature:ᔓ - [$C_n$mim][Tf_2N] (n = 2 - 10)[7,8]; ◴ - [$C_n$mim][PF_6] (n = 4 - 9)[9]; ③ - [$C_n$mim][BF_4] (n = 2, 3, 6, 8)[10,11]; ◴ - [$C_n$mim][TCB] (n = 2, 4, 6, 8, 10)[12,13]; ⌭ - [$C_n$mim][DCA] (n = 2, 4, 6)[13,14].

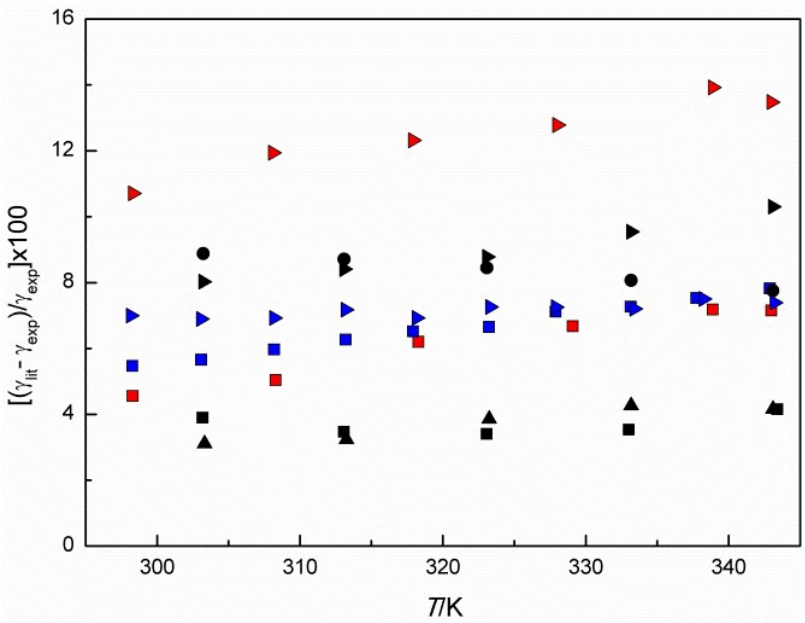

Figure S6: Relative deviation of the experimentally determined surface tension, γ_{exp}, data in this work and literature, γ_{lit}. Same symbols (▶ - [C_2mim][TCM];■ - [C_4mim][TCM]; ▲ - [C_6mim][TCM]; ● – [C_8mim][TCM]) refer to the same IL while the same color (Koller *et al.* (black)[11]; Almeida *et al.* (red)[12]; Součková *et al.* (blue)[13]) to the same research group.

References

1 L. F. Zubeir, G. E. Romanos, W. M. A. Weggemans, B. Iliev, T. J. S. Schubert and M. C. Kroon, *J. Chem. Eng. Data*, 2015, **60**, 1544–1562.

2 T. M. Koller, S. R. Schmid, S. J. Sachnov, M. H. Rausch, P. Wasserscheid and A. P. Fröba, *Int. J. Thermophys.*, 2014, **35**, 195–217.

3 P. J. Carvalho, T. Regueira, L. M. N. B. F. Santos, J. Fernandez and J. A. P. Coutinho, *J. Chem. Eng. Data*, 2010, **55**, 645–652.

4 M. Larriba, P. Navarro, J. García and F. Rodríguez, *Ind. Eng. Chem. Res.*, 2013, **52**, 2714–2720.

5 Y. Yoshida, K. Muroi, A. Otsuka, G. Saito, M. Takahashi and T. Yoko, *Inorg. Chem.*, 2004, **43**, 1458–1462.

6 C. M. S. S. Neves, K. A. Kurnia, J. A. P. Coutinho, I. M. Marrucho, J. N. C. Lopes, M. G. Freire and L. P. N. Rebelo, *J. Phys. Chem. B*, 2013, **117**, 10271–10283.

7 S. M. Mahurin, J. S. Lee, G. A. Baker, H. Luo and S. Dai, *J. Memb. Sci.*, 2010, **353**, 177–183.

8 R. L. Gardas, M. G. Freire, P. J. Carvalho, I. M. Marrucho, I. M. A. Fonseca, A. G. M. Ferreira and J. A. P. Coutinho, *J. Chem. Eng. Data*, 2007, **52**, 1881–1888.

9 M. Królikowski, K. Walczak and U. Domańska, *J. Chem. Thermodyn.*, 2013, **65**, 168–173.

10 S. Bi, T. M. Koller, M. H. Rausch, P. Wasserscheid and A. P. Fröba, *Ind. Eng. Chem. Res.*, 2015, **54**, 3071–3081.

11 T. M. Koller, M. H. Rausch, K. Pohako-esko, P. Wasserscheid and A. P. Fro, *J. Chem. Eng. Data*, 2015, **60**, 2665–2673.

12 H. F. D. Almeida, M. G. Freire, A. M. Fernandes, J. A. Lopes-Da-Silva, P. Morgado, K. Shimizu, E. J. M. Filipe, J. N. Canongia Lopes, L. M. N. B. F. Santos and J. A. P. Coutinho, *Langmuir*, 2014, **30**, 6408–6418.

13 M. Součková, J. Klomfar and J. Pátek, *Fluid Phase Equilib.*, 2015, **406**, 181–193.