Supporting Information

Infinite Dilution Activity Coefficients in the Smectic and Isotropic Phases of Tetrafluoroborate-based Ionic Liquids

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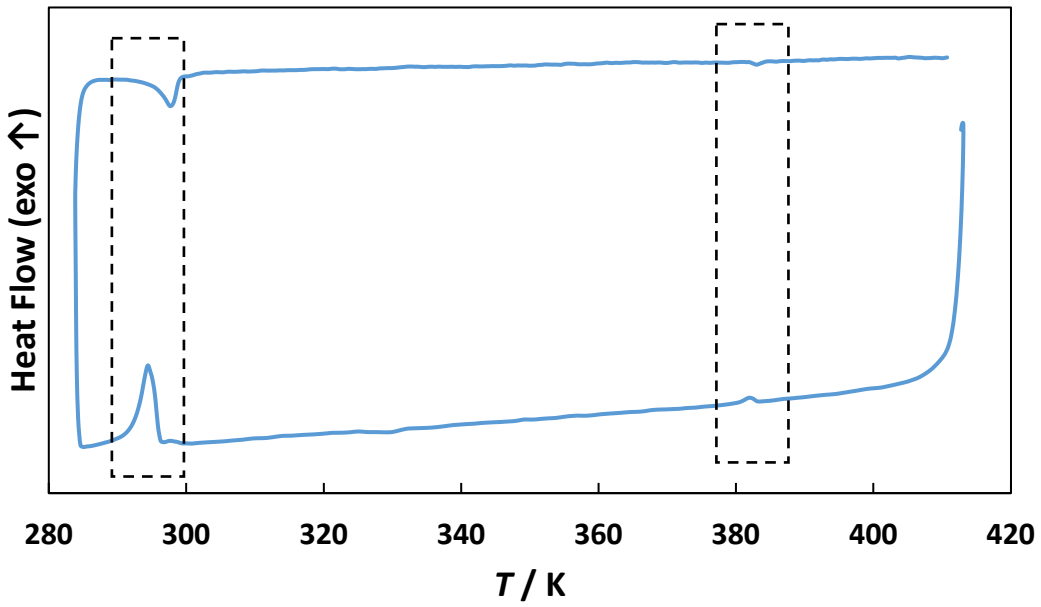

Figure S1. DSC thermogram of 1-tetradecyl-3-imethylimidazolium tetrafluoroborate (heating and cooling rate: 2 K·min^{-1} and 5 K·min^{-1}, respectively; sample mass of approximately 2.5 mg; IL mass purity: > 98.0%).

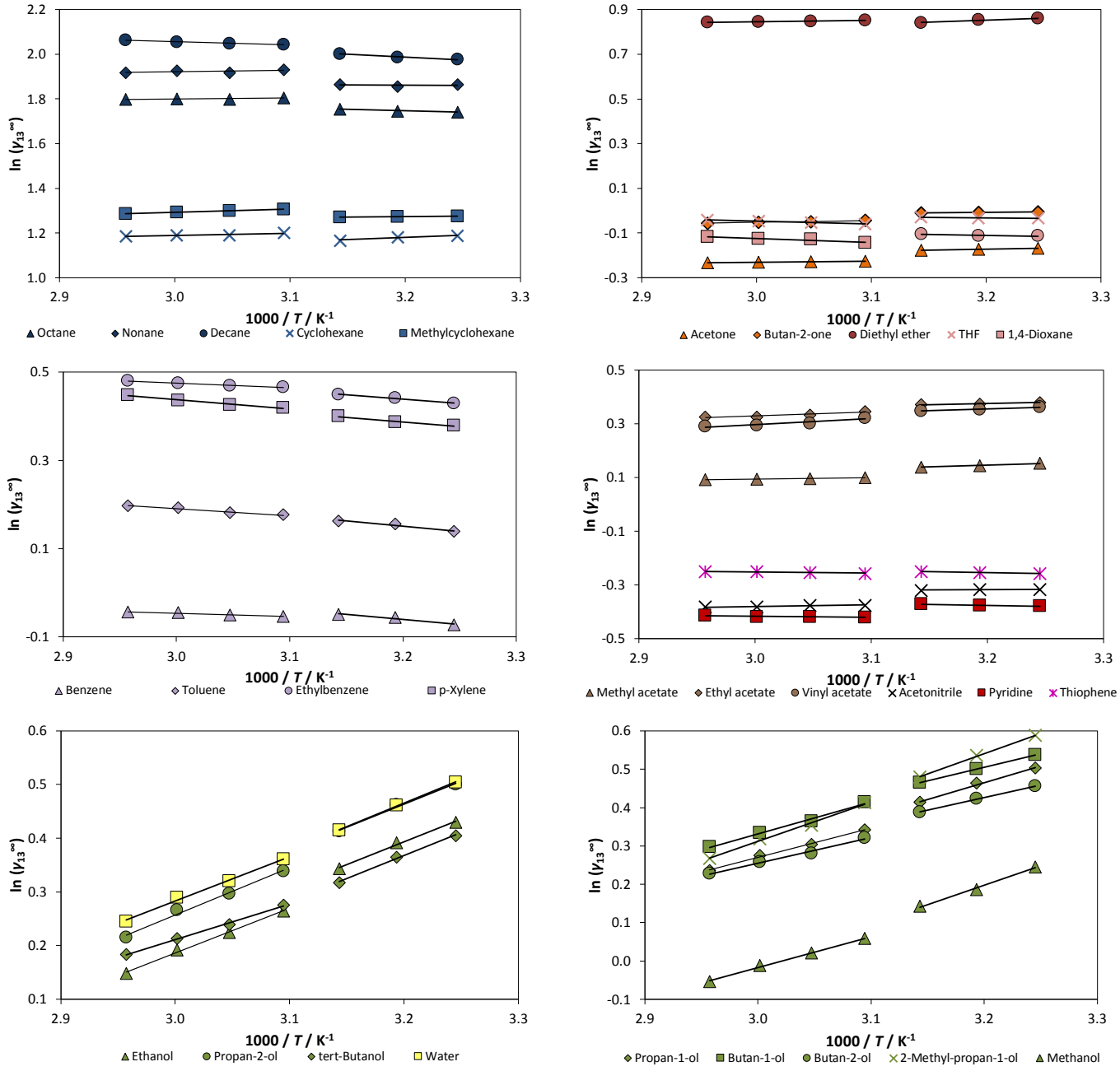

Figure S2. Experimental natural logarithm of activity coefficients at infinite dilution as a function of the reciprocal absolute temperature for all solutes investigated in $[C_{12}mim][BF_4]$.

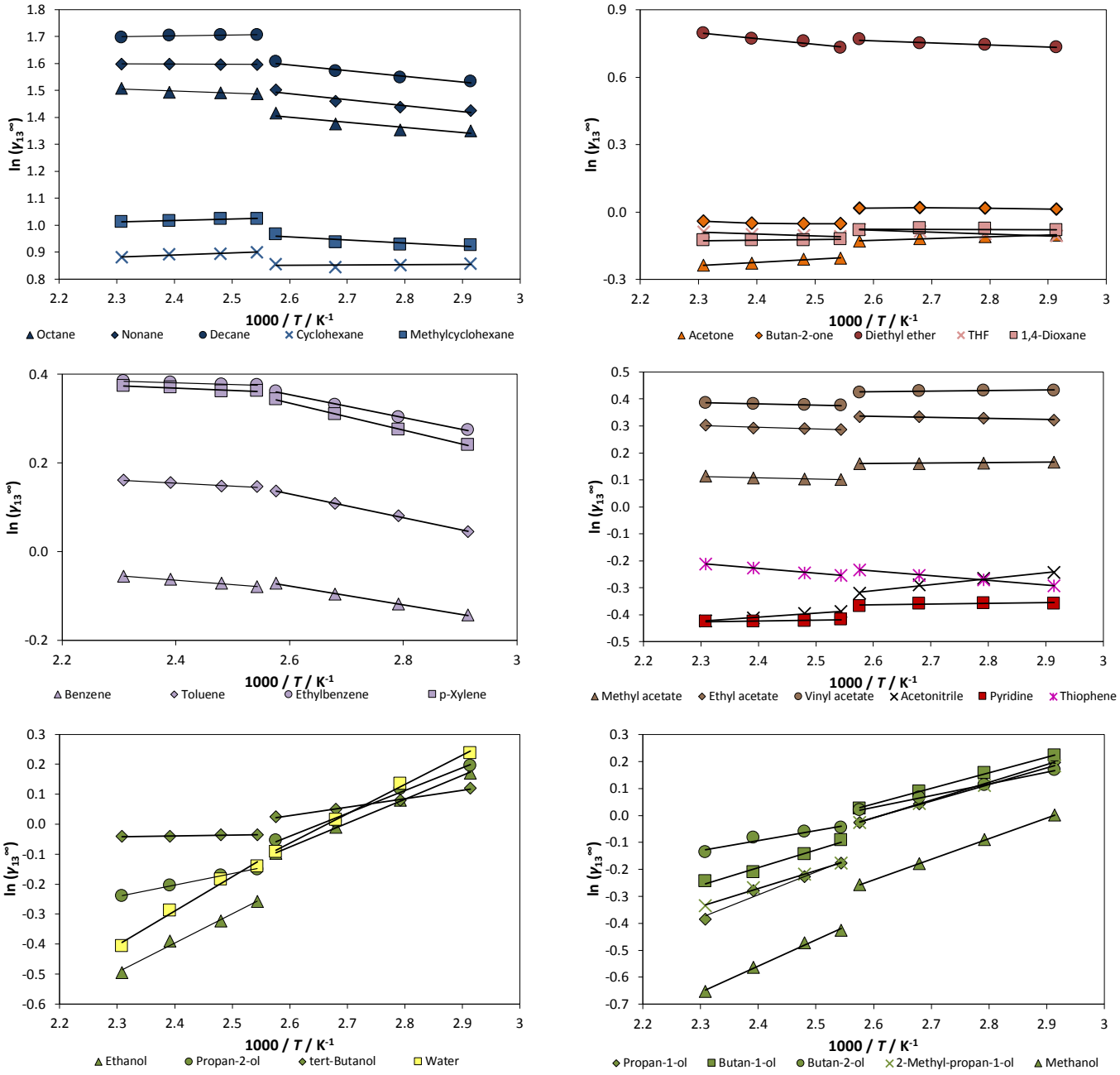

Figure S3. Experimental natural logarithm of activity coefficients at infinite dilution as a function of the reciprocal absolute temperature for all solutes investigated in $[C_{14}mim][BF_4]$.

Table S1. Limiting partial molar excess enthalpies $\overline{H}_m^{E,\infty}$ / kJ·mol^{-1}, excess Gibbs free energies $\overline{G}_m^{E,\infty}$ /kJ·mol^{-1}, and entropies $T_{ref}\overline{S}_m^{E,\infty}$ /kJ·mol^{-1}, for organic solutes and water in ILs.[a]

Organic Solutes	[C_{12}mim][BF_4]						[C_{14}mim][BF_4]					
	T = 313.15 K			T = 328.15 K			T = 358.15 K			T = 403.15 K		
	$\overline{H}_m^{E,\infty}$	$\overline{G}_m^{E,\infty}$	$T\overline{S}_m^{E,\infty}$	$\overline{H}_m^{E,\infty}$	$\overline{G}_m^{E,\infty}$	$T\overline{S}_m^{E,\infty}$	$\overline{H}_m^{E,\infty}$	$\overline{G}_m^{E,\infty}$	$T\overline{S}_m^{E,\infty}$	$\overline{H}_m^{E,\infty}$	$\overline{G}_m^{E,\infty}$	$T\overline{S}_m^{E,\infty}$
Octane	-1.01	4.55	-5.55	0.34	4.91	-4.57	-1.61	4.03	-5.64	-0.65	5.00	-5.65
Nonane	-0.03	4.83	-4.87	0.57	5.23	-4.66	-1.83	4.28	-6.11	-0.06	5.35	-5.41
Decane	-2.05	5.17	-7.22	-1.26	5.59	-6.84	-1.79	4.61	-6.40	0.29	5.72	-5.43
Cyclohexane	1.73	3.08	-1.35	0.78	3.25	-2.47	0.08	2.54	-2.45	0.63	3.00	-2.37
Methylcyclohexane	0.50	3.32	-2.81	1.18	3.55	-2.36	-0.94	2.77	-3.71	0.45	3.43	-2.98
Acetone	0.77	-0.45	1.22	0.46	-0.62	1.08	0.67	-0.33	0.99	1.16	-0.70	1.87
Butan-2-one	0.45	-0.02	0.47	0.69	-0.13	0.82	-0.13	0.05	-0.18	-0.40	-0.17	-0.22
Diethyl ether	1.56	2.22	-0.66	0.47	2.31	-1.84	-0.79	2.22	-3.00	-2.09	2.55	-4.64
THF	-0.34	-0.08	-0.25	-1.07	-0.14	-0.93	-0.73	-0.29	-0.44	-0.66	-0.35	-0.31
1,4-Dioxane	-0.72	-0.29	-0.43	-1.49	-0.35	-1.14	-0.03	-0.22	0.19	0.21	-0.42	0.63
Benzene	-1.91	-0.14	-1.77	-0.61	-0.14	-0.47	-1.75	-0.35	-1.40	-0.82	-0.24	-0.58
Toluene	-1.97	0.41	-2.37	-1.33	0.50	-1.82	-2.24	0.24	-2.48	-0.55	0.50	-1.05
Ethylbenzene	-1.63	1.15	-2.78	-0.88	1.28	-2.16	-2.15	0.90	-3.05	-0.32	1.26	-1.58
p-Xylene	-1.65	1.00	-2.66	-1.76	1.16	-2.93	-2.54	0.82	-3.36	-0.46	1.21	-1.67
Methyl acetate	1.13	0.38	0.75	0.48	0.26	0.22	0.14	0.49	-0.35	-0.40	0.35	-0.75
Ethyl acetate	0.67	0.97	-0.30	1.25	0.91	0.35	-0.35	0.98	-1.33	-0.50	0.98	-1.48
Vinyl acetate	1.14	0.92	0.23	1.92	0.82	1.10	0.19	1.29	-1.10	-0.37	1.27	-1.64
Acetonitrile	0.22	-0.82	1.04	0.51	-1.03	1.53	1.85	-0.79	2.64	1.28	-1.33	2.61
Pyridine	-0.59	-0.98	0.39	-0.33	-1.14	0.81	0.21	-1.06	1.27	0.26	-1.42	1.68
Thiophene	-0.53	-0.66	0.13	-4.92	-0.69	-4.23	-1.41	-0.81	-0.61	-1.49	-0.82	-0.67
Methanol	8.40	0.49	7.91	6.74	0.06	6.68	6.38	-0.27	6.65	8.09	-1.59	9.68
Ethanol	7.02	1.02	6.00	6.92	0.61	6.31	6.60	0.24	6.36	8.13	-1.08	9.21
Propan-1-ol	7.26	1.21	6.05	6.31	0.83	5.48	5.53	0.36	5.17	7.07	-0.76	7.84
Propan-2-ol	7.12	1.20	5.92	7.29	0.81	6.48	6.33	0.35	5.98	3.18	-0.57	3.75
Butan-1-ol	5.92	1.30	4.62	6.86	0.99	5.86	4.83	0.47	4.37	5.50	-0.48	5.98
Butan-2-ol	5.50	1.10	4.40	5.54	0.76	4.78	3.62	0.33	3.29	3.09	-0.20	3.29
2-Methyl-propan-1-ol	8.84	1.40	7.44	8.52	0.96	7.56	5.13	0.33	4.81	5.48	-0.73	6.21

tert-Butanol	7.09	0.95	6.14	5.49	0.65	4.84	2.34	0.24	2.10	0.24	-0.12	0.36
Water	7.31	1.20	6.10	6.91	0.87	6.03	8.16	0.40	7.75	9.54	-0.62	10.16

[a]Standard uncertainties: $u(\overline{H}_m^{E,\infty})$ = ±0.5 kJ·mol^{-1}; $u(\overline{G}_m^{E,\infty})$ = ±0.5 kJ·mol^{-1}; $u(T\overline{S}_m^{E,\infty})$ = ± 0.05 kJ·mol^{-1}.

Table S2. Comparison between the activity coefficients at infinite dilution of this work with values from literature at 323.15 K.

,		Octane	Cyclohexane	Benzene	Methanol	Reference
$[C_2mim][BF_4]$	[a]	186.9	49.73	2.09		[1]
	[a]		46.17	2.51	0.43	[2]
$[C_4mim][BF_4]$	[a]	95.5	24.7	1.5	0.7	[3]
	[a]	127.0	28.30	1.770		[4]
	[b]	329.99	41.50	2.19	1.20	[5]
	[a]		38.38	2.43	1.21	[2]
	[a]	87.12				[6]
	[a]	170.2				[7]
	[a]			2.25		[8]
	[a]				0.65	[9]
$[C_6mim][BF_4]$	[a]	32.00	9.38	1.44	1.07	[10]
	[a]		16.51	1.65	1.08	[2]
	[b]	60.40				[7]
			7.50	1.56		[8]
$[C_8mim][BF_4]$	[a]	11.0	3.9	0.6	0.3	[3]
	[b]	19.60	7.03	1.16	0.91	[11]
	[a]		7.99	1.29	0.94	[2]
$[C_{10}mim][BF_4]$	[a]	10.69	4.43	1.11		[12]
$[C_{12}mim][BF_4]$	[a]	6.08	3.32	0.95	1.06	This Work
$[C_{14}mim][BF_4]$	[a]	3.69	2.35	0.83	1.15	This Work
$[C_{16}mim][BF_4]$	[a]	2.69	1.67	0.78	1.14	[13]

[a]Experimental values;

[b]Interpolated from experimental values;

Table S3. Experimental and estimated densities, ρ, of pure ILCs as a function of temperature, at 0.1 MPa.

	ρ / g·cm^{-3}		
***T* / K**	**[C_{12}mim][BF_4]^a**	**[C_{12}mim][BF_4]^b**	**[C_{14}mim][BF_4]^b**
303.16	1.04565	1.04128	
308.14	1.04226		
313.14	1.03887	1.03623	
318.14	1.03551		1.01532
323.14	1.03231	1.03120	1.01248
328.14	1.02900		1.00953
333.14	1.02568	1.02620	1.00658
338.14	1.02238		1.00365
343.14	1.01908	1.02123	1.00071
348.14	1.01579		0.99778
353.14	1.01253		0.99487
358.14	1.00927		0.99197
363.14	1.00603		0.98908

^{a}Experimental values from ref.[14]; standard uncertainties, u, are $u(\rho) = \pm 5 \cdot 10^{-5}$ g·cm^{-3} and $u(T) = 0.01$ K and $u_r(p) = 0.05$.

^{b}Estimated values.

Table S4. Experimental gas–liquid partition coefficients, K_L, for organic solutes and water in ILCs, at different temperatures and under pressure p = 93.8 kPa.[a]

Organic Solutes	$[C_{12}mim][BF_4]$							$[C_{14}mim][BF_4]$							
T/ K	308.15	313.15	318.15	323.15	328.15	333.15	338.15	343.15	358.15	373.15	388.15	393.15	403.15	418.15	433.15
Octane	432.845	338.911	266.772	203.054	165.183	134.383	110.449	129.693	76.231	46.447	29.259	23.942	18.573	13.141	9.516
Nonane	1154.168	886.278	677.658	493.760	393.153	309.572	249.882	299.374	163.246	93.708	55.781	43.751	32.997	22.338	15.726
Decane	3101.830	2273.884	1676.947	1219.950	930.009	714.536	552.974	671.022	341.600	184.735	104.644	80.340	58.693	38.073	25.888
Cyclohexane	121.464	101.164	85.699	69.638	59.411	50.573	43.504	47.293	31.303	21.708	15.403	13.253	10.942	8.356	6.607
Methylcyclohexane	226.578	185.014	152.368	121.690	102.039	86.236	73.367	81.048	51.608	34.210	23.163	19.563	15.804	11.882	9.124
Acetone	207.621	174.598	147.799	131.666	112.671	96.915	83.911	58.117	39.504	28.105	20.733	20.255	16.952	13.363	10.714
Butan-2-one	416.456	342.376	283.686	244.309	205.775	174.137	148.585	107.539	69.294	46.764	33.118	31.817	25.926	19.515	15.058
Diethyl ether	33.828	29.206	25.488	21.912	19.214	16,886	14.945	13.364	9.531	7.076	5.344	5.074	4.253	3.405	2.757

THF	251.852	209.297	174.731	151.970	128.067	108.936	93.180	77.955	51.560	35.631	25.535	23.780	19.584	14.989	11.721
1,4-Dioxane	1079.415	869.440	701.173	596.554	485.395	401.612	332.871	245.267	150.182	96.976	66.056	60.741	48.432	35.172	26.303
Benzene	435.458	352.533	290.619	243.821	204.626	172.397	146.894	126.139	80.342	53.668	37.301	33.832	27.383	20.567	15.909
Toluene	1108.471	874.411	703.497	566.597	463.643	380.134	315.552	280.376	166.268	104.354	68.617	60.177	47.544	34.207	25.438
Ethylbenzene	2326.856	1795.782	1408.205	1102.360	882.294	710.866	577.820	529.708	298.514	178.475	111.617	95.858	73.790	51.251	36.895
p-Xylene	2664.796	2067.691	1607.584	1254.638	999.461	801.252	645.231	591.839	330.487	195.549	121.253	103.540	79.685	54.910	39.254
Methyl acetate	158.598	132.838	111.848	98.120	83.566	71.589	61.760	44.971	30.312	21.309	15.566	14.971	12.462	9.673	7.677
Ethyl acetate	276.116	226.484	186.151	157.945	133.554	112.893	95.598	74.088	47.195	31.552	22.162	20.859	16.946	12.750	9.827
Vinyl acetate	234.466	193.853	160.669	137.149	117.398	99.684	85.077	57.129	37.034	25.142	17.884	16.866	13.763	10.397	8.082
Acetonitrile	601.410	496.777	414.772	367.356	310.526	264.954	226.077	153.241	102.044	71.233	51.802	49.701	40.850	31.209	24.332

Pyridine	2471.215	1953.444	1550.081	1312.573	1065.196	871.598	715.866	509.561	303.324	190.805	127.067	117.364	91.977	65.365	48.033
Thiophene	619.644	504.669	415.400	347.406	289.783	243.669	206.572	166.675	105.433	70.085	48.473	44.375	35.814	26.516	20.246
Methanol	225.866	191.524	161.634	142.954	121.683	103.817	90.062	64.658	43.147	30.186	21.907	22.943	18.920	14.922	12.121
Ethanol	376.339	305.002	252.059	216.872	180.999	151.189	128.659	93.483	59.172	39.529	27.771	28.613	23.392	17.416	14.111
Propan-1-ol	922.424	725.790	584.532	485.800	394.738	320.718	265.847	201.283	118.925	75.335	50.007	49.612	39.865	28.650	22.716
Propan-2-ol	458.105	364.674	296.691	249.977	206.029	169.755	143.696	108.162	65.836	44.474	30.260	29.008	22.875	16.766	12.774
Butan-1-ol	2579.310	1963.356	1510.099	1195.487	954.737	756.587	609.915	468.744	255.999	151.453	95.234	91.050	70.347	49.249	35.124
Butan-2-ol	1123.372	867.622	680.558	557.657	450.663	361.317	295.200	227.560	130.259	79.778	52.032	47.927	37.053	26.249	19.958
2-Methyl-propan-1-ol	1582.871	1225.381	966.267	779.564	631.270	505.423	414.919	323.016	180.986	108.916	70.312	70.241	54.367	38.498	28.907
tert-Butanol	514.080	407.422	329.364	268.111	219.488	179.633	149.250	117.224	69.580	43.930	29.314	27.304	21.449	15.498	11.678

Water	848.436	684.589	559.197	464.304	384.162	317.071	267.595	198.280	123.466	82.408	56.957	51.481	40.555	30.288	23.858

[a]Standard uncertainties: $u(K_L) < 3$ % and $u(T) = 0.02$ K.

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