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

Decay of Hydrogen Bonding in Mixtures of Aliphatic Heptanols with Bistriflimide Ionic Liquids

Supplementary Information

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Supplementary information contain:

1. Calculated raw data on densities, vaporization enthalpies and self-diffusivities.
2. Information about less significant interactions obtained from simulations.
3. Derivation of reference experimental data.
4. Comparison of the experimental reference data with the literature.

Table S1. Mixtures description table with the amount of IL and alcohol, mass fraction (w_{IL}), molar fraction (x_{IL}) and the average molecular mass of the mixture

m (IL) / mg	**m (alcohol) / mg**	w_{IL}	x_{IL}	**M (mixture) / g·mol^{-1}**	T_{demix}
[C$_4$mim][NTf$_2$] + heptan-1-ol (C$_4$H$_1$)					
318.51	91.00	0.7778	0.4923	265.464	336[1]
[C$_4$mim][NTf$_2$] + heptan-3-ol (C$_4$H$_3$)					
446.11	126.54	0.7790	0.4941	266.010	-
[C$_4$mim][NTf$_2$] + 3-ethylpentan-3-ol (C$_4$E$_3$)					
355.05	98.29	0.7832	0.5002	267.854	276[2]
[C$_6$mim][NTf$_2$] + heptan-1-ol (C$_6$H$_1$)					
448.45	115.92	0.7946	0.5012	282.203	305[3]
[C$_6$mim][NTf$_2$] + heptan-3-ol (C$_6$H$_3$)					
464.49	123.88	0.7895	0.4934	279.613	-
[C$_6$mim][NTf$_2$] + 3-ethylpentan-3-ol (C$_6$E$_3$)					
439.05	114.35	0.7934	0.4993	281.578	259[2]
[C$_8$mim][NTf$_2$] + heptan-1-ol (C$_8$H$_1$)					
423.62	104.47	0.8022	0.4977	295.025	277[2]
[C$_8$mim][NTf$_2$] + heptan-3-ol (C$_8$H$_3$)					
446.41	111.38	0.8003	0.4948	293.979	-
[C$_8$mim][NTf$_2$] + 3-ethylpentan-3-ol (C$_8$E$_3$)					
442.16	103.80	0.8026	0.4985	295.293	246[2]

Table S2. Calculated and literature experimental[a] liquid-phase densities (kg m^{-3})[b]

	300 K		350 K		400 K	
	ρ_{calc}	ρ_{exp}	ρ_{calc}	ρ_{exp}	ρ_{calc}	ρ_{exp} [c]
Pure compound						
heptan-1-ol	812.2	817.6	761.2	780.7	706.5	739.6
heptan-2-ol	814.3	811.7	760.9	771.0	702.4	726.0
heptan-3-ol	813.5	815.6	756.0	772.8	695.5	725.0
2,2-dimethylpentan-1-ol	828.4	-	775.7	-	719.9	-
2,4-dimethylpentan-3-ol	823.3	823.2	766.8	774.7	709.0	723.6
3-ethylpentan-3-ol	825.4	837.7	768.8	791.2	710.1	741.0
[C$_4$mim][NTf$_2$]	1438.9	1434.9	1395.0	1387.9	1350.5	1342.2
Equimolar mixtures with [C$_4$mim][NTf$_2$]						
heptan-1-ol	1236.3	-	1190.0	-	1144.4	-
heptan-2-ol	1239.8	-	1192.3	-	1146.1	-
heptan-3-ol	1240.5	-	1192.6	-	1146.9	-
2,2-dimethylpentan-1-ol	1247.6	-	1200.8	-	1155.6	-
2,4-dimethylpentan-3-ol	1248.5	-	1201.0	-	1155.3	-
3-ethylpentan-3-ol	1251.1	-	1204.0	-	1157.9	-

[a] Reference experimental data were obtained as averages of mutually consistent literature data, see Figs S1-S7.

[b] Uncertainties related to MD sampling are below 1.0 kg m^{-3}.

[c] Data extrapolated over more than 40 K.

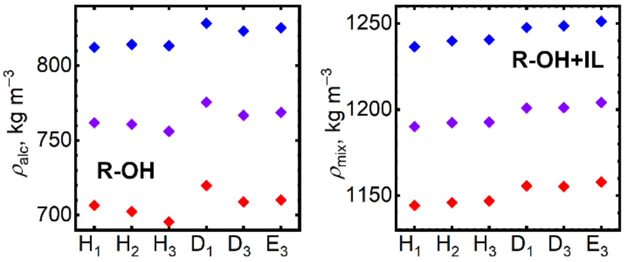

Fig. S1 Calculated liquid-phase densities of the pure alcohols (left) and their equimolar mixtures with [C_4mim][NTf_2] (right) at 300 K (blue), 350 K (purple), and 400 K (red). Abbreviations of the chemical names of individual alcohols: heptan-1-ol (H_1), heptan-2-ol (H_2), heptan-3-ol (H_3), 2,2-dimethylpentan-1-ol (D_1), 2,4-dimethylpentan-3-ol (D_3), and 3-ethylpentan-3-ol (E_3).

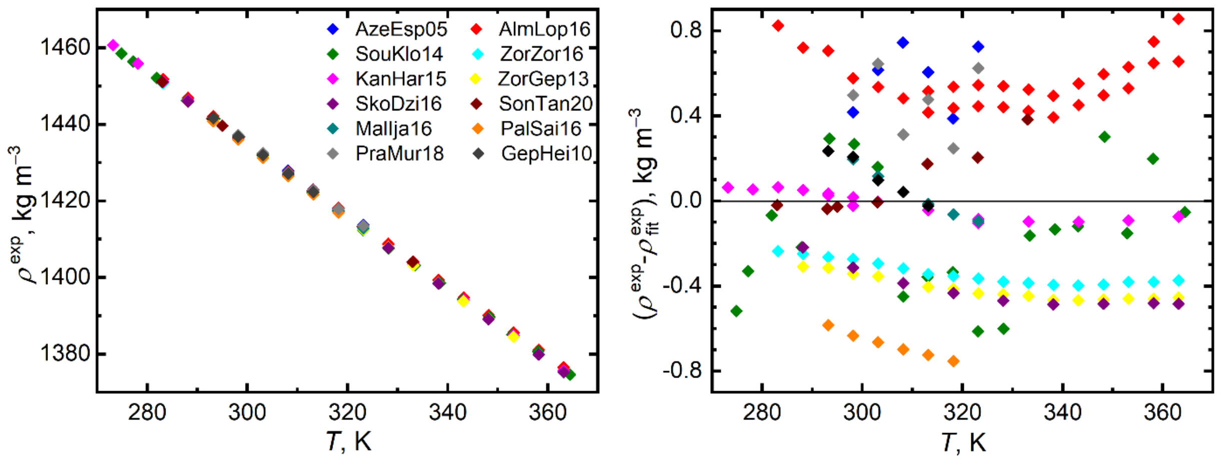

Fig. S2 Comparison of experimental density data sets[4-16] for [C_4mim][NTf_2] that were assessed mutually consistent, and thus selected for the evaluation of the reference density (zero level at right).

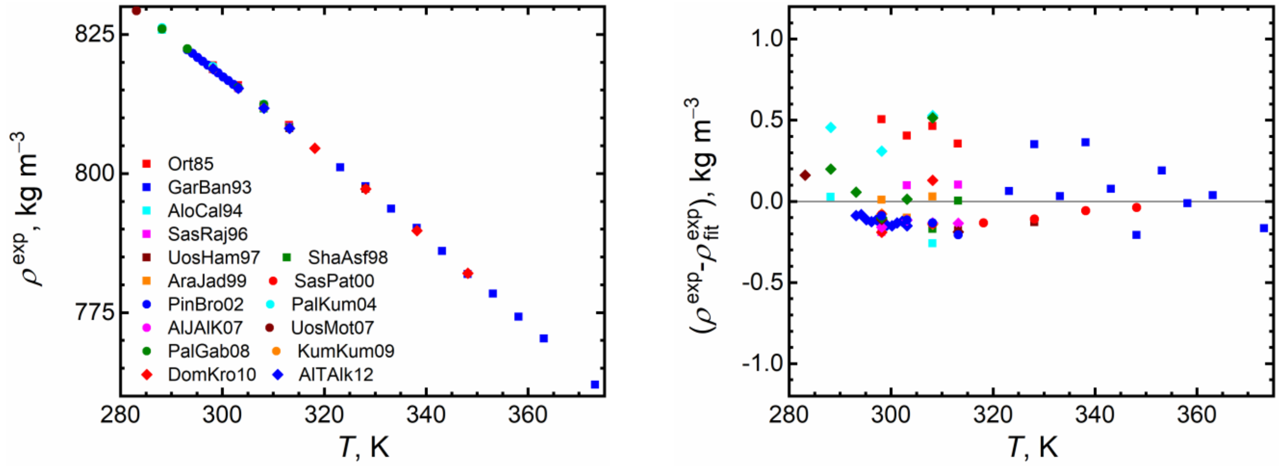

Fig. S3 Comparison of experimental density data sets[17-32] for heptan-1-ol that were assessed mutually consistent, and thus selected for the evaluation of the reference density (zero level at right).

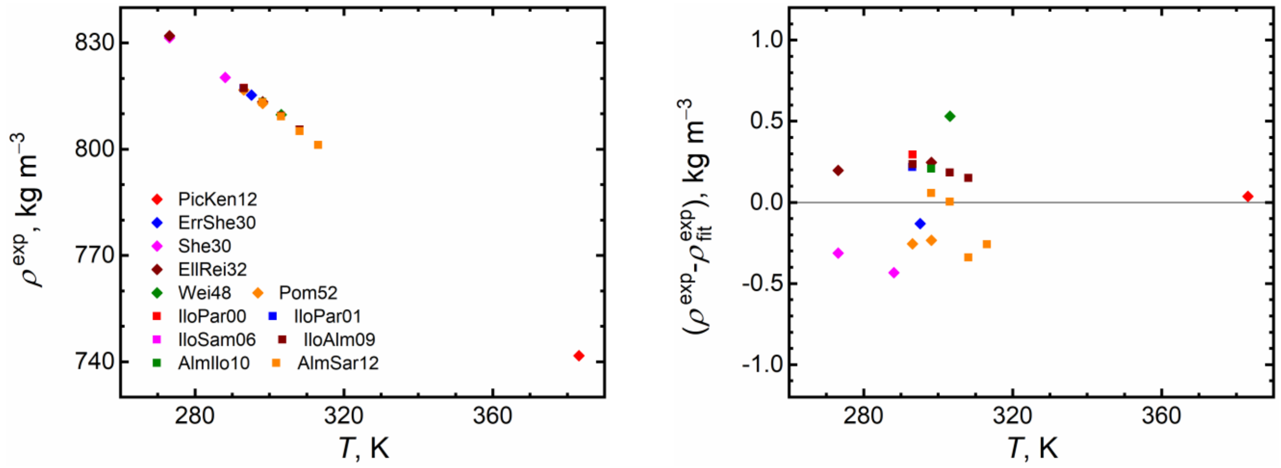

Fig. S4 Comparison of experimental density data sets[33-44] for heptan-2-ol that were assessed mutually consistent, and thus selected for the evaluation of the reference density (zero level at right).

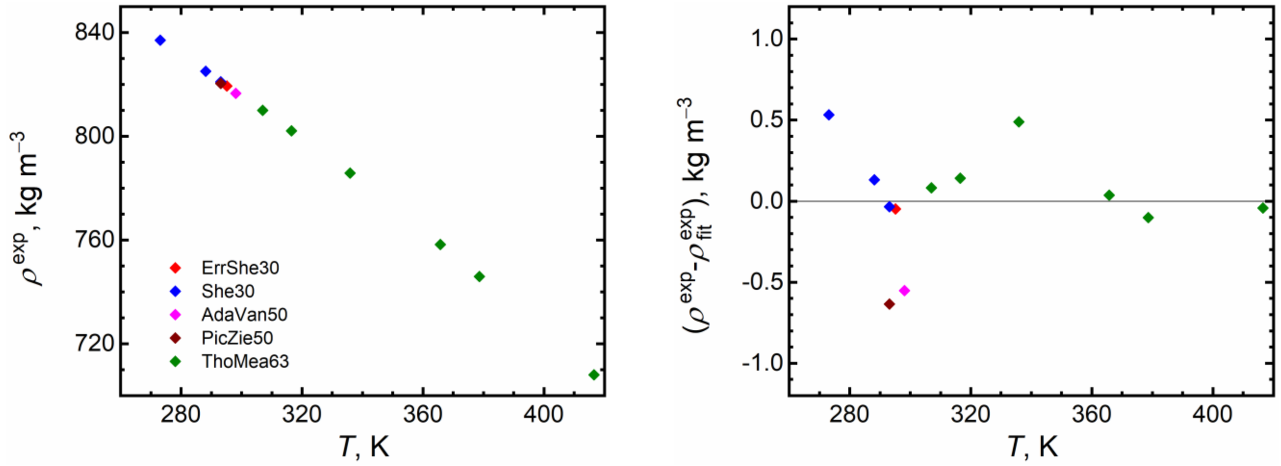

Fig. S5 Comparison of experimental density data sets[42, 43, 45-47] for heptan-3-ol that were assessed mutually consistent, and thus selected for the evaluation of the reference density (zero level at right).

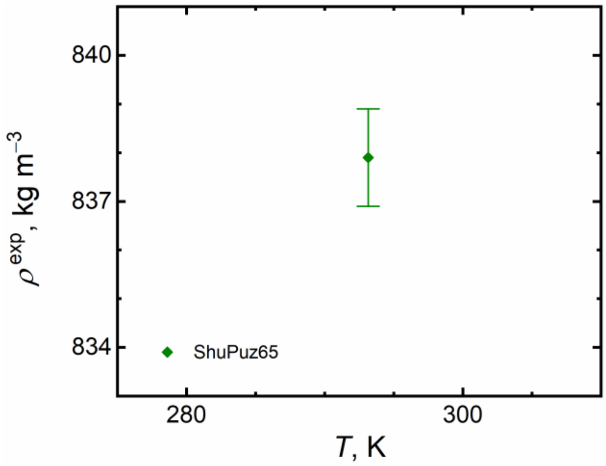

Fig. S6 Experimental density data[48] for 2,2-dimethylpentan-1-ol.

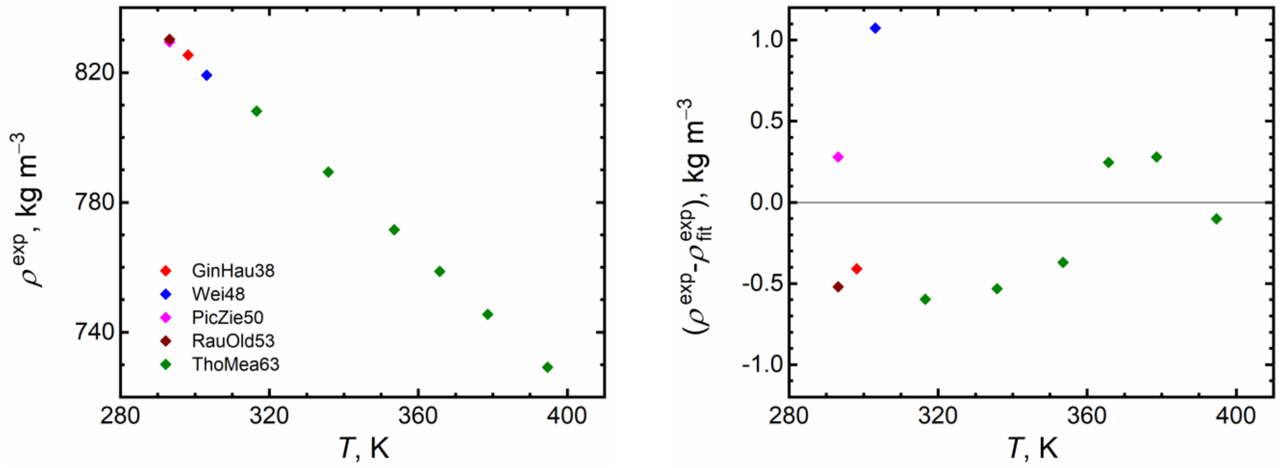

Fig. S7 Comparison of experimental density data sets[40, 45, 46, 49, 50] for 2,4-dimethylpentan-3-ol that were assessed mutually consistent, and thus selected for the evaluation of the reference density (zero level at right).

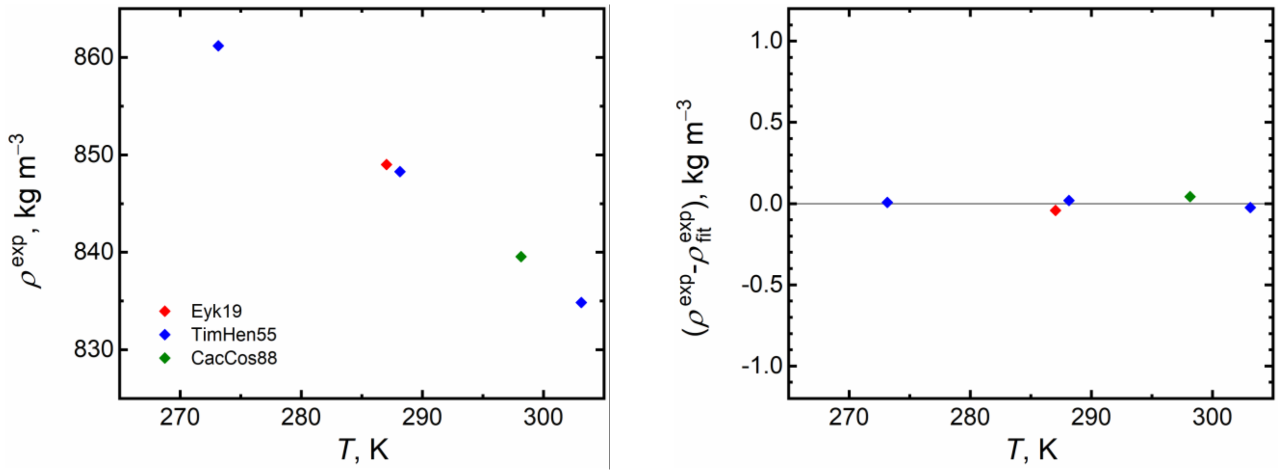

Fig. S8 Comparison of experimental density data sets[51-53] for 3-ethylpentan-3-ol that were assessed mutually consistent, and thus selected for the evaluation of the reference density (zero level at right).

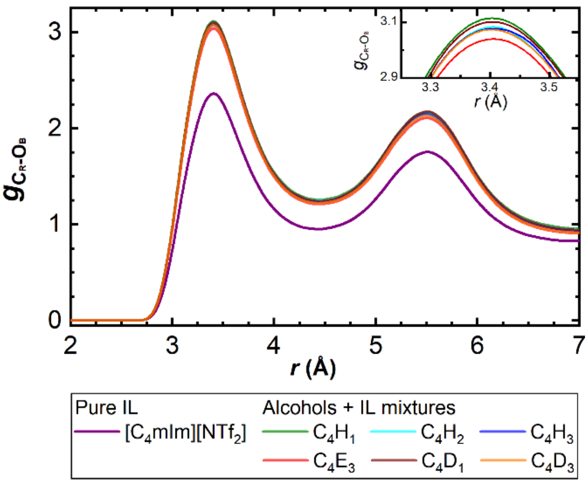

Fig. S9 The closest cation – anion interaction contacts of the cationic C_R and anionic O_B atom types in pure bulk [C$_4$mim][NTf$_2$] and its equimolar mixtures with individual alcohols, all at 350 K. Region of the first peak is given in detail.

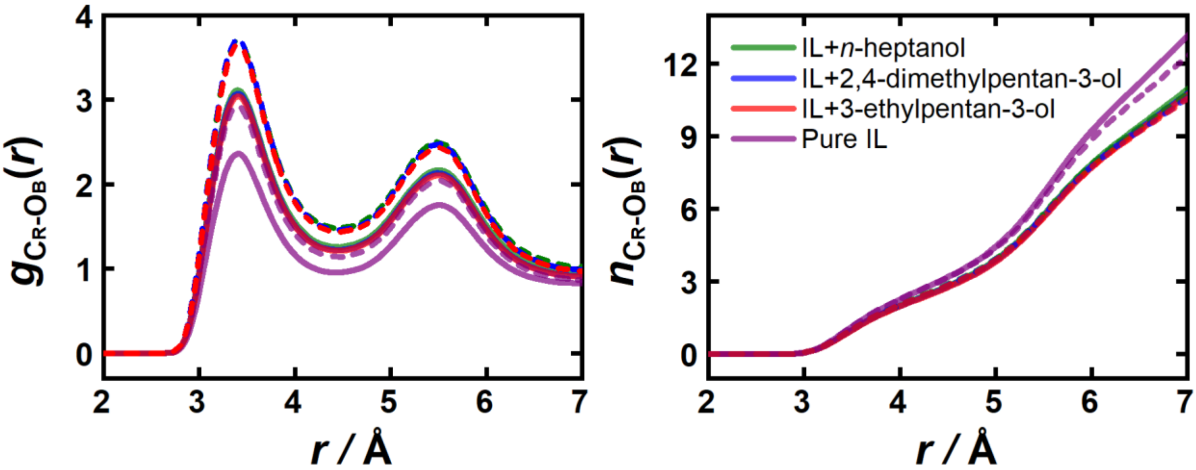

Fig. S10 The closest cation – anion interaction contacts of the cationic C_R and anionic O_B atom types at 350 K. Left – radial distribution functions *g*(*r*), Right – integral coordination numbers *n*(*r*) as functions of the atomic distance. Solid and dashed lines stand for results for [C$_4$mim][NTf$_2$] and [C$_8$mim][NTf$_2$], respectively.

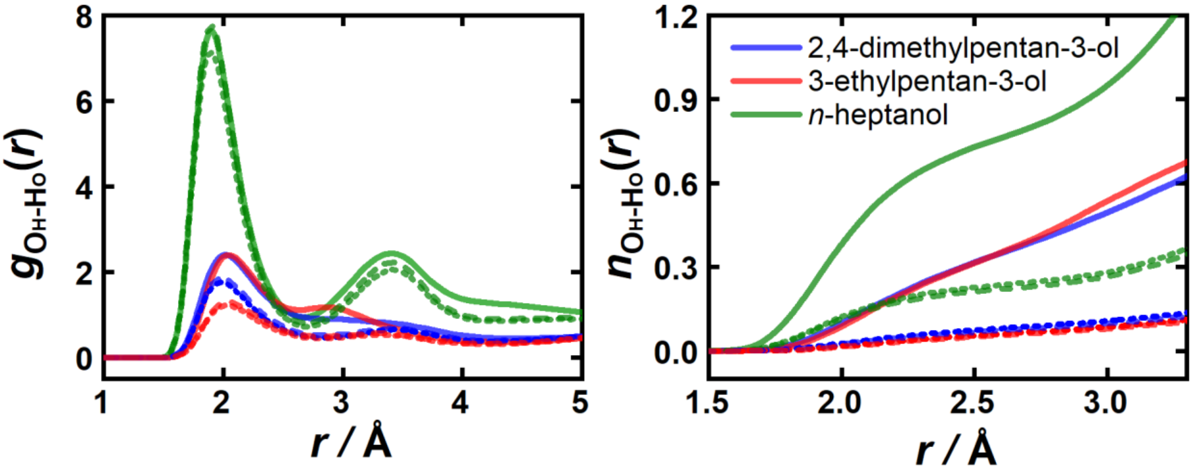

Fig. S11 The closest interaction contacts of the O_H and H_O atom types defining the structure of hydrogen bonds between the hydroxyl groups of alcohol molecules. Left – radial distribution functions, Right – integral coordination numbers as functions of the atomic distance. Solid lines – pure alcohol, Dashed lines – equimolar mixture alcohol+[C_8mim][NTf_2], Dotted lines – equimolar mixture alcohol+[C_4mim][NTf_2].

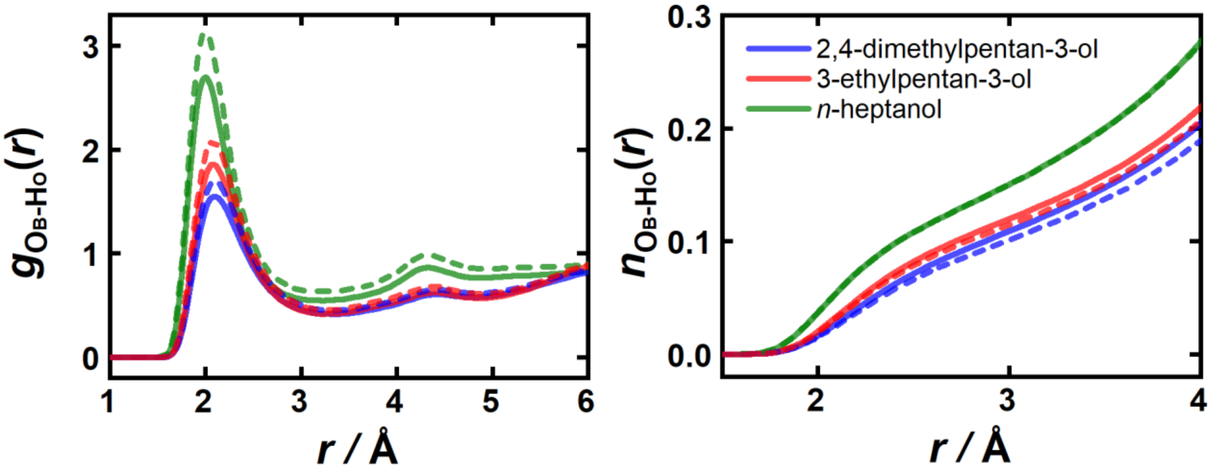

Fig. S12 The closest interaction contacts of the H_O and O_B atom types defining the structure of hydrogen bonds between the hydroxyl groups of alcohol molecules and the [NTf_2] anion. Left – radial distribution functions, Right – integral coordination numbers as functions of the atomic distance. Solid and dashed lines stand for results for [C_4mim][NTf_2] and [C_8mim][NTf_2], respectively.

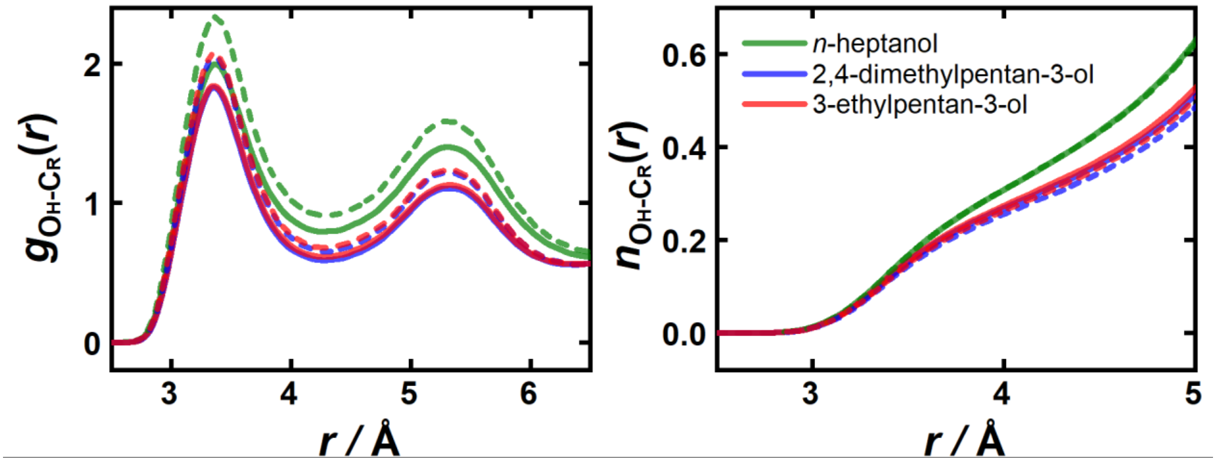

Fig. S13 The closest interaction contacts of the O_H and C_R atom types defining the structure of hydrogen bonds between the hydroxyl groups of alcohol molecules and cation of the ILs. Left – radial distribution functions, Right – integral coordination numbers as functions of the atomic distance. Solid and dashed lines stand for results for $[C_4mim][NTf_2]$ and $[C_8mim][NTf_2]$, respectively.

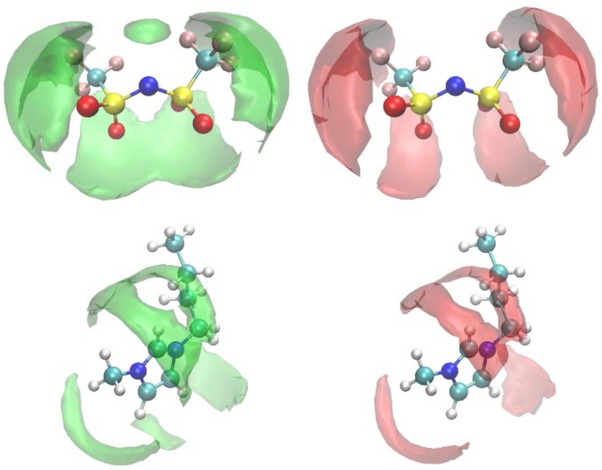

Fig. S14 Spatial distribution functions of the hydroxyl hydrogen atoms around the $[NTf_2]$ anions (isosurfaces represent the SDF value 2.5) and of the hydroxyl oxygen atoms around the $[C_4mim]$ cations (isosurfaces represent the SDF value 5.0). Situation for equimolar mixtures of $[C_4mim][NTf_2]$ with heptan-1-ol, and 3-ethylpentan-3-ol are depicted in green and red, respectively.

Table S3. Calculated coordination numbers ($n_{O\text{-}H}$) representing the average number of hydrogen-bonded hydrogen atoms (from alcohol hydroxyl, H_O) around an oxygen atom in the first solvation shell in bulk liquid. Radii of the first solvation shell ($R_{O\text{-}H}$, in Å) given for comparison

	300 K	350 K	400 K	300 K	350 K	400 K
		$n_{O\text{-}H}$			$R_{O\text{-}H}$	
		Pure compound				
heptan-1-ol	0.917	0.785	0.621	2.63	2.67	2.71
heptan-2-ol	0.873	0.697	0.511	2.64	2.67	2.69
heptan-3-ol	0.814	0.594	0.432	2.64	2.67	2.77
2,2-dimethylpentan-1-ol	0.731	0.555	0.416	2.67	2.73	2.78
2,4-dimethylpentan-3-ol	0.588	0.471	0.298	2.68	2.94	2.88
3-ethylpentan-3-ol	0.577	0.367	0.266	2.54	2.64	2.81

Equimolar mixtures with [C_4mim][NTf_2], coordination of alcohol oxygen O_H						
heptan-1-ol	0.307	0.243	0.185	2.67	2.68	2.73
heptan-2-ol	0.255	0.201	0.151	2.68	2.71	2.76
heptan-3-ol	0.245	0.178	0.123	2.72	2.73	2.73
2,2-dimethylpentan-1-ol	0.189	0.145	0.112	2.73	2.77	2.82
2,4-dimethylpentan-3-ol	0.136	0.095	0.074	2.82	2.83	2.73
3-ethylpentan-3-ol	0.092	0.071	0.058	2.77	2.78	2.82
Equimolar mixtures with [C_4mim][NTf_2], coordination of [NTf_2] oxygen O_B						
heptan-1-ol	0.162	0.159	0.159	3.02	3.09	3.23
heptan-2-ol	0.166	0.156	0.147	3.07	3.17	3.24
heptan-3-ol	0.153	0.144	0.135	3.14	3.22	3.29
2,2-dimethylpentan-1-ol	0.153	0.151	0.132	3.18	3.37	3.33
2,4-dimethylpentan-3-ol	0.146	0.136	0.117	3.22	3.37	3.41
3-ethylpentan-3-ol	0.162	0.137	0.118	3.21	3.23	3.33

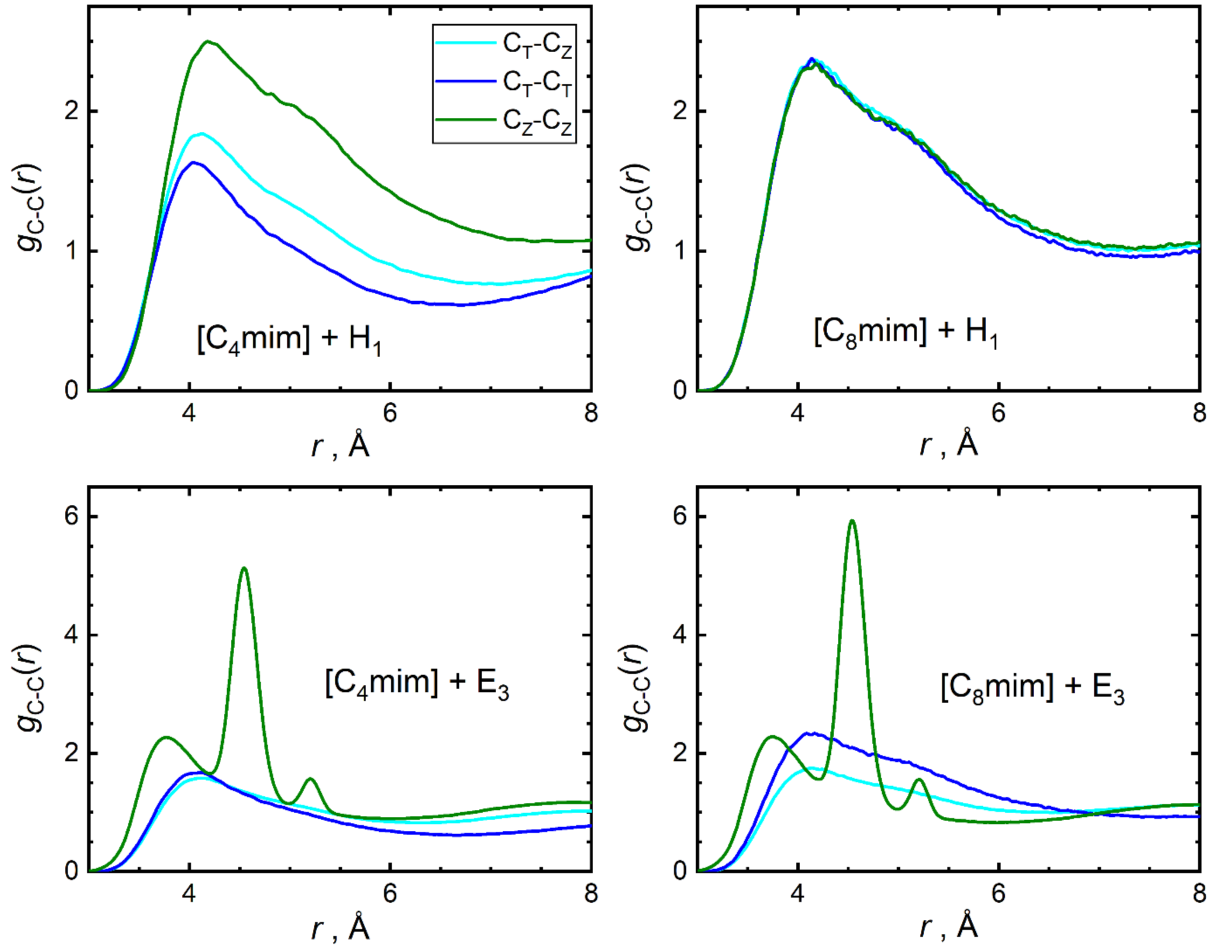

Fig. S15 The closest interaction contacts of the C_T (terminal carbon site of the longer alkyl side-chain of the cations) and C_Z (terminal carbon atoms of the alkyl chains of alcohols) atom types at 350 K. Data are compared for equimolar mixtures of heptan-1-ol (H_1) or 3-ethylpentan-3-ol (H_3) with [C_4mim][NTf_2]or [C_8mim][NTf_2].

Table S4. Calculated structure and interaction energies (kJ mol^{-1}) of vapor-phase simulation-annealed dimers.

	d(O…H−O), Å [a]	α(O…H−O), deg. [a]	E_{int} [b]	E_{elec} [b]	E_{exch} [b]	E_{indu} [b]	E_{disp} [b]
alcohol-alcohol dimers							
heptan-1-ol	1.88	174.4	-39.2	-54.0	75.0	-16.4	-43.8
heptan-2-ol	1.89	164.7	-35.2	-46.5	65.1	-14.6	-39.2
heptan-3-ol	1.86	175.0	-37.4	-53.6	70.4	-16.8	-37.4
2,2-dimethylpentan-1-ol	1.85	170.5	-31.3	-50.1	57.5	-15.2	-23.4
2,4-dimethylpentan-3-ol	1.88	172.2	-35.6	-47.8	60.6	-15.2	-33.2
3-ethylpentan-3-ol	1.86	176.1	-34.0	-51.8	60.4	-16.2	-26.4
alcohol-[NTf$_2$] clusters							
heptan-1-ol	1.98	165.2	-60.0	-57.7	57.8	-22.2	-37.9
heptan-2-ol	1.92	173.3	-49.2	-53.8	59.4	-20.8	-34.0
heptan-3-ol	1.93	171.3	-53.9	-57.7	66.3	-25.6	-36.9
2,2-dimethylpentan-1-ol	1.90	169.6	-57.5	-59.2	63.8	-24.6	-37.4
2,4-dimethylpentan-3-ol	1.91	171.1	-52.2	-57.0	64.2	-22.8	-36.7
3-ethylpentan-3-ol	1.90	175.5	-47.5	-51.3	60.9	-21.8	-35.3

[a] Simulation-annealed clusters further reoptimized with B3LYP-D3/aug-cc-pVDZ.

[b] Interaction energies and its decomposition at the sSAPT0/jun-cc-pVDZ level of theory.

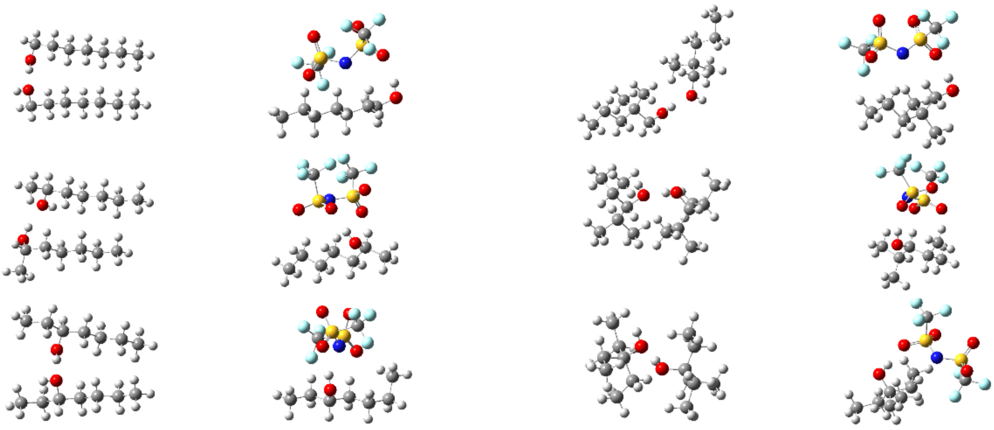

Fig. S16 Geometries of the simulation-annealed vapor-phase clusters of alcohol-alcohol dimers (odd columns) and alcohol-[NTf2] clusters (even columns).

Table S5. Calculated vaporization enthalpies (kJ mol^{-1})[a]

	300 K	350 K	400 K	300 K	298.15 K
		$\Delta_{\mathrm{vap}}H^{\mathrm{calc}}$		$\Delta_{\mathrm{vap}}H^{\mathrm{exp,\,b}}$	$\Delta_{\mathrm{vap}}H^{\mathrm{lit,\,c}}$
	Pure compound				
heptan-1-ol	61.0	52.7	44.5	66.3 ± 0.4	67.0 ± 2.0
heptan-2-ol	57.4	48.0	39.1	63.3 ± 0.4	62.1 ± 0.4
heptan-3-ol	59.0	48.0	39.0	62.1 ± 0.4	63.0[d] ± 2.0
2,2-dimethylpentan-1-ol	55.6	47.6	40.5		
2,4-dimethylpentan-3-ol	55.0	45.7	38.8	56.3 ± 0.4	58.5[e] ± 2.0
3-ethylpentan-3-ol	48.5	39.9	33.6	56.8 ± 0.4	57.3 ± 0.2
[C_4mim][NTf_2]	175.2	167.5	160.6		
	Equimolar mixtures with [C_4mim][NTf_2]				
heptan-1-ol	116.3	108.8	102.4		
heptan-2-ol	114.7	107.2	100.4		
heptan-3-ol	115.5	107.6	101.0		
2,2-dimethylpentan-1-ol	115.2	108.1	101.7		
2,4-dimethylpentan-3-ol	115.6	107.9	101.5		
3-ethylpentan-3-ol	112.8	105.5	99.3		

[a] Uncertainties related to MD sampling are below 1.0 kJ mol^{-1}.

[b] Unpublished data by Štejfa and Fulem.[54]

[c] Literature data from the NIST database (webbook.nist.gov).

[d] Interpolated from available data at different temperatures.

[e] Extrapolated from available data at different temperatures (extrapolation by 24 K).

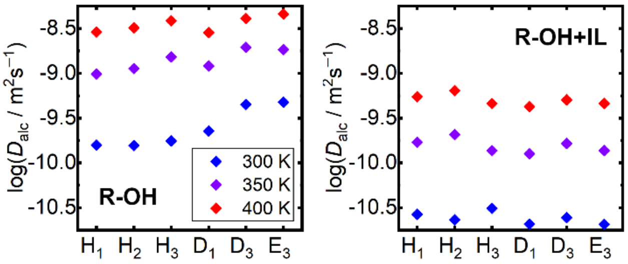

Fig. S17 Calculated self-diffusivities of the pure alcohols (left) and their equimolar mixtures with [C$_4$mim][NTf$_2$] (right) at 300 K (blue), 350 K (purple), and 400 K (red). Chemical names of individual alcohols are abbreviated as follows: heptan-1-ol (H$_1$), heptan-2-ol (H$_2$), heptan-3-ol (H$_3$), 2,2-dimethylpentan-1-ol (D$_1$), 2,4-dimethylpentan-3-ol (D$_3$), and 3-ethylpentan-3-ol (E$_3$).

Table S6. Calculated self-diffusion data for alcohol molecules (10^{-9} m^2 s^{-1})[a]

	300 K	350 K	400 K
Pure compound			
heptan-1-ol	0.157	0.984	2.890
heptan-2-ol	0.157	1.125	3.203
heptan-3-ol	0.175	1.522	3.849
2,2-dimethylpentan-1-ol	0.226	1.203	2.833
2,4-dimethylpentan-3-ol	0.447	1.945	4.079
3-ethylpentan-3-ol	0.475	1.828	4.570
Equimolar mixtures with [C$_4$mim][NTf$_2$]			
heptan-1-ol	0.027	0.170	0.546
heptan-2-ol	0.023	0.207	0.638
heptan-3-ol	0.031	0.138	0.462
2,2-dimethylpentan-1-ol	0.021	0.126	0.425
2,4-dimethylpentan-3-ol	0.025	0.164	0.504
3-ethylpentan-3-ol	0.021	0.138	0.462

[a] Uncertainties related to MD sampling are below 10^{-11} m^2 s^{-1}.

Table S7. Experimental Liquid Phase Heat Capacities c_p of Heptan-1-ol, Heptan-3-ol, and 3-Ethylpentan-3-ol at $p = (100 \pm 5)$ kPa[a,b]

T / K	c_p / J·K^{-1}·g^{-1}	δ_{rel}[c]	T / K	c_p / J·K^{-1}·g^{-1}	δ_{rel}[c]	T / K	c_p / J·K^{-1}·g^{-1}	δ_{r}[c]
heptan-1-ol			heptan-3-ol			3-ethylpentan-3-ol		
349.7	2.834	0.08	349.6	3.118	-0.24	349.8	3.151	0.38
345.0	2.794	0.16	345.0	3.091	-0.08	345.0	3.169	0.20
340.0	2.755	0.35	340.0	3.066	0.27	340.0	3.193	0.30
335.0	2.709	0.33	335.0	3.033	0.40	335.0	3.199	0.00
330.0	2.657	0.06	330.0	2.986	0.13	330.0	3.207	-0.05
325.0	2.604	-0.24	325.0	2.934	-0.23	325.0	3.208	-0.15
320.0	2.557	-0.31	320.0	2.886	-0.42	320.0	3.217	0.22
315.0	2.517	-0.11	315.0	2.842	-0.44	315.0	3.223	0.74
310.0	2.473	-0.08	310.0	2.796	-0.43	310.0	3.199	0.57
305.0	2.435	0.19	305.0	2.749	-0.41	305.0	3.159	0.20
300.0	2.384	-0.04	300.0	2.702	-0.35	300.0	3.116	0.01
295.0	2.346	0.29	295.0	2.662	0.09	295.0	3.071	0.13
291.1	2.319	0.65	291.0	2.631	0.51	291.0	3.022	0.01

[a] Standard uncertainty u is $u(T) = 0.05$ K, and the combined expanded uncertainty of the heat capacity is $U_{\mathrm{c}}(C_{p,\mathrm{m}}) = 0.01 C_{p,\mathrm{m}}$ (0.95 level of confidence).

[b] Values are reported with one digit more than is justified by the experimental uncertainty to avoid round-off errors in calculations based on these results.

[c] $\delta_{\mathrm{r}} = 100 \times \left(c_p - c_p^{\mathrm{calc}}\right) / c_p^{\mathrm{calc}}$, where c_p^{calc} is heat capacity calculated from eqn (S1) with parameters from Table S9.

Table S8. Experimental Liquid Phase Heat Capacities c_p of [C$_4$mim][NTf$_2$], [C$_6$mim][NTf$_2$], and [C$_8$mim][NTf$_2$] at $p = (100 \pm 5)$ kPa[a,b]

T / K	c_p / J·K^{-1}·g^{-1}	δ_{rel}[c]	T / K	c_p / J·K^{-1}·g^{-1}	δ_{rel}[c]	T / K	c_p / J·K^{-1}·g^{-1}	δ_{r}[c]
[C$_4$mim][NTf$_2$]			[C$_6$mim][NTf$_2$]			[C$_8$mim][NTf$_2$]		
352.6	1.428	-0.07	352.6	1.545	0.15	352.7	1.545	-0.09
350.0	1.424	-0.15	350.0	1.540	0.11	350.0	1.541	-0.10
345.0	1.416	-0.23	345.0	1.530	0.08	345.0	1.532	-0.19
340.0	1.411	-0.08	340.0	1.520	0.01	340.0	1.525	-0.09
335.0	1.406	0.04	335.0	1.510	-0.07	335.0	1.519	0.04
330.0	1.398	-0.01	330.0	1.502	0.01	330.0	1.512	0.07
325.0	1.389	-0.10	325.0	1.494	0.06	325.0	1.505	0.16
320.0	1.381	-0.18	320.0	1.486	0.12	320.0	1.496	0.07
315.0	1.376	-0.03	315.0	1.479	0.15	315.0	1.483	-0.31
310.0	1.373	0.32	310.0	1.470	0.16	310.0	1.471	-0.60
305.0	1.368	0.49	305.0	1.461	0.09	305.0	1.472	-0.04
300.0	1.355	0.13	300.0	1.452	-0.01	300.0	1.466	0.06
295.0	1.348	0.16	295.0	1.444	-0.03	295.0	1.458	0.02
290.9	1.345	0.41	291.0	1.440	0.13	290.9	1.454	0.17

[a] Standard uncertainty u is $u(T) = 0.05$ K, and the combined expanded uncertainty of the heat capacity is $U_{\mathrm{c}}(C_{p,\mathrm{m}}) = 0.01 C_{p,\mathrm{m}}$ (0.95 level of confidence).

[b] Values are reported with one digit more than is justified by the experimental uncertainty to avoid round-off errors in calculations based on these results.

[c] $\delta_{\mathrm{r}} = 100 \times \left(c_p - c_p^{\mathrm{calc}}\right) / c_p^{\mathrm{calc}}$, where c_p^{calc} is heat capacity calculated from eqn (S1) with parameters from Table S9.

Experimental specific heat capacities obtained in this work have been described by a polynomial function (S1). Parameters for pure compounds are listed in Table S9, parameters for equimollar mixtures are listed in Table S11 and parameters for excess specific heat capacities of equimollar mixtures are listed in Table S12.

$$c_p = \sum_{i=0}^{n} A_{i+1}\left(\frac{T}{100\ \mathrm{K}}\right)^{i} . \qquad \text{(S1)}$$

Table S9. Parameters of eqn (S1) for liquid phase heat capacities of pure compounds in $\mathrm{J \cdot K^{-1} \cdot g^{-1}}$

Compound	A_1 / $\mathrm{J \cdot K^{-1} \cdot g^{-1}}$	A_2 / $\mathrm{J \cdot K^{-1} \cdot g^{-1}}$	A_3 / $\mathrm{J \cdot K^{-1} \cdot g^{-1}}$	A_4 / $\mathrm{J \cdot K^{-1} \cdot g^{-1}}$	T_{min} - T_{max}/K	s_{r}[a]
heptan-1-ol	-4.08944E-1	9.58706E-1	-9.15273E-3	-	291-358	0.216
heptan-3-ol	-3.45423E0	3.10334E0	-3.49410E-1	-	291-353	0.272
3-ethylpentan-3-ol	-4.45470E1	3.96470E1	-1.08286E1	9.69594E-1	276-355	0.177
[C$_4$mim][NTf$_2$]	7.40600E-1	2.56163E-1	-1.72657E-2	-	276-358	0.175
[C$_6$mim][NTf$_2$]	1.26674E0	-3.19584E-2	3.12620E-2	-	291-350	0.282
[C$_8$mim][NTf$_2$]	1.11923E0	8.03016E-2	1.16165E-2	-	291-353	0.165

[a] $s_{\mathrm{r}} = 100\left\{\sum_{i=1}^{n}\left[\left(c_p - c_p^{\mathrm{calc}}\right)/c_p^{\mathrm{calc}}\right]_i^2 \Big/ \left(n-m\right)\right\}^{1/2}$, where n is the number of fitted data points, and m is the number of independent adjustable parameters.

Table S10. Overview of the literature liquid phase heat capacities for pure compounds studied in this work[a]

Reference	N[b]	(T_{min}-T_{max})/K	$u_{\mathrm{r}}(C_{p\mathrm{m}})$/%[c]	mole fraction purity	method
heptan-1-ol					
Parks et al.[55]	7	240.03 - 299.99	1.0	0.997	Aneroid
Calvo et al.[56]	1	298.15	nosp.	>0.99	flow
van Miltenburg et al.[57]	**78**	**241.56 - 369.74**	**0.2**	**0.999**	**Adiabatic**
Serra et al.[58]	50	261.15 – 380.00	1.0	0.996	Tian-Calvet
This Work	13	291.07 - 349.71	1.0	0.999	Tian-Calvet
heptan-3-ol					
Serra et al.[58]	51	261.41 – 382.85	1.0	0.998	Tian-Calvet
This Work	**13**	**290.95 - 349.65**	**1.0**	**0.996**	**Tian-Calvet**
3-ethylpentan-3-ol					
Cáceres-Alonso et al.[51]	1	298.15	nosp.	>0.98	flow
Cerdeiriña et al.[59]	60	278.15 – 337.15	0.2	>0.98	Tian-Calvet
Serra et al.[58]	42	262.09 – 357.94	1.0	0.992	Tian-Calvet
This Work	**13**	**291.05 - 349.84**	**1.0**	**0.993**	**Tian-Calvet**
[C$_4$mim][NTf$_2$]					
Holbrey et al.[60]	17	293.15 - 453.15	nosp.	0.98	MDSC
Fredlake et al.[61]	2	298.15 - 323.15	3.6	>0.99	DSC
Troncoso et al.[62]	20	283.15 - 328.15	0.2 J/mol/K	>0.998	Tian-Calvet
Zhang and Reddy[63]	S	273.15 – 473.15	nosp.	nosp.	DSC
Shimizu et al.[64]	12	250 - 300	0.2	0.997	Adiabatic
Blokhin et al.[65]	**149**	**183.41 - 367.49**	**0.4**	**0.985**	**Adiabatic**

Reference	N[b]	$(T_{\mathrm{min}}$-$T_{\mathrm{max}})$/K	$u_r(C_{pm})$/%[c]	mole fraction purity	method
Ge et al.[66]	14	293 - 358	5.0	nosp.	DSC
Nieto de Castro et al.[67]	12	308.16 - 363.18	1.5	nosp.	DSC
Rocha et al.[68]	1	298.15	0.3	>0.99	drop
Gómez et al.[69]	41	293.15 - 333.15	5.0	>0.98	DSC
Makino et al.[70]	S	293.15 - 363.15	0.2	>0.997	Tian-Calvet
This Work	14	290.94 - 352.58	1.0	>0.990	Tian-Calvet
[C_6mim][NTf_2]					
Crosthwaite et al.[71]	2	298 - 323	5.0	nosp.	DSC
Archer[72]	164	196 - 370	1.1	0.995	DSC
Blokhin et al.[73]	**176**	**188.06 - 370**	**0.4**	**>0.995**	**Adiabatic**
Diedrichs and Ghmehling[74]	61	318.17 - 425.15	5.0	>0.999	DSC
Diedrichs and Ghmehling[74]					MDSC
Diedrichs and Ghmehling[74]					Tian-Calvet
Shimizu et al.[75]	6	272.1 - 310	0.5 J/mol/K	0.9983	Adiabatic
Ge et al.[66]	14	293 - 358	5.0	nosp.	DSC
Bochmann and Hefter[76]	21	325.02 - 564.85	0.3	nosp.	Tian-Calvet
Hughes et al.[77]	15	302.86 - 372.64	3.0	nosp.	Tian-Calvet
Rocha et al.[68]	1	298.15	0.3	>0.99	drop
Gómez et al.[69]	41	293.15 - 333.15	5.0	>0.99	DSC
This Work	14	290.99 - 352.60	1.0	>0.990	Tian-Calvet
[C_8mim][NTf_2]					
Crosthwaite et al.[71]	2	298 - 323	5.0	nosp.	DSC
Paulechka et al.[78]	**86**	**187.58 - 367.13**	**0.4**	**0.986**	**Adiabatic**
Ge et al.[66]	14	293 - 358	0.4	nosp.	DSC
Bochmann and Hefter[76]	21	325.02 – 564.84	0.3	nosp.	Tian-Calvet
Hughes et al.[77]	18	281.99 - 372.66	3.0	nosp.	Tian-Calvet
Chatel et al.[79]	13	265.02 - 385.03	3.0	nosp.	DSC
Rocha et al.[68]	1	298.15	0.3	>0.99	drop
This Work	14	290.94-352.73	1.0	>0.990	Tian-Calvet

[a] The data from references written in bold have been used as C_{pm}^{ref} in Fig. S17.

[b] N stands for number of data points.

[c] $u_r(C_{pm})$ stands for relative uncertainty in heat capacity as stated by the authors.

All available experimental heat capacities of pure compounds are compared in Fig. S17. Where possible, heat capacity values obtained by adiabatic calorimetry in a wide temperature range have been selected as reference. If no such data were available (in the case of heptan-3-ol and 3-ethylpentan-3-ol), our data have been used instead. In the case of [C_6mim][NTf_2], our data deviates by up to 4% from Blokhin et al.[73] However, data by other authors (Diedrichs and Ghmehling[74], Archer[72], Hughes et al.[77] and Ge et al.[66]) are in a better agreement with our data. We believe this disparity might be caused by the sample rather than the experimental method. Excess heat capacities are not influenced by differences between heat capacities of pure compounds obtained in this work and in the literature.

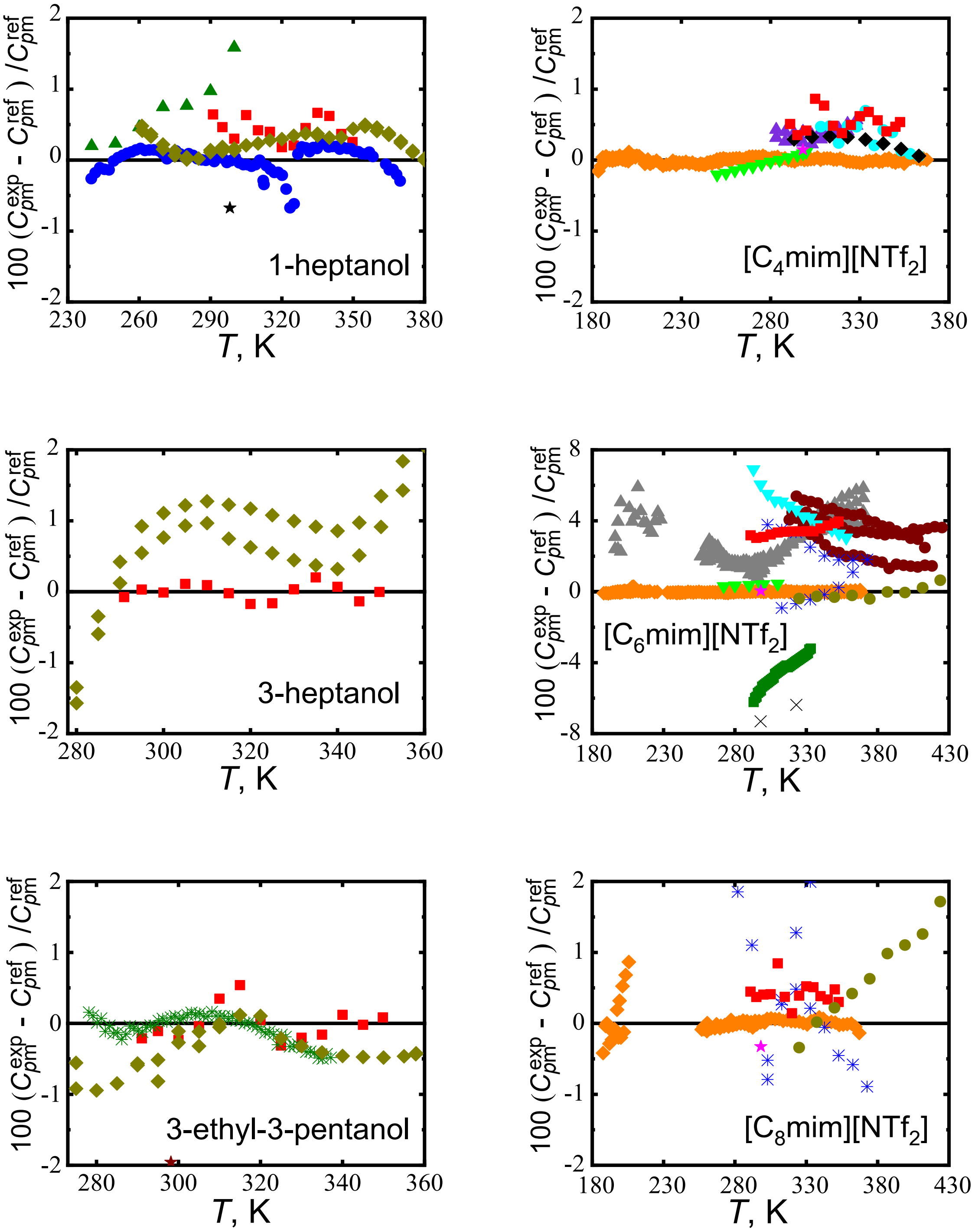

Fig. S18 Relative deviations $100\left(C_{pm}^{\mathrm{exp}}-C_{pm}^{\mathrm{ref}}\right)/C_{pm}^{\mathrm{ref}}$ of individual experimental heat capacities C_{pm}^{exp} from the reference C_{pm}^{ref} written in bold in Table 2. Red ■, This Work; Blue ●, van Miltenburg et al.[57]; Dark green ▲, Parks et al.[55]; Black ★, Calvo et al.[56]; Brown ★, Cáceres-Alonso et al.[51]; Dark green ✳; Cerdeiriña et al.[59], Orange ◆, Blokhin and coworkers[65, 73, 80]; Violet ▲, Troncoso et al.[62]; Black ◆, Makino et al.[70]; Cyan ▼, Ge et al.[66]; Cyan ●, Nieto de Castro et al.[67]; Green ▼, Shimizu et al. [64, 75]; Dark green ■, Gómez et al.[69]; Magenta ★, Rocha et al.[68]; Brown ●, Diedrichs and Ghmehling[74]; Grey ▲, Archer[81]; Olive ●, Bochmann and Hefter[76]; Blue ✳, Hughes et al.[77]; Black ×, Crosthwaite et al.[71]; Olive ◆, Serra et al.[58] Other data from Table S10 are not displayed, because they are out of scale.

Table S11. Parameters of eqn (S1) for liquid phase heat capacities of equimolar mixtures in $J\cdot K^{-1}\cdot g^{-1}$

Mixture[a]	A_1	A_2	A_3	T_{min}–T_{max}/K	s_r[b]
C_4H_1	1.59974E0	3.84473E-2	-	348-358	0.033
C_4H_3	2.84581E-2	8.71694E-1	-1.05382E-1	291-353	0.125
C_4E_3	1.43363E0	-2.39490E-3	2.32332E-2	296-354	0.058
C_6H_1	1.67896E0	-1.25001E-1	4.40540E-2	325-351	0.033
C_6H_3	1.72311E0	-1.27203E-1	4.45707E-2	291-349	0.128
C_6E_3	2.78389E0	-7.81168E-1	1.44693E-1	291-349	0.276
C_8H_1	1.79567E0	-2.18248E-1	6.31760E-2	291-353	0.379
C_8H_3	1.88228E0	-2.33465E-1	6.10361E-2	291-353	0.214
C_8E_3	1.96909E0	-2.69323E-1	6.50696E-2	291-345	0.191

[a] Abbreviations described in Table S1.

[b] $s_r = 100\left\{\sum_{i=1}^{n}\left[\left(c_p - c_p^{\mathrm{calc}}\right)/c_p^{\mathrm{calc}}\right]_i^2 \Big/ \left(n-m\right)\right\}^{1/2}$, where n is the number of fitted data points, and m is the number of independent adjustable parameters.

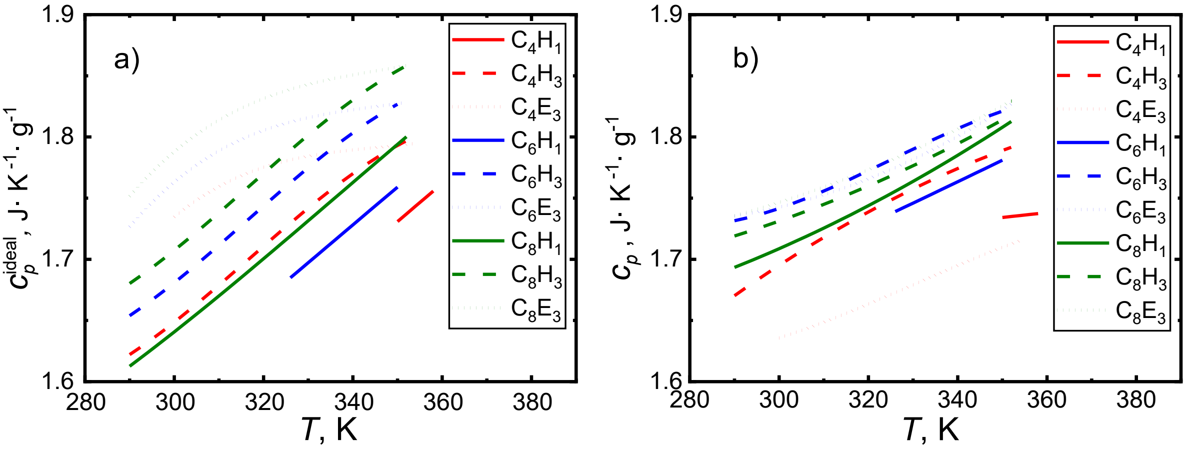

Fig. S19 Heat capacities of mixtures studied in this work with molar fraction $x_{IL} = 0.50 \pm 0.01$ (listed in Table S1). a) ideal mixture based on selected data from Table S10, b) real mixture calculated by the means of eqn (S1) with parameters from table S11.

Table S12. Parameters of eqn (S1) for excess heat capacities of equimolar mixtures in $J\cdot K^{-1}\cdot g^{-1}$

Mixture[a]	A_1	A_2	A_3	A_4	T_{min}–T_{max}/K
C_4H_1	4.32435E0	-2.22572E0	2.82339E-1	-	350-358
C_4H_3	4.59952E-1	-1.74780E-1	1.15085E-2	-	290-352
C_4E_3	2.25532E1	-1.99622E1	5.82796E0	-5.63603E-1	300-354
C_6H_1	1.48377E0	-7.36678E-1	8.77769E-2	-	326-352
C_6H_3	9.04018E-1	-4.19438E-1	4.17447E-2	-	290-350
C_6E_3	1.36784E1	-1.14955E1	3.15942E0	-2.84438E-1	290-350
C_8H_1	1.12601E0	-5.72756E-1	7.15642E-2	-	290-352
C_8H_3	2.04810E0	-1.14896E0	1.57024E-1	-	290-352
C_8E_3	1.64132E1	-1.43072E1	4.10373E0	-3.88908E-1	290-352

[a] Abbreviations described in Table S1

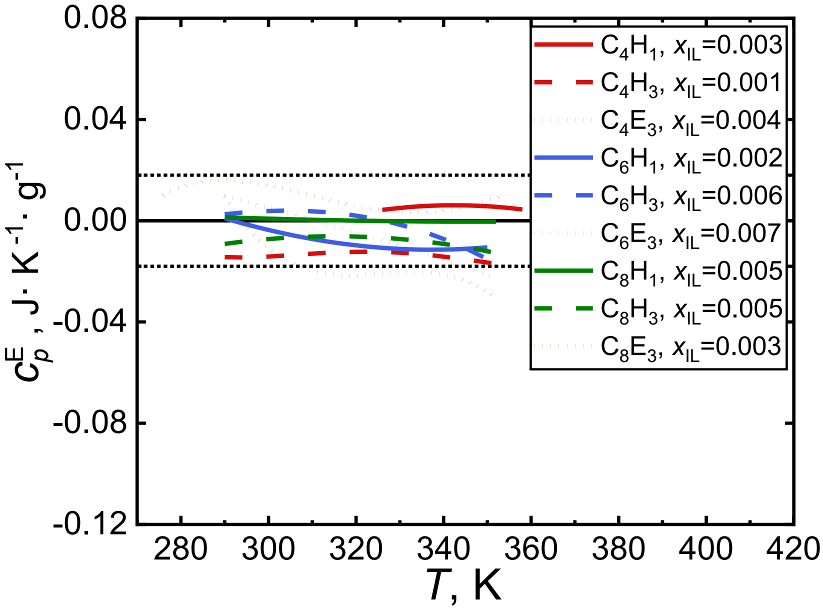

Fig. S20 Heat capacity of Alcohol-rich mixture with a drop of IL. $x_{IL} < 0.01$.

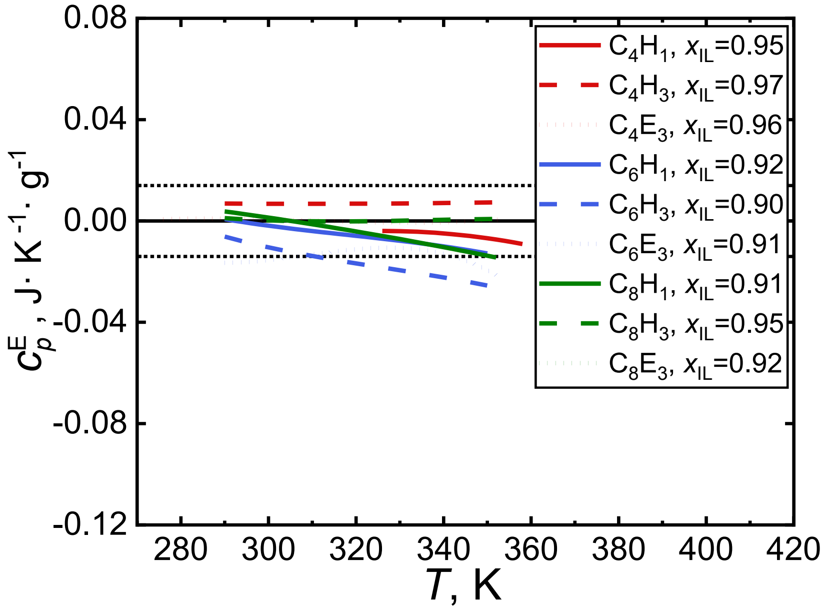

Fig. S21 Heat capacity of IL-rich mixture with a drop of alcohol. $x_{IL} > 0.9$.

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