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Solvation of Alcohols in Ionic Liquids – understanding the effect of the Anion and Cation

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Table S1. List of the studied compounds, the CAS number, purity, molar mass, density and water content

compound	CAS	source	purity	$\frac{\text{molar mass}}{\text{g}\cdot\text{mol}^{-1}}$	$\frac{\rho}{\text{Kg}\cdot\text{m}^{-3}}$	$\frac{\text{water}}{\text{ppm}}$
ionic liquids						
$[C_4py][NTf_2]$	187863-42-9	IoLiTec	99 %	416.36	–	60
$[C_4C_1pip][NTf_2]$	623580-02-9	IoLiTec	99 %	436.44	1380.8[15]	40
$[C_4C_1pirr][NTf_2]$	223437-11-4	IoLiTec	99 %	422.41	1394.9[16]	48
$[C_4C_1pirr][FAP]$	851856-47-8	Merck	> 99 %	587.27	1583.15[17]	108
$[C_4C_1im][FAP]$	917762-91-5	Merck	> 99 %	584.23	1625.32[18]	102
$[C_4C_1im][DCA]$	448245-52-1	IoLiTec	> 98 %	205.26	1060.5[19]	94
$[C_4C_1im][TFA]$	174899-94-6	IoLiTec	99 %	252.23	1212.8[20]	318
$[C_3C_1C_1im][NTf_2]$	169051-76-7	IoLiTec	> 98 %	419.36	1456.4[21]	33
Alcohol						
propan-1-ol	71-23-8	Sigma Aldrich	99.7 %	60.10	799.62[22]	52

Table S2. Results of the quantum chemical calculation of the interaction energy between the propan-1-ol and the anion X in the gas phase.

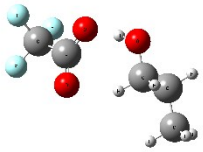
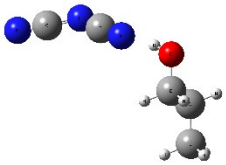
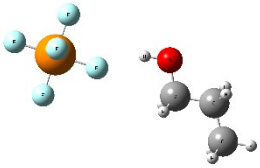
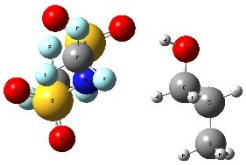
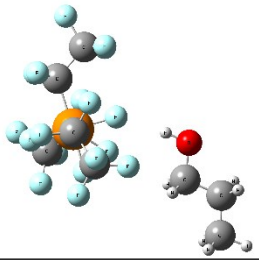
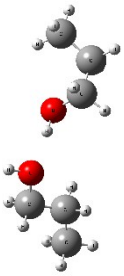
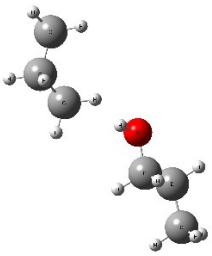
X	Interaction orientation	$\frac{E_{\text{int}}}{\text{kJ} \cdot \text{mol}^{-1}}$
	Anions	
TFA		– 62.90
DCA		– 52.60
PF_6		– 30.24
NTf_2		– 28.03
FAP		– 17.55
	Others	
propan-1-ol		– 18.46
propane		– 0.68

Table S3. Internal configurational energies, U_{cfg}, obtained from the molecular dynamic simulations results.

	U_{cfg} / kJ·mol^{-1} [a]
90 · [C4C1im][TFA] (l)	–8262.0 ± 38.9
90 · [C4C1im][DCA] (l)	–26735.8 ± 43.5
90 · [C4C1im][FAP] (l)	34356.8 ± 36.8
90 · [C4C1im][PF_6] (l)	–23373.2 ± 37.4
90 · [C4C1im][NTf_2] (l)	–4111.2 ± 41.8
{ 90 · [C4C1im][TFA] + 1 · propan-1-ol } (sol)	–8291.0 ± 45.2
{ 90 · [C4C1im][DCA] + 1 · propan-1-ol } (sol)	–26755.0 ± 36.2
{ 90 · [C4C1im][FAP] + 1 · propan-1-ol } (sol)	34360.5 ± 43.3
{ 90 · [C4C1im][PF_6] + 1 · propan-1-ol } (sol)	–23367.6 ± 39.5
{ 90 · [C4C1im][NTf_2] + 1 · propan-1-ol } (sol)	–4123.7 ± 40.8
1 · Propanol (g)	29.6 ± 0.4

[a] the uncertainties quoted correspond to the standard deviation of 24 values (20 in the case of propanol) obtained in the independent simulation runs.

Table S4. Standard (p^o=0.1 MPa) molar enthalpy of solvation at infinite dilution, $\Delta_{solv}H_m^{o,\infty}$, of propan-1-ol in the studied ionic liquids at 298.15 K, obtained from the data in Table S3.

Ionic Liquid	$-\Delta_{solv}H_m^{o,\infty}$ / kJ·mol^{-1}
[C4C1im][TFA]	61.1 ± 59.6
[C4C1im][DCA]	51.3 ± 56.6
[C4C1im][FAP]	28.4 ± 56.8
[C4C1im][PF_6]	26.5 ± 54.4
[C4C1im][NTf_2]	44.6 ± 58.4

Table S5. Standard (p^o=0.1 MPa) molar enthalpy of solvation at infinite dilution at 298.15 K, $\Delta_{solv}H_m^{o,\infty}$, for propan-1-ol in $[C_4C_1im][TFA]$, computed from the 24 U_{cfg}(sol) and U_{cfg}(IL, l) values found from the independent simulation runs, and U_{cfg}(Prop, g) = 29.6 ± 0.4 kJ·mol^{-1}. All data in kJ·mol^{-1}.

	U_{cfg}(sol)																						
U_{cfg}(IL)	-8293.5	-8291.1	-8285.3	-8402.0	-8283.9	-8262.7	-8279.1	-8260.9	-8263.7	-8262.7	-8355.1	-8263.6	-8324.9	-8266.3	-8313.9	-8234.0	-8270.7	-8361.7	-8269.0	-8201.5	-8323.9	-8249.5	-8348.9	-8315.6
-8227.0	-98.6	-96.2	-90.4	-207.1	-89.0	-67.8	-84.2	-66.0	-68.8	-67.8	-160.2	-68.7	-130.0	-71.4	-119.0	-39.1	-75.8	-166.8	-74.1	-6.6	-129.0	-54.6	-154.0	-120.7
-8268.9	-56.7	-54.4	-48.5	-165.2	-47.2	-25.9	-42.4	-24.2	-26.9	-25.9	-118.3	-26.8	-88.1	-29.5	-77.1	2.8	-33.9	-124.9	-32.2	35.3	-87.1	-12.7	-112.2	-78.8
-8291.1	-34.4	-32.1	-26.2	-143.0	-24.9	-3.6	-20.1	-1.9	-4.6	-3.6	-96.1	-4.6	-65.9	-7.3	-54.9	25.1	-11.7	-102.7	-9.9	57.6	-64.9	9.5	-89.9	-56.6
-8220.2	-105.4	-103.1	-97.2	-214.0	-95.9	-74.6	-91.1	-72.9	-75.6	-74.6	-167.0	-75.5	-136.8	-78.2	-125.9	-45.9	-82.7	-173.6	-80.9	-13.4	-135.8	-61.5	-160.9	-127.5
-8205.8	-119.8	-117.4	-111.6	-228.3	-110.2	-89.0	-105.4	-87.2	-89.9	-88.9	-181.4	-89.9	-151.2	-92.6	-140.2	-60.2	-97.0	-188.0	-95.2	-27.8	-150.2	-75.8	-175.2	-141.9
-8235.8	-89.8	-87.5	-81.6	-198.3	-80.3	-59.0	-75.5	-57.3	-60.0	-59.0	-151.4	-59.9	-121.2	-62.6	-110.3	-30.3	-67.0	-158.0	-65.3	2.2	-120.2	-45.8	-145.3	-111.9
-8266.2	-59.4	-57.0	-51.2	-167.9	-49.8	-28.6	-45.0	-26.8	-29.6	-28.5	-121.0	-29.5	-90.8	-32.2	-79.8	0.1	-36.6	-127.6	-34.9	32.6	-89.8	-15.4	-114.8	-81.5
-8231.9	-93.6	-91.3	-85.4	-202.2	-84.1	-62.8	-79.3	-61.1	-63.8	-62.8	-155.3	-63.8	-125.0	-66.5	-114.1	-34.1	-70.9	-161.9	-69.1	-1.6	-124.0	-49.7	-149.1	-115.8
-8255.7	-69.8	-67.5	-61.6	-178.4	-60.3	-39.0	-55.5	-37.3	-40.0	-39.0	-131.5	-40.0	-101.3	-42.7	-90.3	-10.3	-47.1	-138.1	-45.3	22.2	-100.3	-25.9	-125.3	-92.0
-8252.7	-72.9	-70.5	-64.7	-181.4	-63.3	-42.1	-58.5	-40.3	-43.1	-42.0	-134.5	-43.0	-104.3	-45.7	-93.3	-13.4	-50.1	-141.1	-48.3	19.1	-103.3	-28.9	-128.3	-95.0
-8314.2	-11.4	-9.1	-3.2	-119.9	-1.9	19.4	2.9	21.1	18.4	19.4	-73.0	18.5	-42.8	15.8	-31.8	48.1	11.4	-79.6	13.1	80.6	-41.8	32.6	-66.9	-33.5
-8225.1	-100.5	-98.2	-92.3	-209.0	-91.0	-69.7	-86.2	-68.0	-70.7	-69.7	-162.1	-70.6	-131.9	-73.3	-120.9	-41.0	-77.7	-168.7	-76.0	-8.5	-130.9	-56.5	-156.0	-122.6
-8249.0	-76.6	-74.3	-68.4	-185.2	-67.1	-45.8	-62.3	-44.1	-46.8	-45.8	-138.2	-46.7	-108.0	-49.4	-97.1	-17.1	-53.9	-144.8	-52.1	15.4	-107.0	-32.6	-132.1	-98.7
-8249.8	-75.8	-73.5	-67.6	-184.3	-66.3	-45.0	-61.5	-43.3	-46.0	-45.0	-137.4	-45.9	-107.2	-48.6	-96.3	-16.3	-53.0	-144.0	-51.3	16.2	-106.2	-31.8	-131.3	-97.9
-8293.2	-32.4	-30.1	-24.2	-140.9	-22.9	-1.6	-18.1	0.1	-2.6	-1.6	-94.0	-2.5	-63.8	-5.2	-52.9	27.1	-9.6	-100.6	-7.9	59.6	-62.8	11.6	-87.9	-54.5
-8225.8	-99.8	-97.4	-91.6	-208.3	-90.2	-69.0	-85.4	-67.2	-70.0	-68.9	-161.4	-69.9	-131.2	-72.6	-120.2	-40.3	-77.0	-168.0	-75.2	-7.8	-130.2	-55.8	-155.2	-121.9
-8194.8	-130.8	-128.5	-122.6	-239.3	-121.3	-100.0	-116.5	-98.3	-101.0	-100.0	-192.4	-100.9	-162.2	-103.6	-151.3	-71.3	-108.0	-199.0	-106.3	-38.8	-161.2	-86.8	-186.3	-152.9
-8274.1	-51.5	-49.2	-43.3	-160.1	-42.0	-20.7	-37.2	-19.0	-21.7	-20.7	-113.1	-21.6	-82.9	-24.3	-72.0	8.0	-28.8	-119.7	-27.0	40.5	-81.9	-7.6	-107.0	-73.6
-8275.0	-50.6	-48.2	-42.4	-159.1	-41.0	-19.8	-36.2	-18.0	-20.8	-19.8	-112.2	-20.7	-82.0	-23.4	-71.0	8.9	-27.8	-118.8	-26.1	41.4	-81.0	-6.6	-106.0	-72.7
-8267.6	-57.9	-55.6	-49.7	-166.5	-48.4	-27.1	-43.6	-25.4	-28.1	-27.1	-119.6	-28.1	-89.4	-30.8	-78.4	1.6	-35.2	-126.2	-33.4	34.1	-88.4	-14.0	-113.4	-80.1
-8285.7	-39.9	-37.5	-31.7	-148.4	-30.3	-9.1	-25.5	-7.3	-10.0	-9.0	-101.5	-10.0	-71.3	-12.7	-60.3	19.7	-17.1	-108.1	-15.3	52.1	-70.3	4.1	-95.3	-62.0
-8357.4	31.9	34.2	40.1	-76.7	41.4	62.7	46.2	64.4	61.7	62.7	-29.8	61.8	0.5	59.0	11.4	91.4	54.6	-36.4	56.4	123.9	1.5	75.8	-23.6	9.8
-8305.4	-20.2	-17.9	-12.0	-128.8	-10.7	10.6	-5.9	12.3	9.6	10.6	-81.8	9.7	-51.6	7.0	-40.7	39.3	2.5	-88.4	4.3	71.8	-50.6	23.8	-75.7	-42.3
-8316.7	-8.9	-6.5	-0.7	-117.4	0.7	21.9	5.5	23.7	20.9	22.0	-70.5	21.0	-40.3	18.3	-29.3	50.6	13.9	-77.1	15.7	83.1	-39.3	35.1	-64.3	-31.0

$<\Delta_{solv}H_m^{o,\infty}>$ = –61.1 ± 58.4 kJ·mol^{-1}; $\Delta_{solv}H_m^{o,\infty}$ (Max) = +123.9 kJ·mol^{-1}; $\Delta_{solv}H_m^{o,\infty}$ (Min) = –239.3 kJ·mol^{-1}

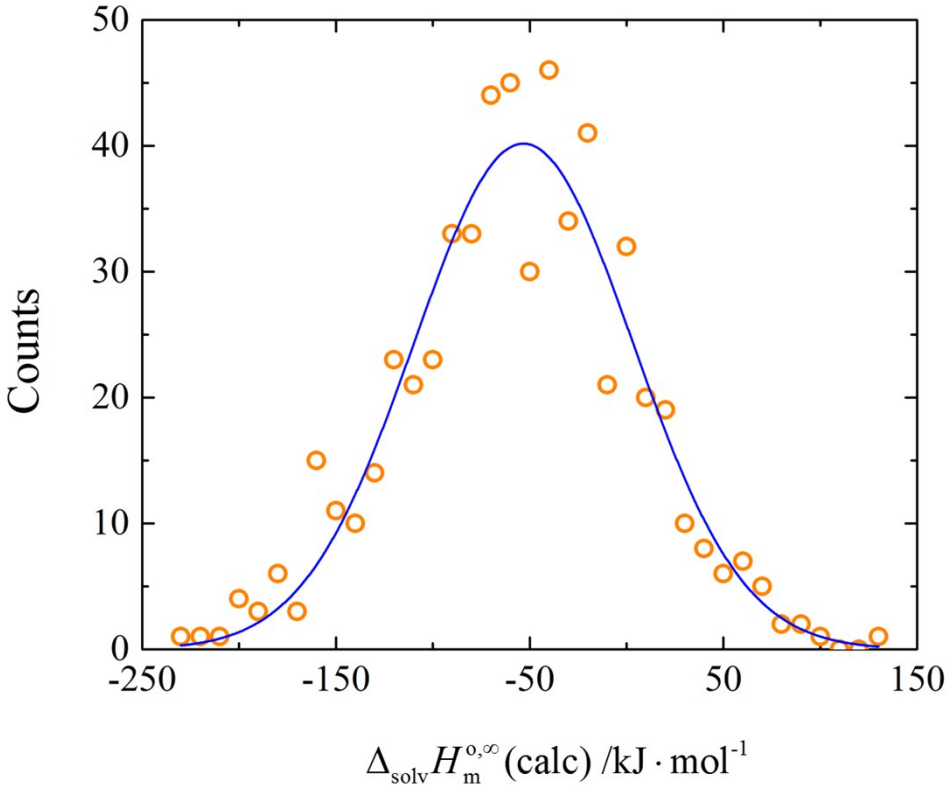


Figure S1. Histogram analysis of the 24 × 24 = 576 values of solvation enthalpy of propan-1-ol in [C4C1im][TFA] showing a wide Gaussian distribution centered around – 60 kJ·mol^{-1} and standard deviation intervals of around 50 kJ·mol^{-1}.