

Electronic Supplementary Information (ESI) for PCCP

Alcohols as Molecular Probes in Ionic Liquids: Evidence for Nanostructuring

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Table S1. Complete list of the schematic structures and abbreviations of the studied ionic liquids

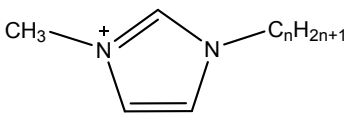
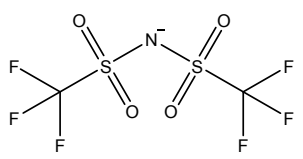
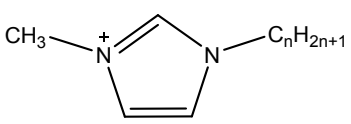
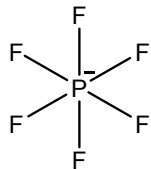
cation	anion	abbreviation
 <p>Imidazolium (im)</p>	 <p>Bis(trifluoromethylsulfonyl)imide (NTf₂)</p>	[C _n C ₁ im][NTf ₂]
R: -CH ₂ -CH ₃		[C ₂ C ₁ im][NTf ₂]
R: -(CH ₂) ₂ -CH ₃		[C ₃ C ₁ im][NTf ₂]
R: -(CH ₂) ₃ -CH ₃		[C ₄ C ₁ im][NTf ₂]
R: -(CH ₂) ₄ -CH ₃		[C ₅ C ₁ im][NTf ₂]
R: -(CH ₂) ₅ -CH ₃		[C ₆ C ₁ im][NTf ₂]
R: -(CH ₂) ₆ -CH ₃		[C ₇ C ₁ im][NTf ₂]
R: -(CH ₂) ₇ -CH ₃		[C ₈ C ₁ im][NTf ₂]
R: -(CH ₂) ₈ -CH ₃		[C ₉ C ₁ im][NTf ₂]
R: -(CH ₂) ₉ -CH ₃		[C ₁₀ C ₁ im][NTf ₂]
R: -(CH ₂) ₁₀ -CH ₃		[C ₁₁ C ₁ im][NTf ₂]
 <p>Imidazolium (im)</p>	 <p>Hexafluorophosphate (PF₆)</p>	[C _n C ₁ im][PF ₆]
R: -(CH ₂) ₃ -CH ₃		[C ₄ C ₁ im][PF ₆]
R: -(CH ₂) ₄ -CH ₃		[C ₅ C ₁ im][PF ₆]
R: -(CH ₂) ₅ -CH ₃		[C ₆ C ₁ im][PF ₆]
R: -(CH ₂) ₆ -CH ₃		[C ₇ C ₁ im][PF ₆]
R: -(CH ₂) ₇ -CH ₃		[C ₈ C ₁ im][PF ₆]
R: -(CH ₂) ₈ -CH ₃		[C ₉ C ₁ im][PF ₆]

Table S2. List of the studied ILs, CAS registry number, purity and molar mass

ionic liquid	CAS registry number	source	purity	MW /g·mol ⁻¹
[C _n C ₁ im][NTf ₂]				
[C ₂ C ₁ im][NTf ₂]	174899-82-2	IoLiTec	99.5 %	391.31
[C ₃ C ₁ im][NTf ₂]	216299-72-8	IoLiTec	99 %	405.34
[C ₄ C ₁ im][NTf ₂]	174899-83-3	IoLiTec	99 %	419.37
[C ₅ C ₁ im][NTf ₂]	280779-53-5	IoLiTec	> 99 %	433.39
[C ₆ C ₁ im][NTf ₂]	382150-50-7	IoLiTec	99 %	447.42
[C ₇ C ₁ im][NTf ₂]	455382-14-5	IoLiTec	> 99 %	461.45
[C ₈ C ₁ im][NTf ₂]	178631-04-4	IoLiTec	99 %	475.47
[C ₉ C ₁ im][NTf ₂]	–	IoLiTec	> 99 %	489.50
[C ₁₀ C ₁ im][NTf ₂]	433337-23-6	IoLiTec	> 98 %	503.53
[C ₁₁ C ₁ im][NTf ₂]	–	IoLiTec	97 %	517.55
[C _n C ₁ im][PF ₆]				
[C ₄ C ₁ im][PF ₆]	174501-64 -5	IoLiTec	99 %	284.18
[C ₅ C ₁ im][PF ₆]	280779-52-4	IoLiTec	> 99 %	298.21
[C ₆ C ₁ im][PF ₆]	304680-35-1	IoLiTec	99 %	312.24
[C ₇ C ₁ im][PF ₆]	357915-04-9	IoLiTec	> 99 %	326.26
[C ₈ C ₁ im][PF ₆]	304680-36-2	IoLiTec	99 %	340.29
[C ₉ C ₁ im][PF ₆]	343952-29-4	IoLiTec	> 99 %	354.32

Table S3. Standard ($p^{\circ}=0.10 \pm 0.01$ MPa) molar enthalpy of solvation at infinite dilution of propan-1-ol, butan-1-ol and pentan-1-ol in the studied ILs, at reference temperature ($T=298.15$ K)

ionic liquid	$\Delta_{\text{solv}} H_{\text{m}}^{\circ, \infty} / \text{kJ} \cdot \text{mol}^{-1}$		
	propan-1-ol	butan-1-ol	pentan-1-ol
[C _n C ₁ im][NTf ₂]			
[C ₂ C ₁ im][NTf ₂]	– 38.73 (± 0.21)	– 42.94 (± 0.23)	– 47.16 (± 0.25)
[C ₃ C ₁ im][NTf ₂]	– 38.87 (± 0.21)	– 43.20 (± 0.22)	– 47.58 (± 0.24)
[C ₄ C ₁ im][NTf ₂]	– 39.08 (± 0.27)	– 43.46 (± 0.28)	– 47.83 (± 0.29)
[C ₅ C ₁ im][NTf ₂]	– 39.11 (± 0.21)	– 43.65 (± 0.21)	– 48.21 (± 0.23)
[C ₆ C ₁ im][NTf ₂]	– 39.32 (± 0.31)	– 44.00 (± 0.27)	– 48.49 (± 0.28)
[C ₇ C ₁ im][NTf ₂]	– 39.07 (± 0.21)	– 43.90 (± 0.21)	– 48.70 (± 0.22)
[C ₈ C ₁ im][NTf ₂]	– 39.03 (± 0.21)	– 43.82 (± 0.21)	– 48.87 (± 0.21)
[C ₉ C ₁ im][NTf ₂]	– 38.98 (± 0.21)	– 43.85 (± 0.21)	– 48.91 (± 0.21)
[C ₁₀ C ₁ im][NTf ₂]	– 39.00 (± 0.21)	– 43.81 (± 0.21)	– 48.84 (± 0.21)
[C ₁₁ C ₁ im][NTf ₂]	– 38.88 (± 0.21)	– 43.68 (± 0.21)	– 48.92 (± 0.21)
[C _n C ₁ im][PF ₆]			
[C ₄ C ₁ im][PF ₆]	– 36.43 (± 0.25)	–	–
[C ₅ C ₁ im][PF ₆]	– 36.80 (± 0.19)	–	–
[C ₆ C ₁ im][PF ₆]	– 36.96 (± 0.24)	–	–
[C ₇ C ₁ im][PF ₆]	– 37.20 (± 0.40)	–	–
[C ₈ C ₁ im][PF ₆]	– 37.29 (± 0.38)	–	–
[C ₉ C ₁ im][PF ₆]	– 37.56 (± 0.37)	–	–

* Uncertainties are the extended standard deviations considering the overall uncertainty.

Table S4. Standard ($p^{\circ}=0.10 \pm 0.01$ MPa) enthalpy of solvation at infinite dilution per unit volume of propan-1-ol, butan-1-ol and pentan-1-ol in the studied ionic liquids, at reference temperature ($T=298.15$ K)

ionic liquid	$\Delta_{\text{solv}} H_v^{\circ, \infty} / \text{kJ} \cdot \text{cm}^{-3}$		
	propan-1-ol	butan-1-ol	pentan-1-ol
[C _n C ₁ im][NTf ₂]			
[C ₂ C ₁ im][NTf ₂]	- 0.5153 (± 0.0028)	- 0.4668 (± 0.0025)	- 0.4339 (± 0.0023)
[C ₃ C ₁ im][NTf ₂]	- 0.5172 (± 0.0028)	- 0.4697 (± 0.0024)	- 0.4378 (± 0.0022)
[C ₄ C ₁ im][NTf ₂]	- 0.5200 (± 0.0036)	- 0.4725 (± 0.0031)	- 0.4401 (± 0.0027)
[C ₅ C ₁ im][NTf ₂]	- 0.5203 (± 0.0028)	- 0.4746 (± 0.0023)	- 0.4436 (± 0.0021)
[C ₆ C ₁ im][NTf ₂]	- 0.5232 (± 0.0042)	- 0.4784 (± 0.0030)	- 0.4461 (± 0.0026)
[C ₇ C ₁ im][NTf ₂]	- 0.5198 (± 0.0028)	- 0.4773 (± 0.0023)	- 0.4481 (± 0.0020)
[C ₈ C ₁ im][NTf ₂]	- 0.5193 (± 0.0028)	- 0.4764 (± 0.0023)	- 0.4496 (± 0.0020)
[C ₉ C ₁ im][NTf ₂]	- 0.5186 (± 0.0028)	- 0.4767 (± 0.0023)	- 0.4500 (± 0.0020)
[C ₁₀ C ₁ im][NTf ₂]	- 0.5189 (± 0.0028)	- 0.4763 (± 0.0023)	- 0.4494 (± 0.0020)
[C ₁₁ C ₁ im][NTf ₂]	- 0.5173 (± 0.0028)	- 0.4749 (± 0.0023)	- 0.4501 (± 0.0020)
[C _n C ₁ im][PF ₆]			
[C ₄ C ₁ im][PF ₆]	- 0.4846 (± 0.0033)	-	-
[C ₅ C ₁ im][PF ₆]	- 0.4896 (± 0.0025)	-	-
[C ₆ C ₁ im][PF ₆]	- 0.4917 (± 0.0032)	-	-
[C ₇ C ₁ im][PF ₆]	- 0.4950 (± 0.0053)	-	-
[C ₈ C ₁ im][PF ₆]	- 0.4962 (± 0.0050)	-	-
[C ₉ C ₁ im][PF ₆]	- 0.4998 (± 0.0049)	-	-

* The uncertainty is the extended standard deviation considering overall uncertainty.