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

Supplementary information:

On the structural origin of free volume in 1-alkyl-3-methylimidazolium ionic liquid mixtures: a SAXS and ^{129}Xe NMR study

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EXPERIMENTAL

General Procedures

Unless otherwise specified, syntheses were performed using standard Schlenk techniques or within a glovebox under a dry nitrogen atmosphere. Reagents purchased were of the highest purity available and were dried from appropriate drying agents.

Synthesis of Ionic Liquids

General Procedure for the Synthesis of 1-Alkyl-3-methylimidazolium chlorides ([$C_xC_1$im]Cl). The haloalkane (1.1 eq) was added dropwise to a stirred 1:1 mixture of 1-methylimidazole (1 eq) and anhydrous ethyl acetate at 0°C. After complete addition the mixture was stirred at ambient temperature for 30 minutes before slowly warming to 60°C. Progress was monitored by ^{1}H NMR. At 10-14 days the mixture was cooled to ambient temperature and the upper layer of the biphasic mixture was removed. Further anhydrous ethyl acetate was added and the mixture stirred vigorously for a few hours to overnight. The upper phase was then removed as above and the lower phase analysed by ^{1}H NMR. The washing step was repeated until the lower phase was free of starting materials. If necessary, depending on the colour of the lower phase, activated decolourising charcoal was added and the mixture stirred at 50°C overnight then cooled and filtered through a bed of Celite®. Additional filtration through a 0.2 µm filter was used to remove any residual particulates. The filtrate was then dried under high vacuum at 55°C.

1-Butyl-3-methylimidazolium chloride, [C_4C_1im]Cl. White crystalline solid (313.4 g, 92%); ^{1}H NMR (400 MHz, acetone-d_6) δH 10.86 (1H, s), 7.96 (1H, m), 7.89 (1H, m), 4.45 (2H, t), 4.10 (3H, s), 1.92 (2H, m), 1.36 (2H, m), 0.94 (3H, t). ^{13}C{^{1}H} NMR (101 MHz, acetone-d_6) δC 139.52, 124.38, 123.14, 49.81, 36.42, 32.98, 20.05, 13.83.

1-Hexyl-3-methylimidazolium chloride, [C_6C_1im]Cl. Clear viscous oil (67.9 g, 72%); ^{1}H NMR (400 MHz, DMSO-d_6) δH 9.38 (1H, s), 7.84 (1H, s), 7.77 (1H, s), 4.18 (2H, t), 3.87 (3H, s), 1.78 (2H, quintet), 1.30-1.21 (6H, m), 0.86 (3H, t). ^{13}C NMR (101 MHz, DMSO-d_6) δC 137.22, 124.03, 122.73, 49.12, 36.16, 31.03, 29.86, 25.61, 22.34, 14.28; m/z 167 ([C_6C_1im]$^+$, 100%), 83, 37, 35 (Cl^-, 100%).

1-Decyl-3-methylimidazolium chloride, [$C_{10}C_1$im]Cl. Clear viscous oil (70.1g, 62%). ^{1}H NMR (400 MHz, DMSO-d_6) δH 9.31 (1H, s), 7.82 (1H, s), 7.75 (1H, s), 4.17 (2H, t), 3.87 (3H, s), 1.78 (2H, quintet), 1.29-1.21 (14H, m), 0.86 (3H, t); ^{13}C NMR (101 MHz, DMSO-d_6) δC 137.20, 124.03, 122.73, 49.14, 36.16, 31.75, 29.91, 29.38, 29.31, 29.14, 28.87, 25.98, 22.55, 14.40; m/z 223 ([$C_{10}C_1$im]$^+$, 100%), 83, 43, 41, 37, 35 (Cl^-, 100%).

1-Ethyl-3-methylimidazolium bromide, [C_2C_1im]Br. Freshly distilled bromoethane (190 mL, 2.50 mol) was added dropwise to freshly distilled 1-methylimidazole (190 mL, 2.38 mol) overnight, under a nitrogen atmosphere and with vigorous stirring. During this time, a white solid formed. The solid was recrystallised from 60:40 acetonitrile/ethyl acetate (300 mL), and the residual solution was carefully decanted off. The solid was washed with diethyl ether (3 x 150 mL) and the solid was dried under vacuum to yield 1-ethyl-3-methylimidazolium bromide (279 g, 61%) as a white crystalline solid.

^{1}H NMR (400 MHz, DMSO-d_6): δH 9.16 (1H, s), 7.80 (1H, t), 7.71 (1H, t), 4.19 (2H, q), 3.85 (3H, s), 1.41 (3H, t). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δC 136.2, 123.5, 122.0, 44.1, 35.7, 15.1. m/z (LSIMS+) 111 ($[C_2C_1im]^+$, 100%). m/z (LSIMS−) 46 ($[EtOH]^-$, 100%), 80 ($[HBr]^-$, 83%), 81 (Br^-, 48%) 79 (Br^-, 47%).

General Procedure for the Preparation of 1-Alkyl-3-methylimidazolium bistrifluoromethanesulfonyl(imides) ($[C_xC_1im][NTf_2]$). In air, $[C_xC_1im]Cl$ or $[C_2C_1im]Br$ (1 eq) and lithium bis(trifluoromethanesulfonyl)imide (1.1 eq) were dissolved separately in water (typically 150 mL each). These aqueous solutions were combined resulting in the immediate formation of a second phase. Dichloromethane (200 mL) was added to increase the volume of the lower phase and the resultant organic phase separated and washed with water until the aqueous phase tested negative for halide using a 0.1 M $AgNO_3$ solution (typically 4 × 150 mL). The dichloromethane solvent was removed and the resultant liquid dried at 50 °C *in vacuo*.

1-Ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[C_2C_1im][NTf_2]$). Clear colourless oil (50.4 g, 95%). ^{1}H NMR (400 MHz, acetone-d_6) δH 9.00 (1H, s), 7.76 (1H, s), 7.69 (1H, s), 4.40 (2H, q), 1.56 (3H, t); ^{13}C{^{1}H} NMR (101 MHz, acetone-d_6) δC 137.20, 124.86, 123.17, 121.06 (q), 45.82, 36.67, 15.62. ^{19}F{^{1}H} NMR (376 MHz, acetone-d_6) δF −79.96 (s).

1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[C_4C_1im][NTf_2]$). Clear colourless oil (187.6 g, 98%). ^{1}H NMR (400 MHz, acetone-d_6) δH 9.00 (1H, s), 7.76 (1H, m), 7.70 (1H, m), 4.36 (2H, t), 4.05 (3H, s), 1.92 (2H, quintet), 1.38 (2H, sextet), 0.94 (3H, t); ^{13}C{^{1}H} NMR (101 MHz, acetone-d_6) δC 137.43, 124.87, 123.48, 121.04 (q), 50.31, 36.71, 32.78, 20.00, 13.67; ^{19}F{^{1}H} NMR (376 MHz, acetone-d_6) δF −79.96 (s).

1-Hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[C_6C_1im][NTf_2]$). Clear colourless oil (33.2 g, 94 %). ^{1}H NMR (400 MHz, acetone-d_6) δH 9.07 (1H, s), 7.80 (1H, m), 7.74 (1H, m), 4.38 (2H, t), 4.08 (3H, s), 1.96 (2H, quintet), 1.24-1.42 (6H, m), 0.87 (3H, t); ^{13}C{^{1}H} NMR (101 MHz, acetone-d_6) δC 137.44, 124.89, 123.50, 121.04 (q), 50.58, 36.71, 31.82, 30.77, 26.46, 23.04, 14.16; ^{19}F{^{1}H} NMR (376 MHz, acetone-d_6) δF −79.95 (s).

1-Decyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[C_{10}C_1im][NTf_2]$). Clear colourless oil (75.2 g, 96 %). ^{1}H NMR (400 MHz, acetone-d_6) δH 9.08 (1H, s), 7.80 (1H, m), 7.74 (1H, m), 4.39 (2H, t), 4.08 (3H, s), 1.97 (2H, quintet), 1.18-1.44 (14H, m), 0.87 (3H, t); ^{13}C{^{1}H} NMR (101 MHz, acetone-d_6) δC 137.52, 124.97, 123.59, 121.16 (q), 50.67, 36.80, 32.67, 30.91, 30.19, 26.89, 23.38, 14.40; ^{19}F{^{1}H} NMR (376 MHz, acetone-d_6) δF −79.95 (s).

Density of IL Mixtures

Table S1. Measured density and the molar volume of each IL or IL mixture. Literature values reported in parentheses.

$[C_2C_1im]_x[C_{10}C_1im]_{1-x}[NTf_2]$

x	M (g mol^{-1})	Density (g mL^{-1})	V_m (cm^3 mol^{-1})	V^E (cm^3 mol^{-1})
0	503.52	1.2787 (1.279,[1] 1.2783)[2]	393.77	-
0.166	484.8915	1.3061	371.24	0.06
0.333	466.1507	1.3370	348.66	0.21
0.500	447.41	1.3728	325.92	0.19
0.667	428.6693	1.4138	303.20	0.21
0.831	410.2652	1.4612	280.78	0.10
1	391.3	1.5186 (1.5185)[3]	257.68	-

$[C_4C_1im]_x[C_{10}C_1im]_{1-x}[NTf_2]$

x	M (g mol^{-1})	Density (g mL^{-1})	V_m (cm^3 mol^{-1})	V^E (cm^3 mol^{-1})
0	503.52	1.2787 (1.279,[1] 1.2783)[2]	393.78	-
0.167	489.47	1.2989	376.84	0.05
0.333	475.49	1.3210	359.96	0.06
0.500	461.44	1.3456	342.93	0.02
0.665	447.55	1.3719	326.24	0.11
0.833	433.41	1.4025	309.03	-0.01
1	419.36	1.4359 (1.4357,[4] 1.4341,[4] 1.4366,[5] 1.4370)[6]	292.05	-

$[C_4C_1im]_x[C_6C_1im]_{1-x}[NTf_2]$

x	M (g mol^{-1})	Density (g mL^{-1})	V_m (cm^3 mol^{-1})	V^E (cm^3 mol^{-1})
0	447.41	1.3716 (1.37[7], 1.3710[8])	326.20	-
0.167	442.72565	1.3813	320.51	0.00
0.334	438.0413	1.3915	314.80	-0.02
0.499	433.41305	1.4019	309.16	-0.03
0.666	428.7287	1.4127	303.47	-0.03
0.833	424.04435	1.4240	297.79	-0.02
1	419.36	1.4356 (1.4357,[4] 1.4341,[4] 1.4366,[5] 1.4370)[6]	292.11	-

SAXS Data

Table S2. Correlation distances for peak I in $[C_2C_1im]_x[C_{10}C_1im]_{1-x}[NTf_2]$, $[C_4C_1im]_x[C_{10}C_1im]_{1-x}[NTf_2]$ and $[C_4C_1im]_x[C_6C_1im]_{1-x}[NTf_2]$ mixtures.

x in $[C_2C_1im]_x[C_{10}C_1im]_{1-x}[NTf_2]$	d (Å)	x in $[C_4C_1im]_x[C_{10}C_1im]_{1-x}[NTf_2]$	d (Å)	x in $[C_4C_1im]_x[C_6C_1im]_{1-x}[NTf_2]$	d (Å)
0	22.6	0	22.6	0	16.2
0.17	22.9	0.17	22.3	0.17	16.2
0.33	23.4	0.33	22.0	0.33	16.0
		0.50	21.3	0.50	15.8
0.67	24.1	0.67	20.4	0.67	16.0
0.83	23.5	0.83	19.1	0.83	NA
1	NA	1	NA	1	NA

Table S3. Correlation distances for peak II in $[C_2C_1im]_x[C_{10}C_1im]_{1-x}[NTf_2]$, $[C_4C_1im]_x[C_{10}C_1im]_{1-x}[NTf_2]$ and $[C_4C_1im]_x[C_6C_1im]_{1-x}[NTf_2]$ mixtures.

x in $[C_2C_1im]_x[C_{10}C_1im]_{1-x}[NTf_2]$	d (Å)	x in $[C_4C_1im]_x[C_{10}C_1im]_{1-x}[NTf_2]$	d (Å)	x in $[C_4C_1im]_x[C_6C_1im]_{1-x}[NTf_2]$	d (Å)
0	7.47	0	7.49	0	7.43
0.17	7.43	0.17	7.46	0.17	7.43
0.33	7.38	0.33	7.46	0.33	7.42
		0.50	7.44	0.50	7.41
0.67	7.24	0.67	7.41	0.67	7.39
0.83	7.18	0.83	7.40	0.83	7.38
1	7.09	1	7.36	1	7.35

^{129}Xe NMR

^{129}Xe NMR Experimental Setup

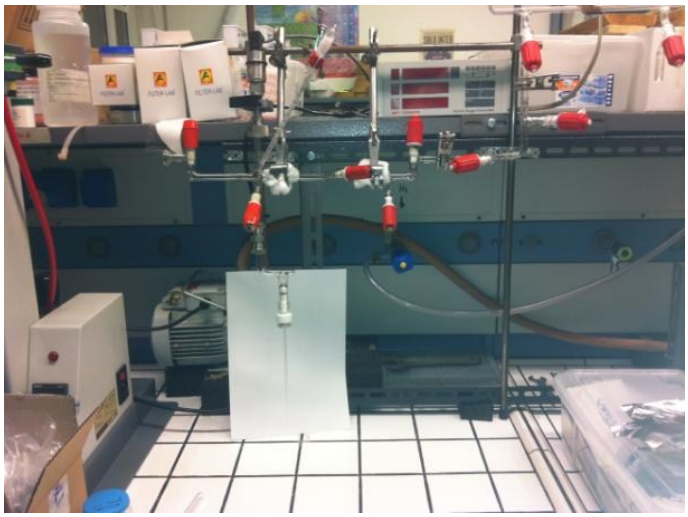

Fig. S1. View of the manifold used for preparing Xe NMR samples.

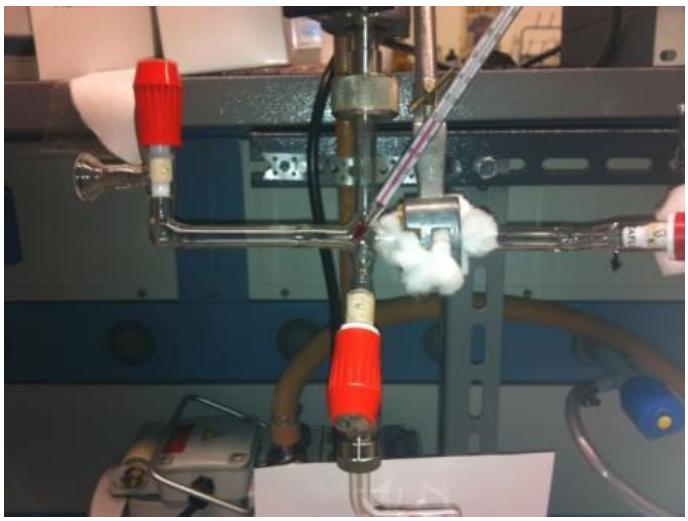

Fig. S2. Details of the cross shaped glass section of the manifold. Bottom: to the NMR tube. Left: inlet for xenon gas. Top: pressure gauge. Right: to the vacuum pump.

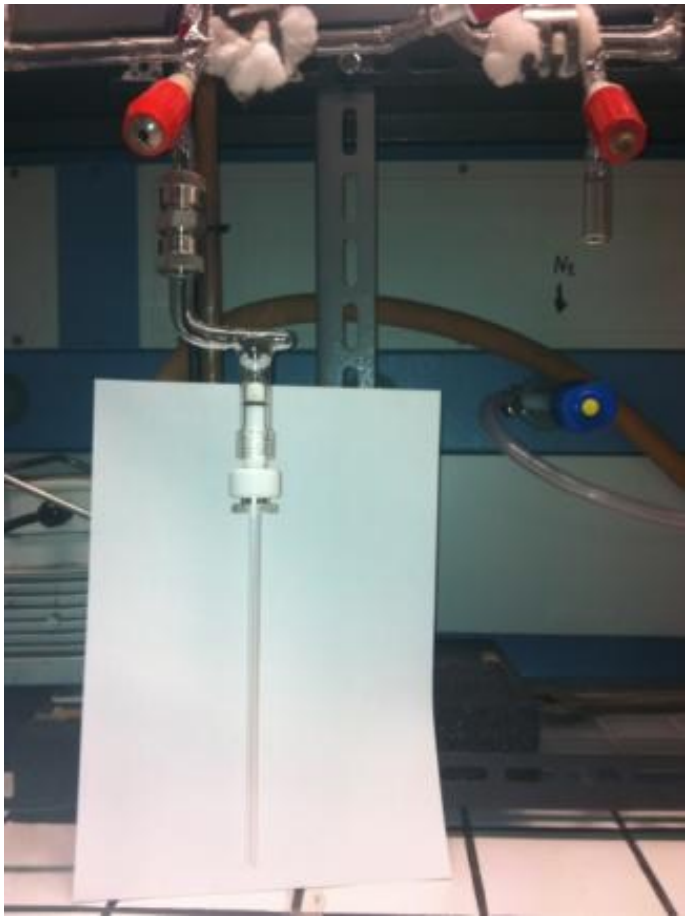

Fig. S3. Details of the connection to the NMR tube. The white teflon screw has an o-ring that can seal the tube by tightening on the glass. The metal part is a second screw (with o-ring) that provides sealing relative to the atmosphere.

^{129}Xe NMR Data

Table S4. ^{129}Xe NMR data for mixture $[C_2C_1im]_x[C_{10}C_1im]_{1-x}[NTf_2]$.

***x* in $[C_2C_1im]_x[C_{10}C_1im]_{1-x}[NTf_2]$**	**δ (ppm)[a]**	**δ_{calcd} (ppm)[b]**	**δ^E (ppm)[c]**
0.00	168.4	168.4	0.0
0.17	167.0	166.1	0.9
0.33	165.4	164.0	1.4
0.50	163.6	161.8	1.8
0.67	161.3	159.5	1.8
0.83	158.5	157.4	1.1
1.00	155.1	155.1	0.0

[a] Experimental value

[b] Calculated. $\delta_{calcd} = x\delta_1+(1-x)\delta_2$, where δ_1 and δ_2 are the experimental chemical shifts of the pure components.

[c] Excess ^{129}Xe chemical shift for a given molar fraction *x*. $\delta^E = \delta - (x\delta_1+(1-x)\delta_2)$.

Table S5. ^{129}Xe NMR data for mixture $[C_4C_1im]_x[C_{10}C_1im]_{1-x}[NTf_2]$.

***x* in $[C_4C_1im]_x[C_{10}C_1im]_{1-x}[NTf_2]$**	**δ (ppm)[a]**	**δ_{calcd} (ppm)[b]**	**δ^E (ppm)[c]**
0.00	168.4	168.4	0.0
0.17	167.1	166.7	0.4
0.33	165.9	165.1	0.8
0.50	164.1	163.4	0.7
0.67	162.4	161.7	0.7
0.83	160.4	160.1	0.3
1.00	158.1	158.1	0.0

[a] Experimental value

[b] Calculated. $\delta_{calcd} = x\delta_1+(1-x)\delta_2$, where δ_1 and δ_2 are the experimental chemical shifts of the pure components.

[c] Excess ^{129}Xe chemical shift for a given molar fraction *x*. $\delta^E = \delta - (x\delta_1+(1-x)\delta_2)$.

Table S6. ^{129}Xe NMR data for mixture $[C_4C_1im]_x[C_6C_1im]_{1-x}[NTf_2]$.

***x* in $[C_4C_1im]_x[C_6C_1im]_{1-x}[NTf_2]$**	**δ (ppm)[a]**	**δ_{calcd} (ppm)[b]**	**δ^E (ppm)[c]**
0.00	158.1	158.1	0.0
0.17	158.9	158.8	0.1
0.33	159.6	159.4	0.2
0.50	160.15	160.1	0.1
0.67	160.8	160.7	0.1
0.83	161.4	161.3	0.1
1.00	162.0	162.0	0.0

[a] Experimental value

[b] Calculated. $\delta_{calcd} = x\delta_1+(1-x)\delta_2$, where δ_1 and δ_2 are the experimental chemical shifts of the pure components.

[c] Excess ^{129}Xe chemical shift for a given molar fraction *x*. $\delta^E = \delta - (x\delta_1+(1-x)\delta_2)$.

^{129}Xe NMR Model

The preferential solvation model for the ^{129}Xe NMR chemical shift assumed an equilibrium of the form given by Eq. S1 below where $Xe_{[CnC1im][NTf2]}$ refers to Xe solvated by $[C_nC_1im][NTf_2]$ and $[C_mC_1im][NTf_2]$ refers to the IL that is not interacting with a Xe atom. The equilibrium constant, K, for this process in terms of the mole fraction of each component is then given by Eq. S2 below.

$$Xe_{[CnC1im][NTf2]} + [C_mC_1im][NTf_2] \rightleftharpoons Xe_{[CmC1im][NTf2]} + [C_nC_1im][NTf_2] \quad \text{(S1)}$$

$$K = \frac{x_{[CnC1im][NTf2]}x_{Xe[CnC1im][NTf2]}}{x_{[CmC1im][NTf2]}x_{Xe[CmC1im][NTf2]}} \quad \text{(S2)}$$

$x_{[CnC1im][NTf2]}$ is taken be equivalent to the composition (x) of the IL mixture. $x_{[CnC1im][NTf2]} = 1 - x_{[CnC1im][NTf2]}$. $x_{Xe[CnC1im][NTf2]}$ is calculated by Eq. S3 where δ_2 is the ^{129}Xe NMR chemical shift in $[C_mC_1im][NTf_2]$, δ_1 is the chemical shift within $[C_nC_1im][NTf_2]$ and δ the chemical shift of the mixture. $x_{Xe[CmC1im][NTf2]} = 1 - x_{Xe[CnC1im][NTf2]}$. As discussed in the main text, the mole fractions calculated in this way are not the precise mole fraction within the mixture as the absolute mole fraction of solvated Xe is unknown. Nonetheless, the use of these mole fractions leads to the same numerical value of K as any increase in the mole fraction of solvated Xe, and hence $x_{Xe[CnC1im][NTf2]}$ and $x_{Xe[CmC1im][NTf2]}$ will be exactly offset by the decrease in free IL and hence $x_{[CnC1im][NTf2]}$ and $x_{[CmC1im][NTf2]}$. Therefore, given their equivalence for the simple model proposed the effective mole fractions we define here are used rather than the absolute mole fraction in the solution.

$$\chi_{Xe[CnC1im][NTf2]} = \frac{\delta_2 - \delta}{\delta_2 - \delta_1} \quad \text{(S3)}$$

The parameters obtained from this model for each composition of each mixture are given in Tables S7-S9.

Table S7. Model parameters obtained for the $[C_2C_1im]_x[C_{10}C_1im]_{1-x}[NTf_2]$ mixtures.

$x_{[C2C1im][NTf2]}$	$x_{Xe[C2C1im][NTf2]}$	K
0	0	
0.166	0.105	1.74
0.333	0.226	1.69
0.500	0.361	1.77
0.667	0.534	1.77
0.831	0.744	1.68
1	1	

Table S8. Model parameters obtained for the $[C_4C_1im]_x[C_{10}C_1im]_{1-x}[NTf_2]$ mixtures.

$x_{[C4C1im][NTf2]}$	$x_{Xe[C4C1im][NTf2]}$	K
0	0	
0.167	0.126	1.42
0.333	0.243	1.54
0.500	0.417	1.40
0.665	0.583	1.46
0.833	0.777	1.40
1	1	

Table S9. Model parameters obtained for the $[C_4C_1im]_x[C_6C_1im]_{1-x}[NTf_2]$ mixtures.

$x_{[C4C1im][NTf2]}$	$x_{Xe[C4C1im][NTf2]}$	K
0	0	
0.167	0.154	1.13
0.334	0.308	1.11
0.499	0.474	1.11
0.666	0.615	1.27
0.833	0.795	1.26

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