

Supplementary Information

Playing with ionic liquid mixtures to design engineered CO₂ separation membranes

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Density measurements

Densities of the pure ionic liquids (ILs) and their mixtures were measured in the temperature range from 293.15 K to 353.15 K and are reported in Table S1 and S2, and illustrated in Figure S1 and S2, respectively. Additionally, a comparison of these results with literature values is shown in Table S3. When comparing the experimental results obtained in this work with those published in the literature for the same pure ILs, it can be observed that they are consistent with each other, with the exception of the pure [C₂mim][C₁SO₄], in which a deviation of 0.31 % for density and 16.1 % for viscosity values were observed. These differences can be attributed to the content of water in the IL. However, a direct comparison cannot be made since some of the authors do not report the quantity of water in their samples.

The density decreases linearly with temperature, for all pure ILs and their mixtures, in the whole temperature range studied. The linear equation (S1) was used to correlate the temperature dependence of the density:

$$\rho = a + b(T) \quad (\text{S1})$$

where ρ corresponds to density (g·cm⁻³), T is the temperature (K) and a and b are the fitting parameters. The a and b values, derived from the equation (S1), obtained for all the studied samples are presented in Table S4.

The molar volumes (V_m) of the pure ILs and their mixtures are presented in Table S5 and S6, respectively. The excess molar volume (V^E) of the IL mixtures was calculated by equation (S2):

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho_M} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \quad (\text{S2})$$

where ρ corresponds to the density (g·cm⁻³), x is the molar fraction and the M corresponds to the molar mass (g·mol⁻¹). The subscript 1 and 2 refer to the two pure ILs and the subscript M denotes the IL mixture. The calculated excess molar volumes are listed in Table S7 and depicted in Figure S3 for 293.15K.

As expected, Figure S1 and Figure S2 show that the density values of mixtures are in between those of the pure ILs. The density values can be grouped into two distinct groups: the sulfate-based ILs (values from 1.2 to 1.3 g·cm⁻³) and the cyano-based ILs (values from 1.0 to 1.15 g·cm⁻³). The density values of pure ILs decrease with the increase in the alkyl chain length in the sulfate and with the increase in the number of cyano groups in the anion of the IL (Figure S1). Accordingly, at a fixed

temperature, the densities of the pure ILs can be ranked according to the following anion order: $[\text{C}_1\text{SO}_4]^- > [\text{C}_2\text{SO}_4]^- > [\text{SCN}]^- > [\text{N}(\text{CN})_2]^- > [\text{C}(\text{CN})_3]^- > [\text{B}(\text{CN})_4]^-$.

The excess molar volumes (V^E) are the result of contributions from several effects, namely: chemical, physical and structural modifications. Physical contributions originate positive V^E values, which are non-specific interactions between the real species present in the mixture.⁶ Negative V^E values is a result of chemical contributions (charge-transfer type forces, changes in hydrogen bonding equilibrium or electrostatic interactions) or structural contributions (geometrical fitting or changes of free volume).⁶ The V^E obtained for all the studied mixtures at different temperatures present positive values, with the exception of those obtained for the $[\text{C}_2\text{mim}][\text{C}_1\text{SO}_4]_{0.5}[\text{N}(\text{CN})_2]_{0.5}$ mixture, that present a negative V^E in the whole range temperature, and for the $[\text{C}_2\text{mim}][\text{SCN}]_{0.5}[\text{N}(\text{CN})_2]_{0.5}$ mixture that presented a negative V^E values for higher temperatures (from 343.15 K to 353.15K).

Table S1 Measured densities, ρ ($\text{g}\cdot\text{cm}^{-3}$), of the pure ionic liquids studied in this work.

T (K)	$[\text{C}_2\text{mim}][\text{C}_1\text{SO}_4]$	$[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$	$[\text{C}_2\text{mim}][\text{SCN}]^*$	$[\text{C}_2\text{mim}][\text{N}(\text{CN})_2]^*$	$[\text{C}_2\text{mim}][\text{C}(\text{CN})_3]$	$[\text{C}_2\text{mim}][\text{B}(\text{CN})_4]$
293.15	1.294	1.241	1.119	1.106	1.085	1.040
298.15	1.291	1.237	1.116	1.103	1.081	1.036
303.15	1.287	1.234	1.113	1.099	1.077	1.032
308.15	1.284	1.231	1.110	1.096	1.074	1.029
313.15	1.281	1.227	1.107	1.093	1.070	1.025
318.15	1.278	1.224	1.104	1.090	1.067	1.021
323.15	1.274	1.221	1.101	1.086	1.064	1.017
328.15	1.271	1.218	1.098	1.083	1.060	1.013
333.15	1.268	1.214	1.095	1.080	1.057	1.010
338.15	1.265	1.211	1.092	1.077	1.054	1.006
343.15	1.261	1.208	1.089	1.074	1.050	1.002
348.15	1.258	1.205	—	—	1.047	0.999
353.15	1.255	1.201	—	—	1.043	0.995

*Values taken from Tomé *et al.*¹

Table S2 Measured densities, ρ ($\text{g}\cdot\text{cm}^{-3}$), of the ionic liquid mixtures studied in this work.

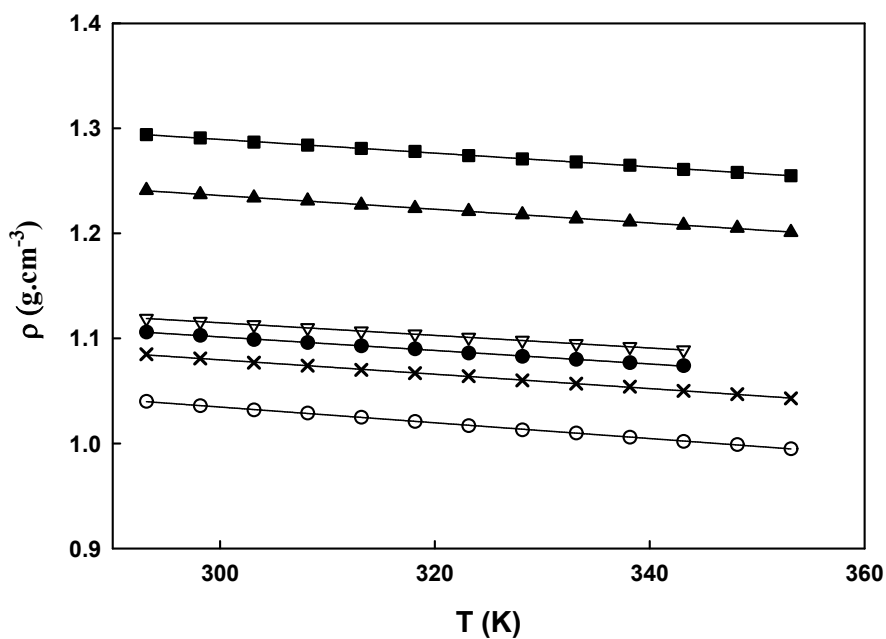
<i>T</i> (K)	[C ₂ mim]	[C ₂ mim]	[C ₂ mim]	[C ₂ mim]	[C ₂ mim]	[C ₂ mim]	[C ₂ mim]
	[C ₁ SO ₄] _{0.5}	[C ₁ SO ₄] _{0.5}	[C ₁ SO ₄] _{0.5}	[C ₁ SO ₄] _{0.5}	[SCN] _{0.5}	[SCN] _{0.5}	[SCN] _{0.5}
	[SCN] _{0.5}	[N(CN) ₂] _{0.5}	[C(CN) ₃] _{0.5}	[B(CN) ₄] _{0.5}	[N(CN) ₂] _{0.5}	[C(CN) ₃] _{0.5}	[B(CN) ₄] _{0.5}
293.15	1.211	1.203	1.179	1.144	1.112	1.099	1.070
298.15	1.208	1.200	1.176	1.140	1.108	1.096	1.067
303.15	1.205	1.196	1.172	1.137	1.105	1.092	1.063
308.15	1.201	1.193	1.169	1.133	1.102	1.089	1.060
313.15	1.198	1.190	1.165	1.129	1.099	1.086	1.056
318.15	1.195	1.186	1.162	1.126	1.096	1.083	1.053
323.15	1.192	1.183	1.159	1.122	1.093	1.080	1.049
328.15	1.189	1.180	1.155	1.119	1.090	1.076	1.046
333.15	1.186	1.177	1.152	1.115	1.087	1.073	1.042
338.15	1.183	1.174	1.149	1.111	1.084	1.070	1.039
343.15	1.180	1.170	1.145	1.108	1.081	1.067	1.036
348.15	1.177	1.167	1.142	1.104	1.078	1.064	1.032
353.15	1.174	1.164	1.139	1.101	1.075	1.060	1.029

Table S3 Comparison of density (ρ) and viscosity (η) values of the pure ionic liquids measured in this work with those from literature at 298.15 K.

Ionic liquids	ρ ($\text{g}\cdot\text{cm}^{-3}$)		η (mPa.s)	
	This Work	Literature	This Work	Literature
	[C ₂ mim][C ₁ SO ₄]	1.291	1.287 ²	100.021
[C ₂ mim][C ₂ SO ₄]	1.237	1.237 ³	92.677	95.90 ³
[C ₂ mim][C(CN) ₃]	1.081	1.081 ⁴	14.187	14.610 ⁵
[C ₂ mim][B(CN) ₄]	1.036	1.036 ⁵	17.793	18.565 ⁵

Table S4 Fitted parameters Equation (S1) for the studied ILs and their mixtures.

Ionic Liquids	$b \times 10^{-4}$	a	r^2
[C ₂ mim][C ₁ SO ₄]	-6.52	1.485	0.9995
[C ₂ mim][C ₂ SO ₄]	-6.55	1.433	0.9994
[C ₂ mim][SCN]	-6.00	1.295	1.0000
[C ₂ mim][N(CN) ₂]	-6.44	1.295	0.9992
[C ₂ mim][C(CN) ₃]	-6.85	1.485	0.9995
[C ₂ mim][B(CN) ₄]	-7.49	1.260	0.9996
[C ₂ mim][C ₁ SO ₄] _{0.5} [SCN] _{0.5}	-6.16	1.391	0.9994
[C ₂ mim][C ₁ SO ₄] _{0.5} [N(CN) ₂] _{0.5}	-6.51	1.394	0.9994
[C ₂ mim][C ₁ SO ₄] _{0.5} [C(CN) ₃] _{0.5}	-6.71	1.376	0.9995
[C ₂ mim][C ₁ SO ₄] _{0.5} [B(CN) ₄] _{0.5}	-7.20	1.355	0.9996
[C ₂ mim][SCN] _{0.5} [N(CN) ₂] _{0.5}	-6.07	1.289	0.9996
[C ₂ mim][SCN] _{0.5} [C(CN) ₃] _{0.5}	-6.42	1.287	0.9994
[C ₂ mim][SCN] _{0.5} [B(CN) ₄] _{0.5}	-6.89	1.272	0.9995

**Figure S1** Densities (ρ) of the pure ionic liquids measured in this work as a function of temperature (T): [C₂mim][C₁SO₄] (■), [C₂mim][C₂SO₄] (▲), [C₂mim][SCN] (▽), [C₂mim][N(CN)₂] (●), [C₂mim][C(CN)₃] (◩), [C₂mim][B(CN)₄] (○).

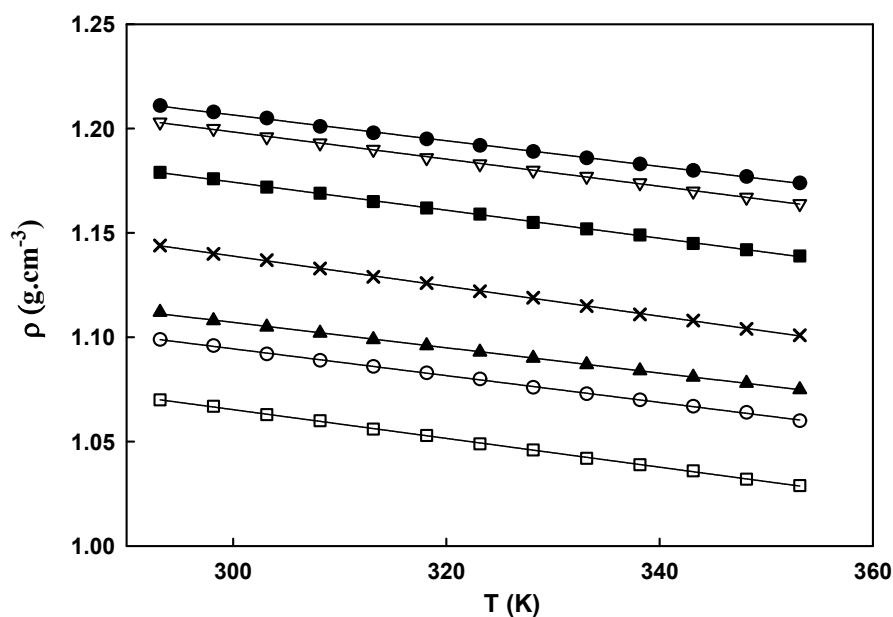


Figure S2 Densities (ρ) of the ionic liquid mixtures measured in this work as a function of temperature (T): $[\text{C}_2\text{mim}][\text{C}_1\text{SO}_4]_{0.5}[\text{SCN}]_{0.5}$ (●), $[\text{C}_2\text{mim}][\text{C}_1\text{SO}_4]_{0.5}[\text{N}(\text{CN})_2]_{0.5}$ (▽), $[\text{C}_2\text{mim}][\text{C}_1\text{SO}_4]_{0.5}[\text{C}(\text{CN})_3]_{0.5}$ (■), $[\text{C}_2\text{mim}][\text{C}_1\text{SO}_4]_{0.5}[\text{B}(\text{CN})_4]_{0.5}$ (×), $[\text{C}_2\text{mim}][\text{SCN}]_{0.5}[\text{N}(\text{CN})_2]_{0.5}$ (▲), $[\text{C}_2\text{mim}][\text{SCN}]_{0.5}[\text{C}(\text{CN})_3]_{0.5}$ (○), $[\text{C}_2\text{mim}][\text{SCN}]_{0.5}[\text{B}(\text{CN})_4]_{0.5}$ (□).

Table S5 Molar volumes, V_m ($\text{cm}^3\cdot\text{mol}^{-1}$), of the pure ionic liquids studied in this work.

T (K)	$[\text{C}_2\text{mim}][\text{C}_1\text{SO}_4]$	$[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$	$[\text{C}_2\text{mim}][\text{SCN}]^*$	$[\text{C}_2\text{mim}][\text{N}(\text{CN})_2]^*$	$[\text{C}_2\text{mim}][\text{C}(\text{CN})_3]$	$[\text{C}_2\text{mim}][\text{B}(\text{CN})_4]$
293.15	171.62	190.26	151.24	160.24	185.42	226.89
298.15	172.07	190.79	151.66	160.73	186.04	227.76
303.15	172.51	191.31	152.08	161.22	186.64	228.63
308.15	172.95	191.83	152.50	161.70	187.26	229.49
313.15	173.38	192.35	152.91	162.19	187.87	230.33
318.15	173.82	192.85	153.33	162.65	188.46	231.20
323.15	174.27	193.37	153.74	163.13	189.06	232.07
328.15	174.71	193.89	154.15	163.61	189.67	232.94
333.15	175.16	194.41	154.55	164.10	190.27	233.80
338.15	175.61	194.94	154.96	164.59	190.88	234.67
343.15	176.07	195.46	155.38	165.08	191.49	235.54
348.15	176.53	196.00	—	—	192.11	236.35
353.15	177.00	196.55	—	—	192.74	237.25

*Values taken from Tomé *et al.*¹

Table S6 Molar volumes, V_m ($\text{cm}^3\cdot\text{mol}^{-1}$), of the ionic liquid mixtures studied in this work.

T (K)	[C ₂ mim] [C ₁ SO ₄] _{0.5} [SCN] _{0.5}	[C ₂ mim] [C ₁ SO ₄] _{0.5} [N(CN) ₂] _{0.5}	[C ₂ mim] [C ₁ SO ₄] _{0.5} [C(CN) ₃] _{0.5}	[C ₂ mim] [C ₁ SO ₄] _{0.5} [B(CN) ₄] _{0.5}	[C ₂ mim] [SCN] _{0.5} [N(CN) ₂] _{0.5}	[C ₂ mim] [SCN] _{0.5} [C(CN) ₃] _{0.5}	[C ₂ mim] [SCN] _{0.5} [B(CN) ₄] _{0.5}
293.15	161.55	165.94	179.41	200.24	155.85	168.48	189.34
298.15	161.99	166.41	179.95	200.89	156.31	169.01	189.99
303.15	162.42	166.88	180.49	201.55	156.76	169.52	190.62
308.15	162.85	167.34	181.02	202.21	157.21	170.03	191.26
313.15	163.26	167.81	181.56	202.85	157.66	170.54	191.89
318.15	163.69	168.27	182.10	203.48	158.10	171.04	192.51
323.15	164.12	168.74	182.63	204.14	158.54	171.54	193.15
328.15	164.55	169.18	183.14	204.79	158.98	172.04	193.78
333.15	164.98	169.64	183.67	205.45	159.42	172.54	194.43
338.15	165.41	170.10	184.21	206.10	159.86	173.06	195.06
343.15	165.83	170.56	184.74	206.76	160.30	173.58	195.70
348.15	166.26	171.04	185.28	207.42	160.75	174.10	196.35
353.15	166.71	171.50	185.82	208.08	161.21	174.62	196.99

Table S7 Excess molar volumes, V^E ($\text{cm}^3\cdot\text{mol}^{-1}$), of the ionic liquid mixtures studied in this work.

T (K)	[C ₂ mim] [C ₁ SO ₄] _{0.5} [SCN] _{0.5}	[C ₂ mim] [C ₁ SO ₄] _{0.5} [N(CN) ₂] _{0.5}	[C ₂ mim] [C ₁ SO ₄] _{0.5} [C(CN) ₃] _{0.5}	[C ₂ mim] [C ₁ SO ₄] _{0.5} [B(CN) ₄] _{0.5}	[C ₂ mim] [SCN] _{0.5} [N(CN) ₂] _{0.5}	[C ₂ mim] [SCN] _{0.5} [C(CN) ₃] _{0.5}	[C ₂ mim] [SCN] _{0.5} [B(CN) ₄] _{0.5}
293.15	0.1451	-0.0791	0.8889	0.9872	0.0487	0.1800	0.2998
298.15	0.1483	-0.0779	0.8954	0.9790	0.0530	0.1842	0.3036
303.15	0.1560	-0.0697	0.9121	0.9771	0.0548	0.1883	0.2963
308.15	0.1707	-0.0705	0.9187	0.9877	0.0683	0.1935	0.3127
313.15	0.1627	-0.0552	0.9373	0.9969	0.0705	0.1925	0.3184
318.15	0.1569	-0.0560	0.9558	0.9697	0.0678	0.1926	0.2945
323.15	0.1625	-0.0543	0.9662	0.9740	0.0603	0.1815	0.2893
328.15	0.1636	-0.0717	0.9525	0.9682	0.0478	0.1779	0.2863
333.15	0.1624	-0.0848	0.9553	0.9675	0.0373	0.1719	0.2908
338.15	0.1565	-0.0980	0.9634	0.9590	0.0220	0.1773	0.2797
343.15	0.1412	-0.1240	0.9584	0.9596	-0.0064	0.1796	0.2761
348.15	0.1208	-0.1454	0.9557	0.9791	-0.0446	0.1639	0.2944
353.15	0.1002	-0.1661	0.9483	0.9504	-0.0625	0.1486	0.2548

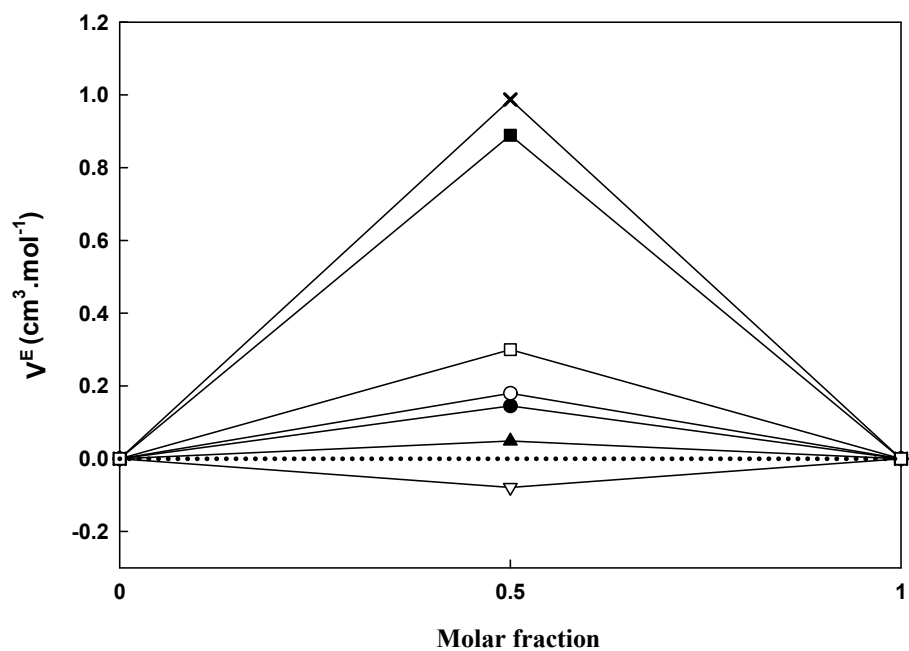


Figure S3 Excess molar volumes of the studied ionic liquid mixtures at 293.15 K: [C₂mim][C₁SO₄]_{0.5}[SCN]_{0.5} (●), [C₂mim][C₁SO₄]_{0.5}[N(CN)₂]_{0.5} (▽), [C₂mim][C₁SO₄]_{0.5}[C(CN)₃]_{0.5} (■), [C₂mim][C₁SO₄]_{0.5}[B(CN)₄]_{0.5} (⊗), [C₂mim][SCN]_{0.5}[N(CN)₂]_{0.5} (▲), [C₂mim][SCN]_{0.5}[C(CN)₃]_{0.5} (○), [C₂mim][SCN]_{0.5}[B(CN)₄]_{0.5} (□).

Viscosity measurements

Viscosity values for the pure ILs and their mixtures, in a range temperature from 293.15 K to 353.15 K, are listed in Table S8 and Table S9 and depicted in Figure S4 and Figure S5, respectively. The viscosity deviations ($\Delta\eta$) for the IL mixtures were calculated using equation (S3).

$$\Delta\ln(\eta) = \ln(\eta_M) - [x_1\ln(\eta_1) + (1-x_1)\ln(\eta_2)] \quad (\text{S3})$$

where η corresponds to viscosity (mPa·s) and x is the molar fraction. The subscript 1 and 2 correspond to the two pure ILs and the subscript M denotes the IL mixture. The calculated viscosity deviations values are presented in Table S10. The viscosity deviations for the studied mixtures are represented in Figure S6, at 293.15K.

For all pure ILs and also their mixtures, the viscosity decreases with temperature. This behaviour with temperature was correlated using a logarithmic equation based on Arrhenius model, described by the expression (S4):

$$\ln(\eta) = \ln(\eta_\infty) - \frac{E_a}{RT} \quad (\text{S4})$$

where η is the viscosity (mPa·s), η_∞ is a pre-exponential constant (mPa·s), E_a is the activation energy ($\text{kJ}\cdot\text{mol}^{-1}$), R is the ideal gas constant and T is the temperature (K). The values corresponding to η_∞ , E_a and the correlation coefficient (r^2) for each ILs are given in Table S11.

As observed for density, the viscosity of the IL mixtures display intermediate values between those of the pure ILs. Accordingly, at a fixed temperature, the viscosity of pure ILs can be ordered by the following order of the anions: $[\text{C}_1\text{SO}_4]^- > [\text{C}_2\text{SO}_4]^- > [\text{SCN}]^- > [\text{B}(\text{CN})_4]^- > [\text{N}(\text{CN})_2]^- > [\text{C}(\text{CN})_3]^-$. Furthermore, the viscosities of the sulfate-based ILs and the cyano-based ILs are very different from each other, meaning that, as density, this property is directly related to the chemical structure of the anion.

Both negative and positive viscosity deviations were found for the IL mixtures studied in this work. As it can be seen from Table S10, all the mixtures studied show negative values for all the IL mixtures prepared, in the entire range of temperatures, with the exception of the following mixtures: $[\text{C}_2\text{mim}][\text{C}_1\text{SO}_4]_{0.5}[\text{SCN}]_{0.5}$, $[\text{C}_2\text{mim}][\text{C}_1\text{SO}_4]_{0.5}[\text{N}(\text{CN})_2]_{0.5}$ and $[\text{C}_2\text{MIM}][\text{C}_1\text{SO}_4]_{0.5}[\text{B}(\text{CN})_4]_{0.5}$, which presented positive viscosity deviations values at some temperatures. Nevertheless, the deviations from ideality are very small. In terms of activation energies, it is interesting to observe that the pure ILs containing sulfate anions, namely $[\text{C}_2\text{mim}][\text{C}_1\text{SO}_4]$ and $[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$, show a more pronounced temperature dependence of viscosity compared to the cyano-based ILs, which is illustrated by their larger E_a value.

The use of equation (S4) to describe the temperature behaviour of viscosity allows the discussion of the energy barrier of a fluid to shear stress, E_a values. The higher the E_a , the more difficult is the ions to move past each other. This can be a direct consequence of the size or entanglement of the ions and/or the presence of stronger interactions within the fluid. The activation energies (E_a) of pure ILs can be interpreted as follows: the pure ILs composed by anions having the sulfate groups exhibited the highest E_a , approximately 30 kJ·mol⁻¹; and the pure ILs combining cyano groups in their anion structure present E_a values of about 20 kJ·mol⁻¹.

Table S8 Measured viscosities, η (mPa·s), of the pure ionic liquids studied in this work.

T (K)	[C ₂ mim][C ₁ SO ₄]	[C ₂ mim][C ₂ SO ₄]	[C ₂ mim][SCN]*	[C ₂ mim][N(CN) ₂]*	[C ₂ mim][C(CN) ₃]	[C ₂ mim][B(CN) ₄]
293.15	127.523	119.987	27.846	17.947	16.624	21.434
298.15	100.021	92.677	23.431	15.426	14.187	17.793
303.15	79.863	73.015	19.937	13.366	12.177	14.933
308.15	64.789	58.563	17.146	11.696	10.578	12.696
313.15	53.474	47.866	14.900	10.323	9.024	10.668
318.15	44.430	39.451	13.058	9.177	8.202	9.490
323.15	37.443	33.041	11.538	8.222	7.314	8.324
328.15	31.902	27.975	10.269	7.410	6.563	7.359
333.15	27.520	23.993	9.200	6.712	5.719	6.354
338.15	23.805	20.676	8.289	6.115	5.379	5.883
343.15	20.794	18.005	7.511	5.597	4.910	5.305
348.15	18.305	15.797	—	—	4.501	4.814
353.15	16.146	13.996	—	—	3.980	4.230

*Values taken from Tomé *et al.*¹

Table S9 Measured viscosities, η (mPa·s), of the ionic liquid mixtures studied in this work.

<i>T</i> (K)	[C ₂ mim]	[C ₂ mim]	[C ₂ mim]	[C ₂ mim]	[C ₂ mim]	[C ₂ mim]	[C ₂ mim]
	[C ₁ SO ₄] _{0.5}	[C ₁ SO ₄] _{0.5}	[C ₁ SO ₄] _{0.5}	[C ₁ SO ₄] _{0.5}	[SCN] _{0.5}	[SCN] _{0.5}	[SCN] _{0.5}
	[SCN] _{0.5}	[N(CN) ₂] _{0.5}	[C(CN) ₃] _{0.5}	[B(CN) ₄] _{0.5}	[N(CN) ₂] _{0.5}	[C(CN) ₃] _{0.5}	[B(CN) ₄] _{0.5}
293.15	60.380	49.200	41.022	53.726	21.287	20.711	23.233
298.15	48.805	40.105	33.341	42.771	18.233	17.560	19.442
303.15	40.075	33.151	27.508	34.690	15.714	15.007	16.435
308.15	33.365	27.778	23.034	28.596	13.678	12.970	14.068
313.15	28.097	23.429	19.346	23.801	11.764	11.070	11.913
318.15	23.981	20.187	16.747	20.377	10.644	9.977	10.607
323.15	20.651	17.491	14.513	17.326	9.494	8.858	9.331
328.15	17.939	15.283	12.688	14.994	8.528	7.925	8.251
333.15	15.697	13.402	11.063	13.026	7.507	6.933	7.158
338.15	13.886	11.943	9.937	11.525	6.999	6.460	6.602
343.15	12.347	10.669	8.885	10.226	6.391	5.880	5.953
348.15	11.045	9.588	7.996	9.135	5.863	5.378	5.404
353.15	9.909	8.614	7.150	8.144	5.252	4.784	4.765

Table S10 Viscosity deviations, $\Delta\eta$ (mPa·s), of the ionic liquid mixtures studied in this work.

<i>T</i> (K)	[C ₂ mim]	[C ₂ mim]	[C ₂ mim]	[C ₂ mim]	[C ₂ mim]	[C ₂ mim]	[C ₂ mim]
	[C ₁ SO ₄] _{0.5}	[C ₁ SO ₄] _{0.5}	[C ₁ SO ₄] _{0.5}	[C ₁ SO ₄] _{0.5}	[SCN] _{0.5}	[SCN] _{0.5}	[SCN] _{0.5}
	[SCN] _{0.5}	[N(CN) ₂] _{0.5}	[C(CN) ₃] _{0.5}	[B(CN) ₄] _{0.5}	[N(CN) ₂] _{0.5}	[C(CN) ₃] _{0.5}	[B(CN) ₄] _{0.5}
293.15	0.0102	0.0557	-0.1155	0.0273	-0.0242	-0.0411	-0.0532
298.15	0.0037	0.0439	-0.1220	0.0138	-0.0232	-0.0420	-0.0534
303.15	-0.0008	0.0356	-0.1255	0.0045	-0.0221	-0.0426	-0.0538
308.15	-0.0044	0.0282	-0.1280	-0.0030	-0.0210	-0.0431	-0.0531
313.15	-0.0027	0.0270	-0.1270	-0.0035	-0.0211	-0.0445	-0.0548
318.15	-0.0110	0.0150	-0.1309	-0.0077	-0.0194	-0.0432	-0.0549
323.15	-0.0136	0.0104	-0.1313	-0.0188	-0.0192	-0.0436	-0.0562
328.15	-0.0164	0.0059	-0.1314	-0.0216	-0.0182	-0.0427	-0.0597
333.15	-0.0125	0.0117	-0.1257	-0.0150	-0.0189	-0.0441	-0.0647
338.15	-0.0203	-0.0017	-0.1299	-0.0265	-0.0172	-0.0417	-0.0649
343.15	-0.0212	-0.0039	-0.1286	-0.0267	-0.0163	-0.0414	-0.0677
348.15	-0.0228	-0.0066	-0.1268	-0.0273	-0.0161	-0.0410	-0.0699
353.15	-0.0152	0.0065	-0.1144	-0.0146	-0.0152	-0.0433	-0.0776

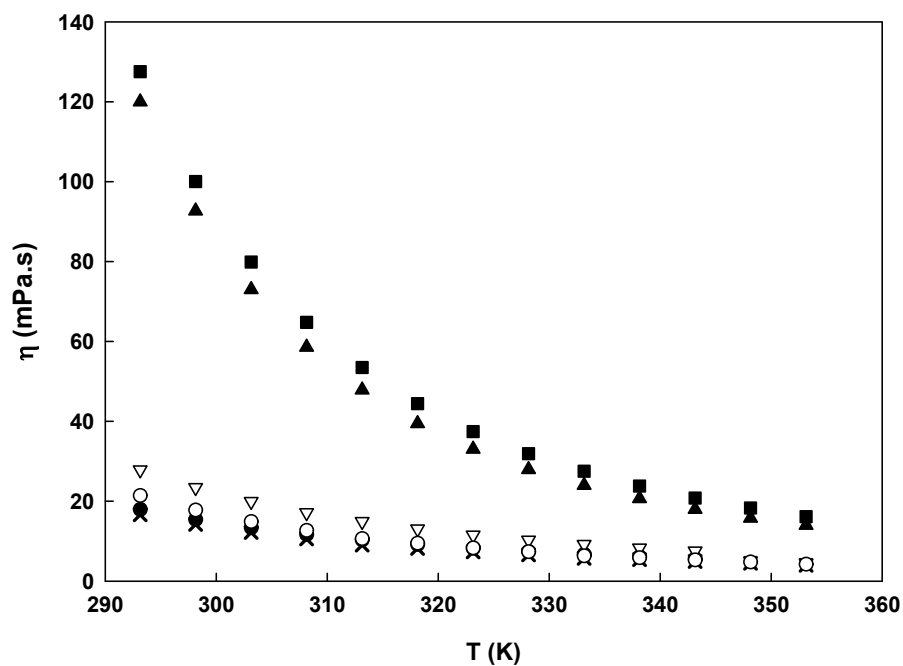


Figure S4 Measured viscosities of the pure ionic liquids studied in this work as a function of temperature (T): $[\text{C}_2\text{mim}][\text{C}_1\text{SO}_4]$ (■), $[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$ (▲), $[\text{C}_2\text{mim}][\text{SCN}]$ (▽), $[\text{C}_2\text{mim}][\text{N}(\text{CN})_2]$ (●), $[\text{C}_2\text{mim}][\text{C}(\text{CN})_3]$ (⊠) and $[\text{C}_2\text{mim}][\text{B}(\text{CN})_4]$ (○).

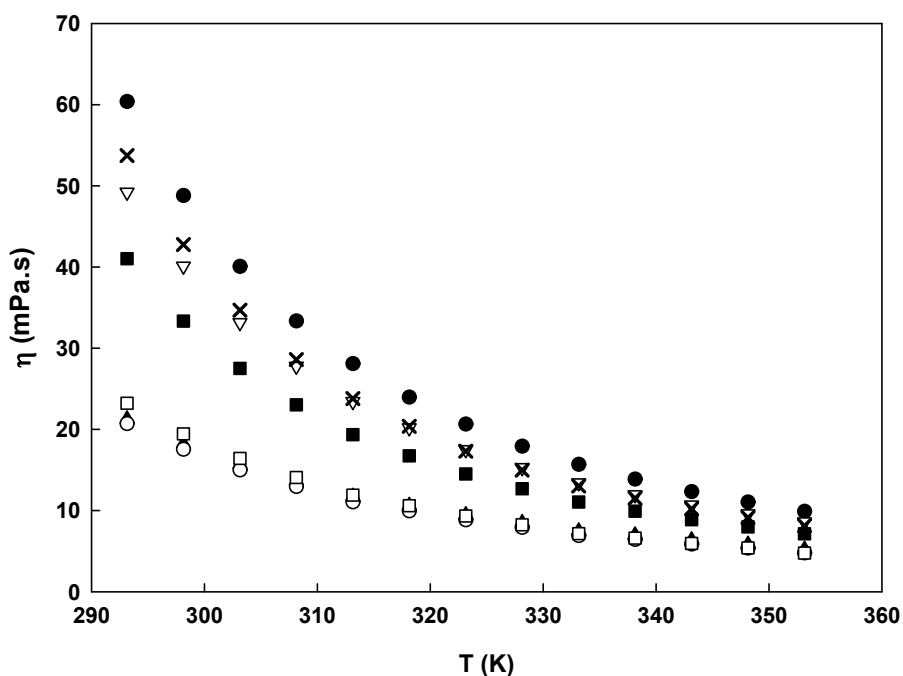


Figure S5 Measured viscosities of the ionic liquid mixtures studied in this work: $[\text{C}_2\text{mim}][\text{C}_1\text{SO}_4]_{0.5}[\text{SCN}]_{0.5}$ (●), $[\text{C}_2\text{mim}][\text{C}_1\text{SO}_4]_{0.5}[\text{N}(\text{CN})_2]_{0.5}$ (▽), $[\text{C}_2\text{mim}][\text{C}_1\text{SO}_4]_{0.5}[\text{C}(\text{CN})_3]_{0.5}$ (■), $[\text{C}_2\text{mim}][\text{C}_1\text{SO}_4]_{0.5}[\text{B}(\text{CN})_4]_{0.5}$ (⊠), $[\text{C}_2\text{mim}][\text{SCN}]_{0.5}[\text{N}(\text{CN})_2]_{0.5}$ (▲), $[\text{C}_2\text{mim}][\text{SCN}]_{0.5}[\text{C}(\text{CN})_3]_{0.5}$ (○), $[\text{C}_2\text{mim}][\text{SCN}]_{0.5}[\text{B}(\text{CN})_4]_{0.5}$ (□).

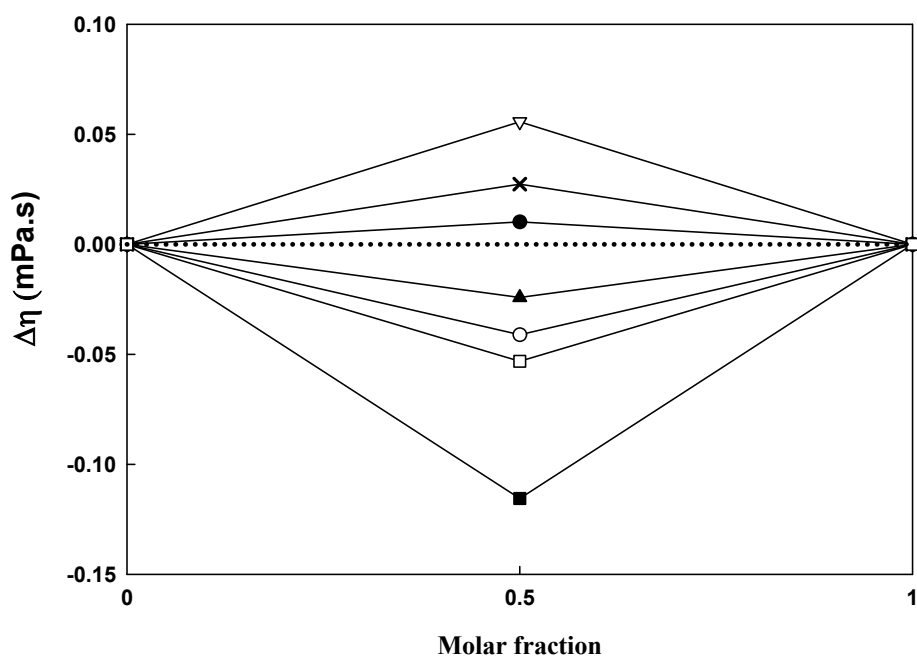


Figure S6 Viscosity deviations of the ionic liquid mixtures studied in this work at 293.15 K: [C₂mim][C₁SO₄]_{0.5}[SCN]_{0.5} (●), [C₂mim][C₁SO₄]_{0.5}[N(CN)₂]_{0.5} (∇), [C₂mim][C₁SO₄]_{0.5}[C(CN)₃]_{0.5} (■), [C₂mim][C₁SO₄]_{0.5}[B(CN)₄]_{0.5} (⊗), [C₂mim][SCN]_{0.5}[N(CN)₂]_{0.5} (▲), [C₂mim][SCN]_{0.5}[C(CN)₃]_{0.5} (○), [C₂mim][SCN]_{0.5}[B(CN)₄]_{0.5} (□).

Table S11 Correlation parameters of Equation (S4).

Ionic Liquids	$\eta_{\infty} \times 10^{-3}$	$-Ea$ (KJ.mol ⁻¹)	r^2
[C ₂ mim][C ₁ SO ₄]	0.683	29.42	0.9972
[C ₂ mim][C ₂ SO ₄]	0.388	30.62	0.9963
[C ₂ mim][SCN]	3.46	21.84	0.9981
[C ₂ mim][N(CN) ₂]	6.02	19.43	0.9983
[C ₂ mim][C(CN) ₃]	4.23	20.07	0.9967
[C ₂ mim][B(CN) ₄]	1.74	22.83	0.9965
[C ₂ mim][C ₁ SO ₄] _{0.5} [SCN] _{0.5}	1.47	25.74	0.9970
[C ₂ mim][C ₁ SO ₄] _{0.5} [N(CN) ₂] _{0.5}	1.77	24.80	0.9969
[C ₂ mim][C ₁ SO ₄] _{0.5} [C(CN) ₃] _{0.5}	1.48	24.79	0.9964
[C ₂ mim][C ₁ SO ₄] _{0.5} [B(CN) ₄] _{0.5}	0.841	26.79	0.9962
[C ₂ mim][SCN] _{0.5} [N(CN) ₂] _{0.5}	6.15	19.77	0.9973
[C ₂ mim][SCN] _{0.5} [C(CN) ₃] _{0.5}	4.16	20.64	0.9969
[C ₂ mim][SCN] _{0.5} [B(CN) ₄] _{0.5}	2.32	22.34	0.9975

References:

1. Tomé, L. C.; Patinha, D. J. S.; Freire, C. S. R.; Rebelo, L. P. N.; Marrucho, I. M., CO₂ separation applying ionic liquid mixtures: the effect of mixing different anions on gas permeation through supported ionic liquid membranes. *RSC Adv.* **2013**, *3* (30), 12220-12229.
2. Bhattacharjee, A.; Varanda, C.; Freire, M. G.; Matted, S.; Santos, L. M. N. B. F.; Marrucho, I. M.; Coutinho, J. A. P., Density and Viscosity Data for Binary Mixtures of 1-Alkyl-3-methylimidazolium Alkylsulfates + Water. *J. Chem. Eng. Data* **2012**, *57* (12), 3473-3482.
3. Pereiro, A. B.; Araujo, J. M. M.; Oliveira, F. S.; Bernardes, C. E. S.; Esperanca, J. M. S. S.; Canongia Lopes, J. N.; Marrucho, I. M.; Rebelo, L. P. N., Inorganic salts in purely ionic liquid media: the development of high ionicity ionic liquids (HIILs). *Chem. Commun.* **2012**, *48* (30), 3656-3658.
4. Fröba, A. P.; Rausch, M. H.; Krzeminski, K.; Assenbaum, D.; Wasserscheid, P.; Leipertz, A., Thermal Conductivity of Ionic Liquids: Measurement and Prediction. *Int. J. Thermophys.* **2010**, *31* (11-12), 2059-2077.
5. Neves, C. M. S. S.; Kurnia, K. A.; Coutinho, J. A. P.; Marrucho, I. M.; Lopes, J. N. C.; Freire, M. G.; Rebelo, L. P. N., Systematic Study of the Thermophysical Properties of Imidazolium-Based Ionic Liquids with Cyano-Functionalized Anions. *J. Phys. Chem. B* **2013**, *117* (35), 10271-10283.
6. Vural, U.S.; Muradoglu, V. and Vural, S., Excess molar volumes, and refractive index of binary mixtures of glycerol + methanol and glycerol + water at 298.15 K and 303.15 K. *B. Chem. Soc. Ethiopia*, **2011**, *25*, 111-118.