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Supplementary Information

CO_2 separation applying ionic liquid mixtures: the effect of mixing different anions on gas permeation through supported ionic liquid membranes

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Density measurements

Density of the pure ionic liquids (ILs) and their mixtures were measured in the temperature range from 293.15 to 343.15 K and are presented in Table S1 and S2 and also illustrated in Figure S1 and S2, respectively. A comparison with literature is shown in Table S3 and the differences observed can be attributed to the low water content of our samples, since few authors do not report the water contents. The density values, ρ ($g{\cdot}cm^{-3}$), are fitted as a function of temperature, T (K), by the method of the least squares using the linear expression given by Equation (S1):

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

where a and b are adjustable parameters which are listed in Table S4. In

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

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

where ρ and x are densities and molar fractions from, respectively, the two pure IL, identified with subscript numbers and subscript M refers to the IL mixture. The calculated excess molar volumes values are listed in

Table S7 and depicted in Figure S3 at 293K.

As can be seen in Figure S1 and Figure S2, the density values of mixtures are in between those of the pure ILs, as expected. This fact is also confirmed for the $[C_2mim][NTf_2][Ac]$ mixture, where the density of the mixture $[C_2mim][NTf_2]_{0.5}[Ac]_{0.5}$ is in between the densities for the other two $[C_2mim][NTf_2][Ac]$ mixtures. It is interesting to see that there are some mixtures with very distinct anions, such as

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[C_2mim][NTf_2][SCN], [C_2mim][NTf_2][DCA] and [C_2mim][NTf_2][Ac], that have similar density values. Regarding the volume changes of a mixture, those can be the result of chemical, physical and structural modifications.[1] Physical contributions cause positive V^E values resulting from non-specific interactions between the real species present in the mixture.[2] The chemical interactions that include charge-transfer type forces, changes in hydrogen bonding equilibrium or electrostatic interactions, as well as the structural contributions that arise from geometrical fitting, contributes to negative V^E values.[3] All the studied mixtures show positive V^E, and therefore, the interactions between pure ILs molecules are stronger than those between different IL. This hinders the packing of the [C_2mim][NTf_2] and thus increases the excess molar volume.

Table S1 Experimental densities (ρ) of the pure ionic liquids studied.

***T* (K)**	**ρ (g·cm^{-3})**				
	[C_2mim][NTf_2]	[C_2mim][SCN]	[C_2mim][Lac]	[C_2mim][DCA]	[C_2mim][Ac]
293.15	1.524	1.119	1.145	1.106	1.101
298.15	1.519	1.116	1.141	1.103	1.098
303.15	1.514	1.113	1.138	1.099	1.095
308.15	1.509	1.110	1.134	1.096	1.092
313.15	1.504	1.107	1.131	1.093	1.089
318.15	1.499	1.104	1.128	1.090	1.086
323.15	1.494	1.101	1.124	1.086	1.083
328.15	1.489	1.098	1.121	1.083	1.080
333.15	1.485	1.095	1.118	1.080	1.077
338.15	1.480	1.092	1.114	1.077	1.074
343.15	1.475	1.089	1.111	1.074	1.071

Table S2 Experimental densities (ρ) of the ionic liquid mixtures studied.

***T* (K)**	***ρ* (g·cm⁻³)**					
	$[C_2mim][NTf_2]_{0.5}[SCN]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[Lac]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[DCA]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[Ac]_{0.5}$	$[C_2mim][NTf_2]_{0.75}[Ac]_{0.25}$	$[C_2mim][NTf_2]_{0.25}[Ac]_{0.75}$
293.15	1.371	1.365	1.362	1.362	1.451	1.249
298.15	1.367	1.361	1.358	1.358	1.447	1.245
303.15	1.363	1.356	1.354	1.353	1.442	1.242
308.15	1.359	1.352	1.349	1.349	1.437	1.238
313.15	1.355	1.348	1.345	1.345	1.433	1.234
318.15	1.350	1.344	1.341	1.341	1.428	1.231
323.15	1.346	1.339	1.337	1.337	1.423	1.227
328.15	1.342	1.335	1.333	1.333	1.419	1.224
333.15	1.338	1.331	1.329	1.329	1.414	1.220
338.15	1.334	1.327	1.325	1.324	1.410	1.216
343.15	1.330	1.323	1.320	1.320	1.405	1.213

Table S3 Density (ρ) and viscosity (η) comparison with literature at 298K.

Ionic liquid sample	***η* (mPa·s)**		***ρ* (g·cm⁻³)**	
	This work	Literature	This work	Literature
$[C_2mim][NTf_2]$	32.4300	33.001 [4]	1.5190	1.51910 [5]
$[C_2mim][Lac]$	246.5070	169.000 [6]	1.1410	1.14606 [6]
$[C_2mim][Ac]$	119.2800	132.910 [7]	1.0979	1.09778 [7]
$[C_2mim][DCA]$	15.4260	14.900 [7]	1.1025	1.10198 [7]
$[C_2mim][SCN]$	23.4310	22.150 [8]	1.1160	1.1168 [9, 10]

Table S4 Fitted parameters of the linear expression given by Equation (S1).

Ionic liquid sample	**b × 10^{-4}**	**a**	**r^2**
[C_2mim][NTf_2]	-9.78	1.5431	0.9999
[C_2mim][SCN]	-5.95	1.1308	0.9998
[C_2mim][Lac]	-6.76	1.1582	0.9998
[C_2mim][DCA]	-6.46	1.1186	0.9999
[C_2mim][Ac]	-5.98	1.1128	0.9999
[C_2mim][NTf_2]$_{0.5}$[SCN]$_{0.5}$	-8.23	1.3876	0.99994
[C_2mim][NTf_2]$_{0.5}$[Lac]$_{0.5}$	-8.48	1.3820	0.99991
[C_2mim][NTf_2]$_{0.5}$[DCA]$_{0.5}$	-8.38	1.3789	0.99994
[C_2mim][NTf_2]$_{0.5}$[Ac]$_{0.5}$	-8.27	1.3781	0.99994
[C_2mim][NTf_2]$_{0.75}$[Ac]$_{0.25}$	-9.16	1.4694	0.99992
[C_2mim][NTf_2]$_{0.25}$[Ac]$_{0.75}$	-7.23	1.2634	0.99996

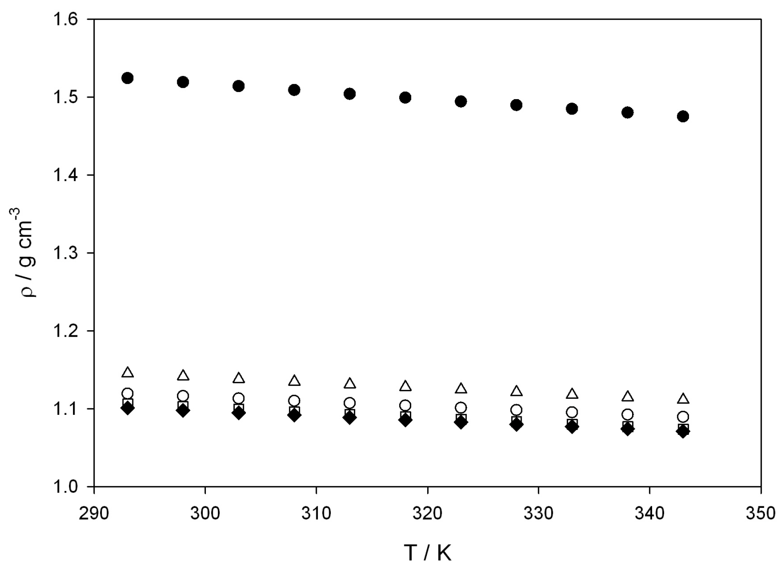

Figure S1 Experimental densities of the pure ionic liquids: [C_2mim][NTf_2] (●), [C_2mim][Ac] (♦), [C_2mim][DCA] (□), [C_2mim][Lac] (Δ), [C_2mim][SCN] (○).

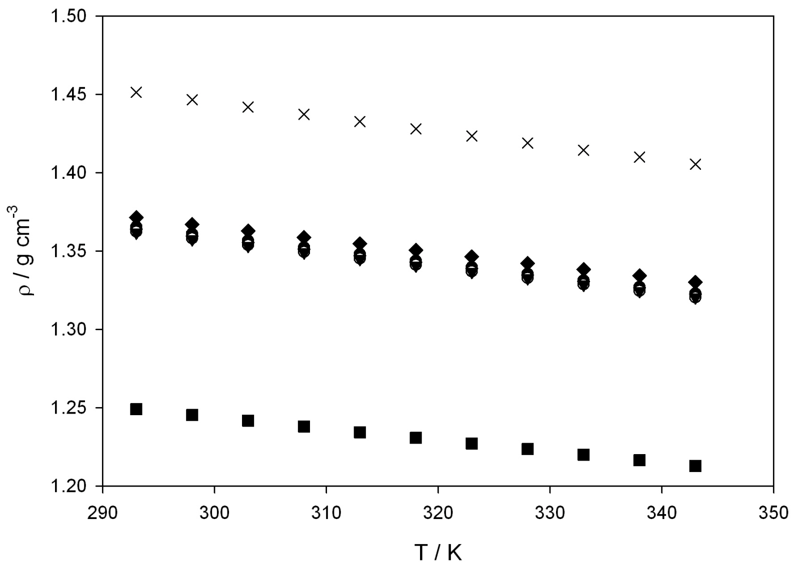

Figure S2 Experimental densities of the ionic liquid mixtures: $[C_2mim][NTf_2]_{0.5}[Lac]_{0.5}$ (●), $[C_2mim][NTf_2]_{0.5}[Ac]_{0.5}$ (▼), $[C_2mim][NTf_2]_{0.75}[Ac]_{0.25}$ (x), $[C_2mim][NTf_2]_{0.25}[Ac]_{0.75}$ (■), $[C_2mim][NTf_2]_{0.5}[DCA]_{0.5}$ (○), $[C_2mim][NTf_2]_{0.5}[SCN]_{0.5}$ (♦).

Table S5 Calculated molar volumes, V_m ($cm^3 \cdot mol^{-1}$), of the pure ionic liquids studied.

T **(K)**	**$[C_2mim][NTf_2]$**	**$[C_2mim][SCN]$**	**$[C_2mim][DCA]$**	**$[C_2mim][Lac]$**	**$[C_2mim][Ac]$**
293.15	256.78	151.24	160.24	174.87	154.61
298.15	257.64	151.66	160.73	175.42	155.04
303.15	258.51	152.08	161.22	175.96	155.47
308.15	259.36	152.50	161.70	176.51	155.90
313.15	260.21	152.91	162.19	177.02	156.34
318.15	261.06	153.33	162.65	177.56	156.77
323.15	261.92	153.74	163.13	178.08	157.19
328.15	262.73	154.15	163.61	178.61	157.62
333.15	263.59	154.55	164.10	179.14	158.05
338.15	264.44	154.96	164.59	179.67	158.49
343.15	265.34	155.38	165.08	180.21	158.93

Table S6 Calculated molar volumes, V_m ($cm^3 \cdot mol^{-1}$), of the ionic liquid mixtures studied.

T (K)	$[C_2mim][NTf_2]_{0.5}[SCN]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[Lac]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[DCA]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[Ac]_{0.5}$	$[C_2mim][NTf_2]_{0.75}[Ac]_{0.25}$	$[C_2mim][NTf_2]_{0.25}[Ac]_{0.75}$
293.15	204.39	216.64	208.66	206.17	231.55	180.53
298.15	205.03	217.34	209.32	206.82	232.30	181.06
303.15	205.66	218.04	209.99	207.46	233.06	181.59
308.15	206.29	218.74	210.66	208.11	233.81	182.13
313.15	206.91	219.44	211.31	208.75	234.57	182.68
318.15	207.55	220.13	211.96	209.40	235.32	183.21
323.15	208.18	220.81	212.63	210.04	236.08	183.75
328.15	208.82	221.51	213.30	210.68	236.83	184.28
333.15	209.45	222.20	213.95	211.33	237.59	184.82
338.15	210.07	222.90	214.62	211.98	238.35	185.37
343.15	210.73	223.61	215.30	212.64	239.09	185.92

Table S7 Calculated excess molar volumes, V^E ($cm^3 \cdot mol^{-1}$), of the ionic liquid mixtures.

T (K)	$[C_2mim][NTf_2]_{0.5}[SCN]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[Lac]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[DCA]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[Ac]_{0.5}$	$[C_2mim][NTf_2]_{0.75}[Ac]_{0.25}$	$[C_2mim][NTf_2]_{0.25}[Ac]_{0.75}$
293.15	0.3730	0.8192	0.1506	0.4800	0.3136	0.3782
298.15	0.3797	0.8102	0.1331	0.4756	0.3113	0.3751
303.15	0.3636	0.8061	0.1227	0.4738	0.3047	0.3658
308.15	0.3610	0.8079	0.1236	0.4810	0.3140	0.3633
313.15	0.3510	0.8174	0.1117	0.4780	0.3235	0.3708
318.15	0.3541	0.8250	0.1046	0.4831	0.3375	0.3700
323.15	0.3486	0.8129	0.1028	0.4902	0.3442	0.3749
328.15	0.3821	0.8353	0.1245	0.5074	0.3762	0.3852
333.15	0.3739	0.8344	0.1097	0.5100	0.3808	0.3880
338.15	0.3706	0.8465	0.1021	0.5119	0.3897	0.3858
343.15	0.3665	0.8365	0.0912	0.5048	0.3578	0.3863

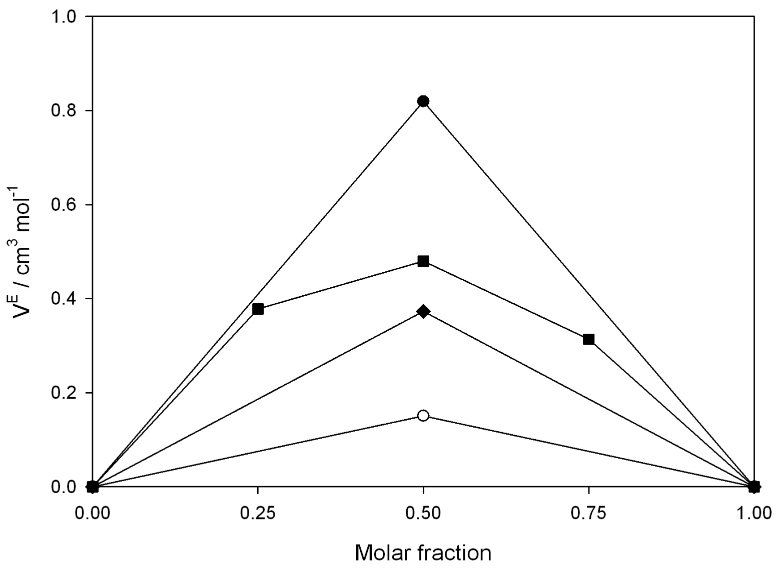

Figure S3 Excess molar volumes of the ionic liquid mixtures at 293.15 K: [C_2mim][NTf_2][Lac] (●), [C_2mim][NTf_2][Ac] (■), [C_2mim][NTf_2][DCA] (○), [C_2mim][NTf_2][SCN] (♦).

Viscosity measurements

Viscosities of the pure ILs and their mixtures from 293.15 to 343.15 K are reported in Table S8 and S9 and Figure S4 Figure S5, respectively. The viscosity deviations ($\Delta\eta$) resulting from the IL mixtures were calculated by Equation (S3):

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

where η and x are respectively, viscosities and molar fractions from the two pure ILs identified with subscript numbers. Subscript M refers to the IL mixture. The calculated values are presented in Table S10. The viscosity deviations calculated at 293K are represented in Figure S6. Dynamic viscosities were fitted as a function of temperature, using an Arrehnius-like law:

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

where E_a is the activation energy, R is the gas constant, T is the temperature in Kelvin, a is the pre-exponential factor and η is the viscosity in mPa·s. The fitted parameters are listed in Table S11.

Taking into account the Table S8 and Table S9, the viscosity trend is similar to that of the density. The viscosity values of the IL mixtures tend to be in between those of the two pure ILs. Concerning the viscosity deviations, negative values are usually obtained for systems where molecular size and shapes of the components and dispersion and dipolar interactions are considered,[11] whereas, charge transfer and hydrogen bonding interactions lead to positive $\Delta\ln(\eta)$ values.[3, 11] In the mixtures studied, only [C_2mim][Lac] shows negative deviation maybe due to the asymmetry and different size of the lactate anion when compared to the other anions, that are linear like thiocyanate or dicyanamide, or have minor sizes, such as the acetate anion. Nevertheless, the deviations from ideality are very small. In terms of activation energies, as can be seen in Table S11, the pure [C_2mim][Lac] shows the higher E_a (45kJ·mol^{-1}), followed by [C_2mim][Ac] (37 kJ·mol^{-1}). Higher activation energies are related to the lower mobility of the ions, due to strong molecular interactions or entanglement of chains. The activation energies of the pure fluids can be ranked in the following order [C_2mim][DCA]<[C_2mim][SCN]<[C_2mim][NTf_2] <[C_2mim][Ac] < [C_2mim][Lac]. The same order is also observed for the mixtures of these ILs with [C_2mim][NTf_2] and the activation energies have values in between those of the pure fluids. The overall viscosities together with activation energies can be increasingly aligned as: [C_2mim][DCA] < [C_2mim][SCN] < [C_2mim][NTf_2]$_{0.5}$[DCA]$_{0.5}$ < [C_2mim][NTf_2] < [C_2mim][NTf_2]$_{0.5}$[SCN]$_{0.5}$ < [C_2mim][NTf_2]$_{0.75}$[Ac]$_{0.25}$ < [C_2mim][NTf_2]$_{0.5}$[Ac]$_{0.5}$ < [C_2mim][NTf_2]$_{0.5}$[Lac]$_{0.5}$ < [C_2mim][NTf_2]$_{0.25}$[Ac]$_{0.75}$ < [C_2mim][Ac] < [C_2mim][Lac].

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Table S8 Experimental viscosities (η) of the pure ionic liquids studied as a function of temperature at atmospheric pressure.

T (K)	η (mPa·s)				
	$[C_2mim][NTf_2]$	$[C_2mim][SCN]$	$[C_2mim][Lac]$	$[C_2mim][DCA]$	$[C_2mim][Ac]$
293.15	39.085	27.846	370.413	17.947	164.930
298.15	32.430	23.431	246.507	15.426	119.280
303.15	27.157	19.937	170.927	13.366	88.883
308.15	23.126	17.146	122.763	11.696	67.973
313.15	19.911	14.900	90.967	10.323	53.129
318.15	17.301	13.058	69.270	9.177	42.369
323.15	15.164	11.538	54.006	8.222	34.377
328.15	13.403	10.269	42.983	7.410	28.328
333.15	11.920	9.200	34.842	6.712	23.670
338.15	10.721	8.289	28.699	6.115	20.017
343.15	9.655	7.511	23.973	5.597	17.116

Table S9 Experimental viscosities (η) of the ionic liquid mixtures studied as a function of temperature at atmospheric pressure.

T (K)	η (mPa·s)					
	$[C_2mim][NTf_2]_{0.5}[SCN]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[Lac]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[DCA]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[Ac]_{0.5}$	$[C_2mim][NTf_2]_{0.75}[Ac]_{0.25}$	$[C_2mim][NTf_2]_{0.25}[Ac]_{0.75}$
293.15	38.600	103.633	29.169	98.011	60.936	127.927
298.15	32.023	79.097	24.537	75.559	48.950	95.812
303.15	26.897	61.728	20.878	59.471	39.967	73.507
308.15	22.855	49.137	17.963	47.661	33.102	57.596
313.15	19.645	39.812	15.603	38.804	27.767	45.972
318.15	17.053	32.787	13.662	32.066	23.561	37.323
323.15	14.918	27.354	12.071	26.848	20.202	30.750
328.15	13.158	23.117	10.731	22.732	17.480	25.681
333.15	11.687	19.744	9.605	19.452	15.261	21.697
338.15	10.447	17.024	8.647	16.807	13.425	18.527
343.15	9.394	14.811	7.827	14.648	11.859	15.976

Table S10 Calculated viscosity deviations, $\Delta\eta$ (mPa·s), of the ionic liquid mixtures at 293.15 K.

T (K)	$[C_2mim][NTf_2]_{0.5}[SCN]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[Lac]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[DCA]_{0.5}$	$[C_2mim][NTf_2]_{0.5}[Ac]_{0.5}$	$[C_2mim][NTf_2]_{0.75}[Ac]_{0.25}$	$[C_2mim][NTf_2]_{0.25}[Ac]_{0.75}$
293.15	0.1571	-0.1493	0.0965	0.1995	0.0841	0.1059
298.15	0.1499	-0.1226	0.0926	0.1946	0.0861	0.1065
303.15	0.1449	-0.0987	0.0915	0.1910	0.0900	0.1065
308.15	0.1378	-0.0810	0.0882	0.1841	0.0891	0.1039
313.15	0.1315	-0.0667	0.0846	0.1765	0.0872	0.1007
318.15	0.1262	-0.0544	0.0809	0.1692	0.0849	0.0971
323.15	0.1203	-0.0452	0.0779	0.1620	0.0822	0.0931
328.15	0.1147	-0.0375	0.0740	0.1541	0.0785	0.0890
333.15	0.1097	-0.0317	0.0712	0.1468	0.0756	0.0845
338.15	0.1028	-0.0299	0.0658	0.1374	0.0688	0.0787
343.15	0.0982	-0.0268	0.0627	0.1306	0.0625	0.0742

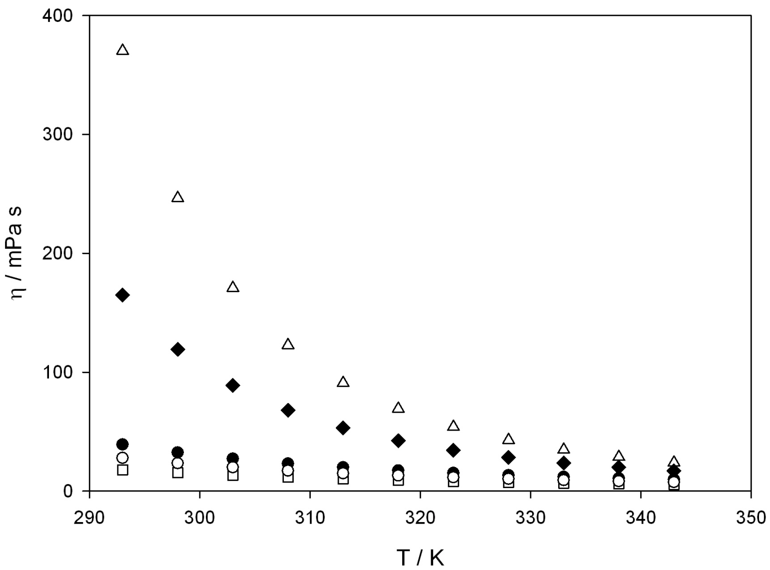

Figure S4 Experimental viscosities of the pure ionic liquids: $[C_2mim][NTf_2]$(●), $[C_2mim][Ac]$ (♦), $[C_2mim][DCA]$ (□), $[C_2mim][Lac]$ (Δ), $[C_2mim][SCN]$ (○).

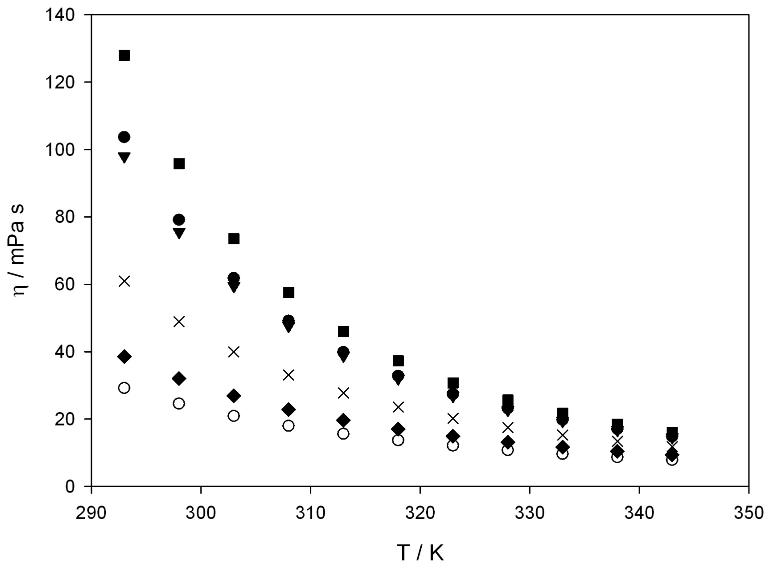

Figure S5 Experimental viscosities of the ionic liquid mixtures: $[C_2mim][NTf_2]_{0.5}[Lac]_{0.5}$ (●), $[C_2mim][NTf_2]_{0.5}[Ac]_{0.5}$ (▼), $[C_2mim][NTf_2]_{0.75}[Ac]_{0.25}$ (x), $[C_2mim][NTf_2]_{0.25}[Ac]_{0.75}$ (■), $[C_2mim][NTf_2]_{0.5}[DCA]_{0.5}$ (○), $[C_2mim][NTf_2]_{0.5}[SCN]_{0.5}$ (♦).

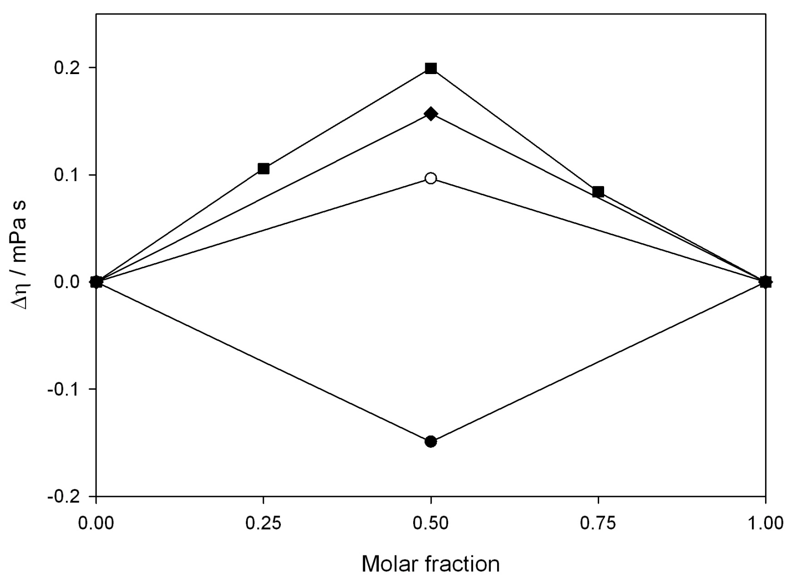

Figure S6 Viscosity deviations of the ionic liquid mixtures at 293.15 K: $[C_2mim][NTf_2][Lac]$ (●), $[C_2mim][NTf_2][Ac]$ (■), $[C_2mim][NTf_2][DCA]$ (○), $[C_2mim][NTf_2][SCN]$ (♦).

Table S11 Fitted parameters of the linear expression given by Equation (S4).

Ionic liquid sample	**ln(a)**	**$-E_a/R$**	**$-E_a$ / kJ·mol^{-1}**	**r^2**
$[C_2mim][NTf_2]$	-5.93 ± 0.15	2801 ± 47	23.3	0.9975 ± 0.0245
$[C_2mim][Ac]$	-10.42 ± 0.33	4525 ± 104	37.6	0.9952 ± 0.0546
$[C_2mim][Lac]$	-12.84 ± 0.48	5459 ± 153	45.4	0.9930 ± 0.0797
$[C_2mim][SCN]$	-5.67 ± 0.12	2627 ± 38	21.8	0.9981 ± 0.0201
$[C_2mim][DCA]$	-5.11 ± 0.10	2337 ± 32	19.4	0.9983 ± 0.0167
$[C_2mim][NTf_2]_{0.5}[SCN]_{0.5}$	-6.04 ± 0.13	2832 ± 42	23.6	0.9980 ± 0.0219
$[C_2mim][NTf_2]_{0.5}[Lac]_{0.5}$	-8.70± 0.25	3889 ± 77	32.3	0.9964 ± 0.0405
$[C_2mim][NTf_2]_{0.5}[DCA]_{0.5}$	-5.66 ±0.12	2637 ± 37	21.9	0.9982 ± 0.0193
$[C_2mim][NTf_2]_{0.5}[Ac]_{0.5}$	-8.46 ± 0.22	3805 ± 70	31.6	0.9970 ± 0.0365
$[C_2mim][NTf_2]_{0.75}[Ac]_{0.25}$	-7.11 ± 0.16	3275 ± 51	27.2	0.9978 ± 0.0269
$[C_2mim][NTf_2]_{0.25}[Ac]_{0.75}$	-9.41 ± 0.26	4161 ± 83	34.6	0.9964 ± 0.0436

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