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Supporting Information:

Hydrogen Bond Redistribution Effects in Mixtures of Protic Ionic Liquids Sharing the Same Cation: Nonideal Mixing with Large Negative Mixing Enthalpies

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S1 MD Simulations

S1.1 Outline/Results of the MD Simulations

To study the pure PILs and mixtures we performed isobaric isothermal (NPT) MD simulations using GROMACS 5.0.6. We investigated eleven compositions between $x_{\mathrm{OMs}} = 0.0$ and $x_{\mathrm{OMs}} = 1.0$ for six temperatures between $T = 300\,\mathrm{K}$ and $T = 400\,\mathrm{K}$ at a pressure of $1\,\mathrm{bar}$. Tables S1 to S11 contain a summary of selected propertees for each performed MD simulation: the average mass density ρ, the average potential energy E_p, the fraction of hydrogen bonds of the [TEA] cations to [OMs] anions y_{OMs}, and the fraction of hydrogen bonds of the [TEA] cations to [OTf] anions y_{OTf}.

Table S1: $x_{\mathrm{OMs}} = 0.0$

T / K	ρ / kg m^{-3}	E_p / kJ mol^{-1}	y_{OMs}	y_{OTf}
300	1245.2	-996	-	0.997
320	1229.1	1186	-	0.995
340	1213.4	3287	-	0.993
360	1198.0	5394	-	0.991
380	1183.3	7461	-	0.988
400	1168.2	9525	-	0.984

Table S2: $x_{\mathrm{OMs}} = 0.1$

T / K	ρ / kg m^{-3}	E_p / kJ mol^{-1}	y_{OMs}	y_{OTf}
300	1232.5	-21008	0.283	0.718
320	1216.8	-18844	0.272	0.725
340	1201.2	-16772	0.274	0.721
360	1186.1	-14677	0.269	0.724
380	1171.6	-12603	0.261	0.729
400	1156.9	-10544	0.255	0.732

Table S3: $x_{\mathrm{OMs}} = 0.2$

T / K	ρ / kg m^{-3}	E_p / kJ mol^{-1}	y_{OMs}	y_{OTf}
300	1220.1	-40840	0.538	0.460
320	1204.2	-38845	0.540	0.457
340	1189.4	-36729	0.525	0.471
360	1175.0	-34631	0.510	0.484
380	1160.3	-32537	0.497	0.496
400	1145.6	-30450	0.482	0.508

Table S4: $x_{\mathrm{OMs}} = 0.3$

T / K	ρ / kg m^{-3}	E_{p} / kJ mol^{-1}	y_{OMs}	y_{OTf}
300	1208.1	-40840	0.734	0.265
320	1192.5	-38845	0.730	0.268
340	1177.3	-36729	0.717	0.280
360	1163.1	-34631	0.707	0.289
380	1148.5	-32537	0.683	0.312
400	1134.1	-30450	0.661	0.331

Table S5: $x_{\mathrm{OMs}} = 0.4$

T / K	ρ / kg m^{-3}	E_{p} / kJ mol^{-1}	y_{OMs}	y_{OTf}
300	1194.3	-79688	0.863	0.136
320	1179.7	-77765	0.869	0.130
340	1165.1	-75594	0.839	0.158
360	1150.6	-73518	0.825	0.172
380	1136.9	-71487	0.806	0.188
400	1122.9	-69461	0.789	0.204

Table S6: $x_{\mathrm{OMs}} = 0.5$

T / K	ρ / kg m^{-3}	E_{p} / kJ mol^{-1}	y_{OMs}	y_{OTf}
300	1181.6	-98623	0.927	0.072
320	1166.7	-96721	0.929	0.069
340	1153.2	-94669	0.918	0.080
360	1139.4	-02582	0.894	0.103
380	1124.9	-90565	0.884	0.112
400	1111.1	-88554	0.869	0.125

Table S7: $x_{\mathrm{OMs}} = 0.6$

T / K	ρ / kg m^{-3}	E_{p} / kJ mol^{-1}	y_{OMs}	y_{OTf}
300	1167.9	-117448	0.966	0.032
320	1154.3	-115502	0.964	0.034
340	1139.7	-113423	0.950	0.047
360	1126.2	-111437	0.939	0.058
380	1112.8	-109500	0.933	0.063
400	1099.3	-107510	0.918	0.076

Table S8: $x_{\mathrm{OMs}} = 0.7$

T / K	ρ / kg m^{-3}	E_{p} / kJ mol^{-1}	y_{OMs}	y_{OTf}
300	1154.2	-136208	0.984	0.015
320	1140.4	-134120	0.972	0.026
340	1126.2	-132153	0.970	0.028
360	1112.8	-130204	0.966	0.031
380	1099.8	-128272	0.956	0.039
400	1086.7	-126348	0.950	0.044

Table S9: $x_{\mathrm{OMs}} = 0.8$

T / K	ρ / kg m^{-3}	E_{p} / kJ mol^{-1}	y_{OMs}	y_{OTf}
300	1139.0	-154745	0.990	0.009
320	1126.2	-152787	0.986	0.012
340	1112.5	-160857	0.983	0.014
360	1099.5	-148934	0.978	0.018
380	1086.6	-147031	0.975	0.020
400	1074.0	-145144	0.970	0.024

Table S10: $x_{\mathrm{OMs}} = 0.9$

T / K	ρ / kg m^{-3}	E_{p} / kJ mol^{-1}	y_{OMs}	y_{OTf}
300	1124.9	-173373	0.993	0.005
320	1111.6	-171490	0.994	0.004
340	1098.2	-169514	0.992	0.005
360	1085.3	-167605	0.988	0.008
380	1073.0	-165740	0.987	0.008
400	1060.4	-163886	0.984	0.010

Table S11: $x_{\mathrm{OMs}} = 1.0$

T / K	ρ / kg m^{-3}	E_{p} / kJ mol^{-1}	y_{OMs}	y_{OTf}
300	1109.5	-191997	0.998	-
320	1096.0	-190126	0.998	-
340	1083.4	-188176	0.997	-
360	1070.7	-186284	0.996	-
380	1058.7	-184451	0.995	-
400	1046.5	-182612	0.993	-

S1.2 Energies of Mixing Obtained from MD Simulation

From the MD simulations we can directly determine the energies of mixing according to

$$\begin{aligned} \Delta U_{\mathrm{mix}} &= U(x_{\mathrm{OMs}}) - x_{\mathrm{OMs}} \cdot U_{[\mathrm{TEA}][\mathrm{OMs}]} \\ &\quad -(1 - x_{\mathrm{OMs}}) \cdot U_{[\mathrm{TEA}][\mathrm{OTf}]} \\ &= E_p(x_{\mathrm{OMs}}) - x_{\mathrm{OMs}} \cdot E_{\mathrm{p},[\mathrm{TEA}][\mathrm{OMs}]} \\ &\quad -(1 - x_{\mathrm{OMs}}) \cdot E_{p,[\mathrm{TEA}][\mathrm{OTf}]} \ , \end{aligned} \tag{1}$$

where $U(x_{\mathrm{OMs}})$ represents the total energy of the mixture [TEA][OTf]/[TEA][OMs] with a given composition x_{OMs}, while $U_{[\mathrm{TEA}][\mathrm{OTf}]}$ and $U_{[\mathrm{TEA}][\mathrm{OMs}]}$ are the energies of the pure PILs. The E_P-values represent the corresponding potential energies. All competed excess energies of mixing are summarised in Table S12.

Table S12: Excess energies of mixing calculated from molecular dynamics simulation data given in Tables S1 to S11.

	ΔU_{mix} / kJ mol^{-1}					
x_{OMs}	300 K	320 K	340 K	360 K	380 K	400 K
0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.1	-1.8±0.3	-1.80±0.23	-1.83±0.18	-1.81±0.17	-1.75±0.17	-1.71±0.16
0.2	-3.3±0.3	-3.54±0.24	-3.45±0.24	-3.38±0.24	-3.23±0.15	-3.09±0.16
0.3	-4.6±0.4	-4.46±0.23	-4.37±0.25	-4.45±0.19	-4.14±0.20	-3.93±0.20
0.4	-4.57±0.23	-4.85±0.23	-4.59±0.24	-4.48±0.23	-4.37±0.19	-4.26±0.19
0.5	-4.23±0.28	-4.50±0.21	-4.45±0.16	-4.27±0.20	-4.14±0.16	-4.02±0.18
0.6	-3.68±0.21	-3.80±0.24	-3.66±0.18	-3.65±0.18	-3.63±0.20	-3.50±0.14
0.7	-3.00±0.19	-2.78±0.22	-2.83±0.22	-2.85±0.18	-2.79±0.18	-2.75±0.14
0.8	-1.86±0.24	-1.9±0.3	-1.95±0.23	-1.97±0.18	-1.92±0.16	-1.92±0.12
0.9	-0.92±0.22	-0.99±0.25	-0.97±0.22	-0.98±0.21	-0.96±0.15	-0.97±0.13
1.0	0.0	0.0	0.0	0.0	0.0	0.0

S2 ^{1}H-NMR-Spectra

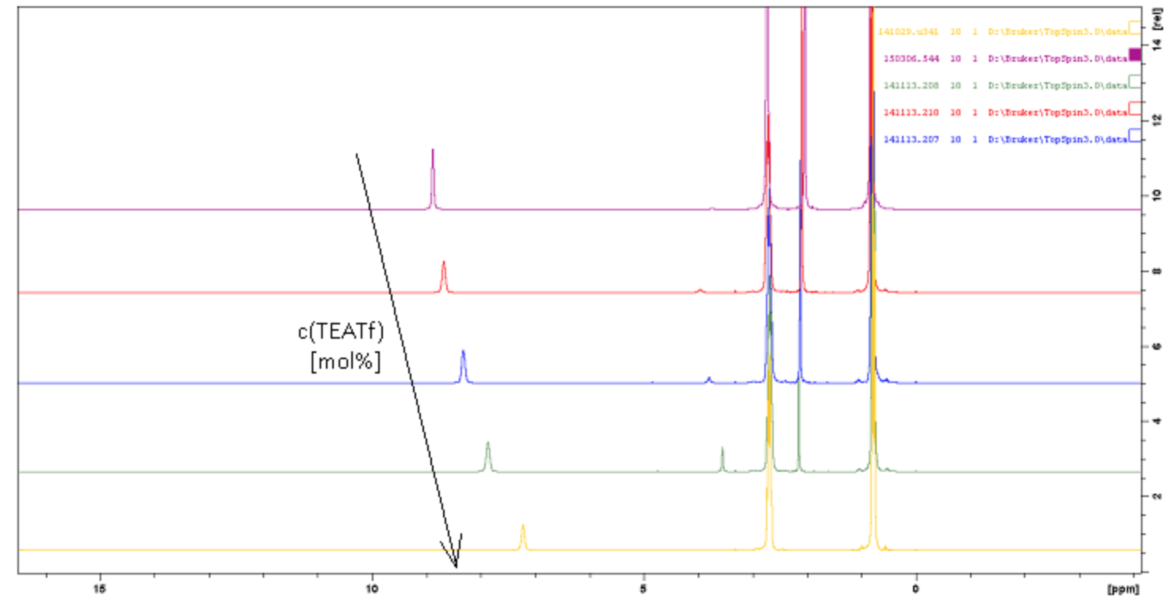

Figure S1: Experimental ^{1}H-NMR spectra obtained at $298\,\mathrm{K}$ for [TEA][OMS]/[TEA][OTf] mixtures with mol fractions $x_{\mathrm{OMs}} = 1.0$, $x_{\mathrm{OMs}} = 0.25$, $x_{\mathrm{OMs}} = 0.5$, $x_{\mathrm{OMs}} = 0.75$, and $x_{\mathrm{OMs}} = 0.0$ (from top to bottom). The arrow indicates the shift of the N-H proton peak as a function of mixture composition.

S3 Experimental Determination of the Excess Enthalpies

S3.1 Apparatus

The partial molar excess enthalpies $\overline{H}^E_{ILj}$ in IL(1) + [TEA][OTf](2) mixtures were measured at T = 298.15 K using the TAM isothermal titration calorimeter (Thermometric, Sweden). The $\overline{H}^E_{ILj}$ in [TEA][OMs](1) + [TEA][OTf](2) system were measured in 4 mL stainless steel reaction cell. Four experiments were conducted: the cell filled with pure [TEA][OMs](1) was titrated with pure [TEA][OTf](2) and vice versa; the cell filled with mixture of [TEA][OMs](1) + [TEA][OTf](2) (x_{OMs} = 0.4602) was titrated with [TEA][OMs](1) or [TEA][OTf](2). 20 injections of 10 μL of pure IL were injected into cell from 250 μL syringe using the Lund pump. The content of the cell was stirred at 85 and 100 rpm using the gold propeller stirrer. The reference cell contained 0.9456 g of [TEA][OMs](1). All four experiments were conducted at 3000 μW range of the calorimeter. The reaction cell and propeller were washed with acetone and dried in oven after experiment termination. Dynamic calibration was performed before start of own titration procedure.

Table S13: Experimental settings of TAM-ITC for measurement of $\overline{H}^E$ in mixture of [TEA][OMs](1) + [TEA][OTf](2) at T = 298.15 K.

m_0^{cell} /g	0.9446	1.4399	1.2815	1.2522
$x_{0,IL1}^{cell}$	1	0	0.4602	0.4602
IL syringe	2	1	1	2
Main section /min	90	90	60	60
Baseline section /min	15	15	15	15

S3.2 Data analysis

The partial molar excess enthalpy of injected IL at i-th injection is directly related to the measured heat

$$\overline{H}^E_{ILj,i} = \frac{\Delta q_i}{\Delta n_{j,i}}, \tag{2}$$

where Δq_i is the measured peak area after injection of Δn_i molar amount of the j-th IL into cell. The measured $\overline{H}^E_{IL,i}$ at i-th injection is tangent to H^E at $(x_{IL,i} + x_{IL,i-1})/2$ between two injections. Here $x_{IL,i}$ and $x_{IL,i-1}$ denote the composition of the mixture in cell after i-th and $(i-1)$th injection.

The molar amount of injected component was calculated from pure IL densities [2] and injected volume. The numerical values of $\overline{H}^E_{ILj,i}$ measured by TAM-ITC and used further for fitting are listed in Tables S14 and S15.

S3.3 Fitting by Redlich-Kister Equation

The composition dependence of H^E by Redlich-Kister equation is given as

$$H^E = x_1x_2[A_1 + A_2(x_1 - x_2) + A_3(x_1 - x_2)^2]. \tag{3}$$

Table S14: Measured $\overline{H}^E$ of [TEA][OMs](1) ionic liquid in mixture of [TEA][OMs](1) + [TEA][OTf](2) at $T = 298.15\,\mathrm{K}$ as function of mixture composition.

x_{OMs}	$\overline{H}^E_{IL1}$ / (J·mol^{-1})	x_{OMs}	$\overline{H}^E_{IL1}$ / (J·mol^{-1})
0.0049	-7935	0.4682	-2675
0.0146	-7764	0.4734	-2632
0.0241	-7679	0.4785	-2580
0.0334	-7582	0.4835	-2538
0.0426	-7572	0.4884	-2494
0.0516	-7399	0.4932	-2469
0.0604	-7305	0.4979	-2394
0.0690	-7174	0.5025	-2360
0.0775	-7134	0.5071	-2307
0.0859	-7071	0.5115	-2264
0.0941	-6949	0.5159	-2205
0.1021	-6827	0.5202	-2187
0.1100	-6783	0.5245	-2138
0.1178	-6639	0.5286	-2111
0.1254	-6588	0.5327	-2076
0.1329	-6492	0.5367	-2015
0.1403	-6384	0.5407	-1987
0.1475	-6330	0.5446	-1930
0.1546	-6261	0.5484	-1938
0.1617	-6210	0.5521	-1884
0.1685	-6116		

Table S15: Measured $\overline{H}^E$ of [TEA][OTf](2) ionic liquid in mixture of [TEA][OMs](1) + [TEA][OTf](2) at $T = 298.15\,\mathrm{K}$ as function of mixture composition.

x_{OMs}	$\overline{H}^E_{IL2}$ / (J·mol^{-1})	x_{OMs}	$\overline{H}^E_{IL2}$ / (J·mol^{-1})
0.9845	-8381	0.4581	-1795
0.9745	-8119	0.4540	-1753
0.9646	-8038	0.4500	-1718
0.9549	-7891	0.4460	-1692
0.9455	-7840	0.4421	-1661
0.9362	-7690	0.4383	-1632
0.9271	-7533	0.4345	-1594
0.9181	-7448	0.4308	-1563
0.9094	-7346	0.4272	-1532
0.9008	-7223	0.4236	-1511
0.8923	-7110	0.4201	-1484
0.8841	-7003	0.4167	-1452
0.8759	-6868	0.4133	-1424
0.8679	-6774	0.4099	-1390
0.8601	-6716	0.4066	-1377
0.8524	-6556	0.4034	-1354
0.8449	-6442	0.4002	-1314
0.8374	-6350	0.3971	-1301
0.8301	-6283	0.394	-1277
0.8230	-6206	0.3909	-1255
0.8159	-6070		

The partial molar enthalpies $\overline{H}^E$ in binary system are calculated from H^E by

$$\overline{H}_1^E = H^E - (1 - x_1)\frac{\partial H^E}{\partial x_1} \tag{4}$$

$$\overline{H}_2^E = H^E - x_1\frac{\partial H^E}{\partial x_1} \tag{5}$$

Applying Eqs. 4 and 5 on Eq. 3 for the measured partial molar excess enthalpies $\overline{H}_{IL1,i}^E$ and $\overline{H}_{IL2,i}^E$ follows

$$\overline{H}_{IL1}^E = x_2^2[A_1 + A_2(4x_1 - 1) + A_3(x_1 - x_2)(6x_1 - 1)], \tag{6}$$

$$\overline{H}_{IL2}^E = x_1^2[A_1 + A_2(1 - 4x_2) + A_3(x_1 - x_2)(1 - 6x_2)]. \tag{7}$$

The partial molar excess enthalpies at infinite dilution then follows

$$\overline{H}_1^{E,\infty} = A_1 - A_2 + A_3 \tag{8}$$

and

$$\overline{H}_2^{E,\infty} = A_1 + A_2 + A_3 \tag{9}$$

To evaluate the parameters A_n of Redlich-Kister equation given above, the experiments were treated by simultaneous linear non-weighted fit using 76 discrete $\overline{H}_{IL,i}^E$ points. Table S16 lists the values for one to three parameter fit of experimental $\overline{H}_{IL1}^E$ and $\overline{H}_{IL2}^E$ by Eqs (6) and (7), respectively, together with the calculated values of partial molar excess enthalpies at infinite dilution $\overline{H}_{IL1}^{E,\infty}$ and $\overline{H}_{IL2}^{E,\infty}$. The $\overline{H}^E$ composition dependence of the excess enthalpies is best represented by three parameter Redlich-Kister equation. Figure S2 illustrates the dependence of the H^E, $\overline{H}_{IL1}^E$ and $\overline{H}_{IL2}^E$ as function of mixture composition. The minimum in H^E is at $x_1 = 0.5083$ with the value $H^E = -2.24\,\mathrm{kJ\cdot mol^{-1}}$.

Table S16: Values of adjustable parameters A_n of Redlich-Kister equations (6) and (7), standard deviation of fit s and calculated partial molar excess enthalpies at infinite dilution $\overline{H}_1^{E,\infty}$ and $\overline{H}_2^{E,\infty}$ by Eqs. (8) and (9) for [TEA][OMs](1) + [TEA][OTf](2) mixture at $T = 298.15\,\mathrm{K}$.

A_1	A_2	A_3	$s/(\mathrm{J\cdot mol^{-1}})$	$\overline{H}_1^{E,\infty}/(\mathrm{kJ\cdot mol^{-1}})$	$\overline{H}_2^{E,\infty}/(\mathrm{kJ\cdot mol^{-1}})$
-8662.17			210	-8.66	-8.66
-8673.45	-385.90		136	-8.29	-9.06
-8974.27	-324.99	804.735	40	-7.85	-8.50

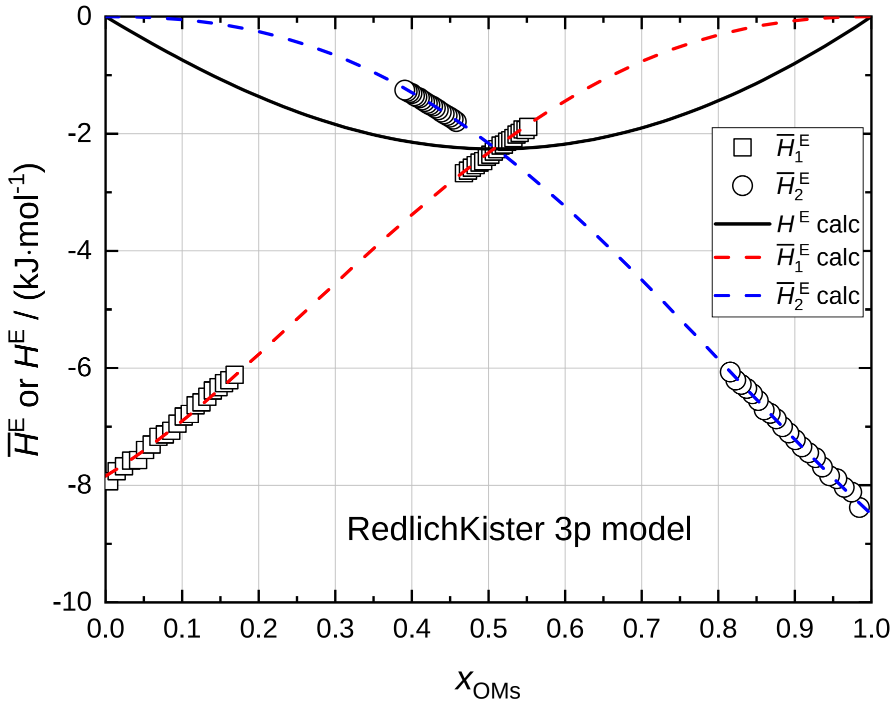

Figure S2: Excess molar enthalpies $\overline{H}^E$ and H^E in the [TEA][OMs](1) + [TEA][OTf](2) mixture at $T = 298.15\,\mathrm{K}$. Points are experimental $\overline{H}^E$: (square) $\overline{H}_1^E$ of [TEA][OMs](1); (circle) $\overline{H}_2^E$ of [TEA][OTf](2). Dashed lines are fits to experimental $\overline{H}_1^E$ and $\overline{H}_2^E$ data by Redlich-Kister Eqs. (6) and (7), with parameters A_n listed in Table S16. Solid line is the calculated H^E by Eq. (3).

S3.4 Fitting by Lattice Model

From the lattice model for ΔU_{mix} at constant pressure for H^E follows

$$\Delta U_{\text{mix}} = H^E = \Delta\epsilon_{\text{HB}} x_1 \frac{(1-x_1)(1-f)}{x_1 + f(1-x_1)} \tag{10}$$

where x_1 is the mole fraction of [TEA][OMs](1) and $f = a + bx_1$

$$\overline{H}_1^E = \Delta\epsilon_{\text{HB}}(1-x_1)\frac{a(ax_1^3 - 3ax_1^2 + 3ax_1 - a - x_1 + 1)}{(ax_1^2 - 2ax_1 + a + x_1)^2} \tag{11}$$

$$\overline{H}_2^E = \Delta\epsilon_{\text{HB}} x_1^2 \frac{2ax_1 - 2a + 1}{(ax_1^2 - 2ax_1 + a + x_1)^2} \tag{12}$$

For the partial molar excess enthalpies at infinite dilution then follows

$$\overline{H}_1^{E,\infty} = \Delta\epsilon_{\text{HB}}(1-a)/a \tag{13}$$

and

$$\overline{H}_2^{E,\infty} = \Delta\epsilon_{\text{HB}}(1-a-b) \tag{14}$$

The following parameters of Eqs. (10) were fitted $\Delta\epsilon_{\mathrm{HB}} = -14.9\,\mathrm{kJ\cdot mol^{-1}}$, $a = 0.6559$, $b = -0.2416$ to experimental $\overline{H}_1^E$ and $\overline{H}_2^E$ data. Figure S3 illustrates the composition dependence of experimental and calculated $\overline{H}^E$ and H^E. The calculated $\overline{H}_1^{E,\infty}$ and $\overline{H}_2^{E,\infty}$ by Eqs. (13) and (14) are $\overline{H}_1^{E,\infty} = -7.83\,\mathrm{kJ\cdot mol^{-1}}$ and $\overline{H}_2^{E,\infty} = -8.74\,\mathrm{kJ\cdot mol^{-1}}$, respectively. The minimum in H^E is at $x_1 = 0.5082$ with the value $H^E = -2.26\,\mathrm{kJ\cdot mol^{-1}}$.

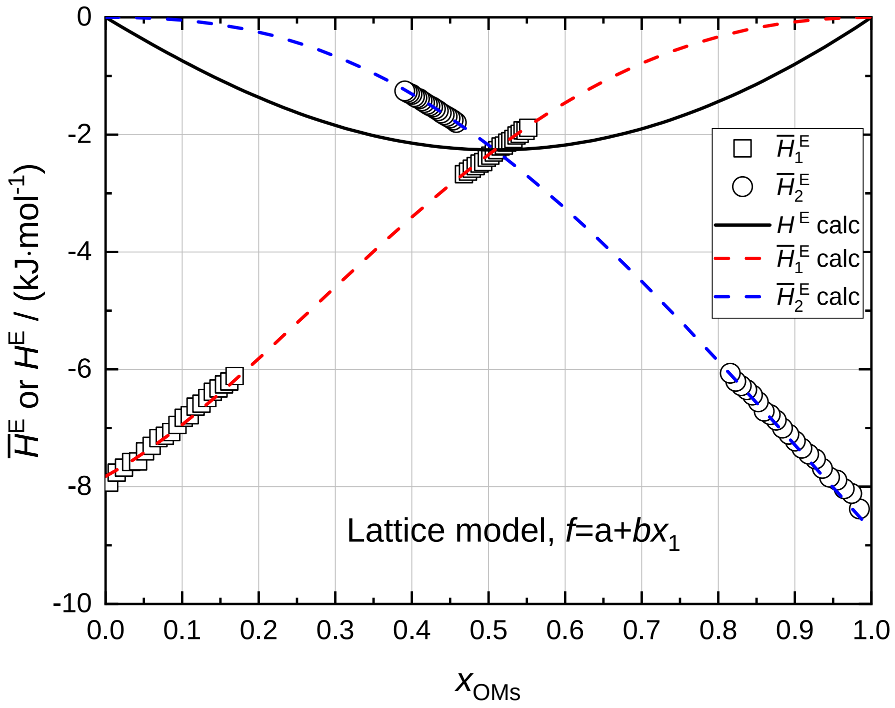

Figure S3: Excess molar enthalpies $\overline{H}^E$ and H^E in the [TEA][OMs](1) + [TEA][OTf](2) mixture at $T = 298.15\,\mathrm{K}$. Points are experimental $\overline{H}^E$: (square) $\overline{H}_1^E$ of [TEA][OMs](1); (circle) $\overline{H}_2^E$ of [TEA][OTf](2). Dashed lines are fits to experimental $\overline{H}_1^E$ and $\overline{H}_2^E$ data by Lattice model, with parameters $\Delta\epsilon_{\mathrm{HB}} = -14.9\,\mathrm{kJ\cdot mol^{-1}}$, $a = 0.6558$, $b = -0.2416$. Solid line is the calculated H^E by Eq. (10).

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