Energetics of Aqueous Solutions of the Ionic Liquid 1-Ethyl-3-methylimidazolium Ethylsulfate.

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BRIEFS (WORD Style "BH_Briefs"). The Energetics of Aqueous Solutions of the Ionic Liquid 1-Ethyl-3-methylimidazolium Ethylsulfate.

Supporting Information

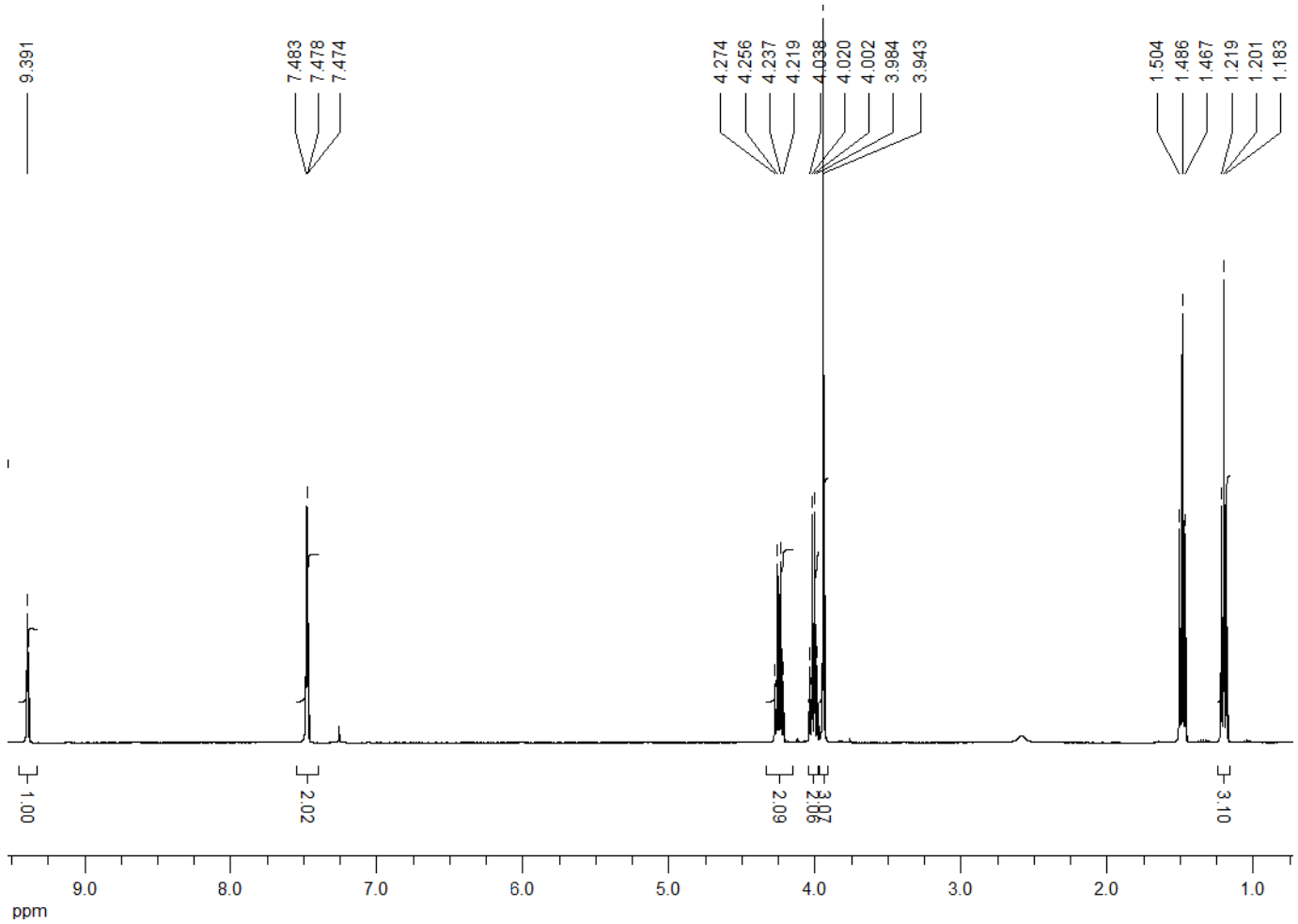

Figure S1. ^{1}H NMR spectrum of 1-ethyl-3-methylimidazolium ethylsulfate, [C_2mim][$EtSO_4$], recorded at ambient temperature in $CDCl_3$. Chemical shifts are given relative to TMS.

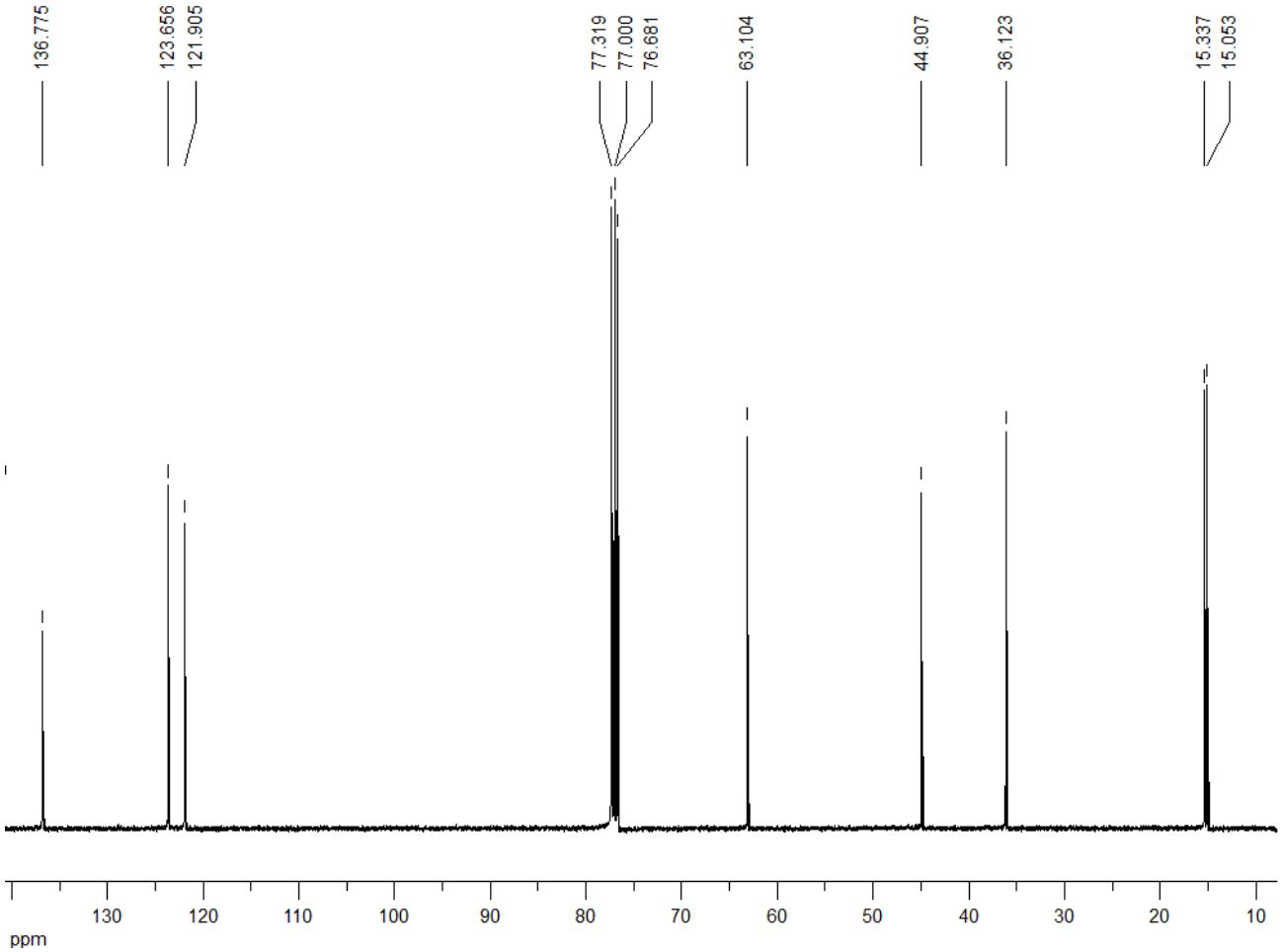

Figure S2. ^{13}C NMR spectrum of 1-ethyl-3-methylimidazolium ethylsulfate, $[C_2mim][EtSO_4]$, recorded at ambient temperature in $CDCl_3$. Chemical shifts are given relative to TMS.

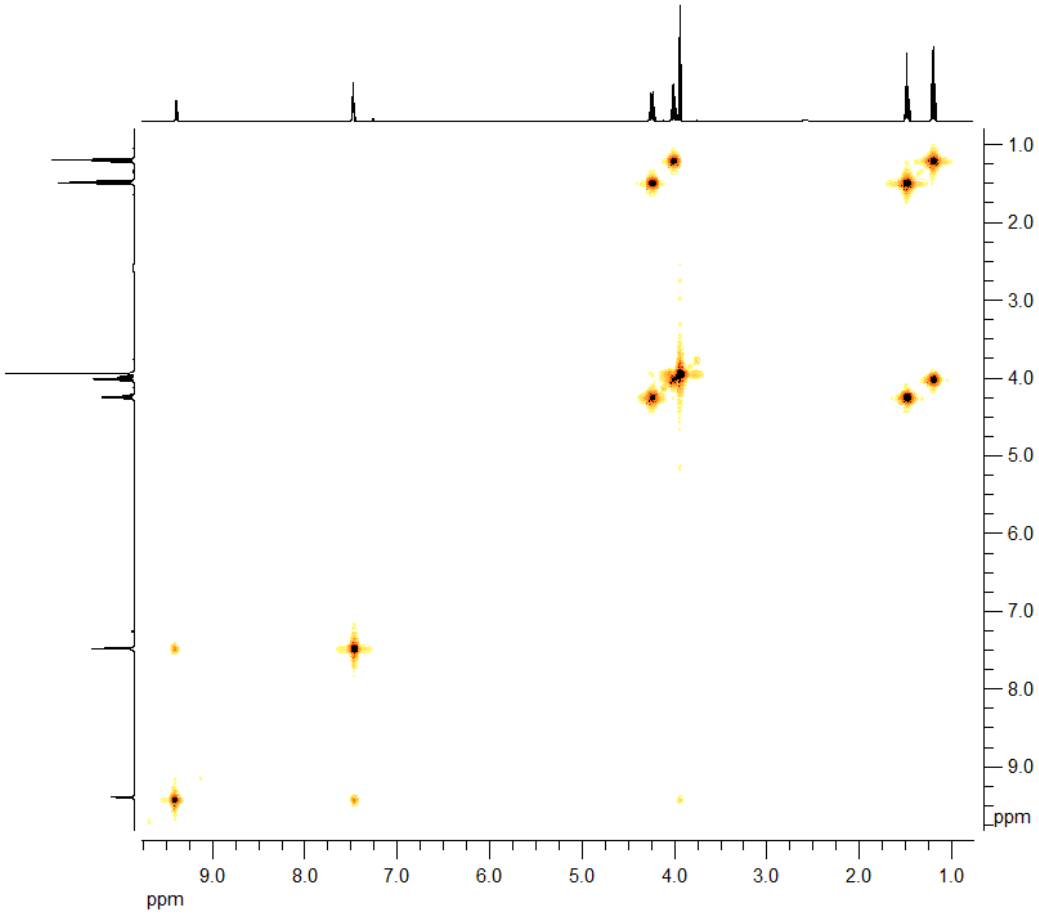

Figure S3. Two-dimensional NMR ^{1}H-^{1}H COSY analysis of 1-ethyl-3-methylimidazolium ethylsulfate, $[C_2mim][EtSO_4]$, recorded at ambient temperature in $CDCl_3$.

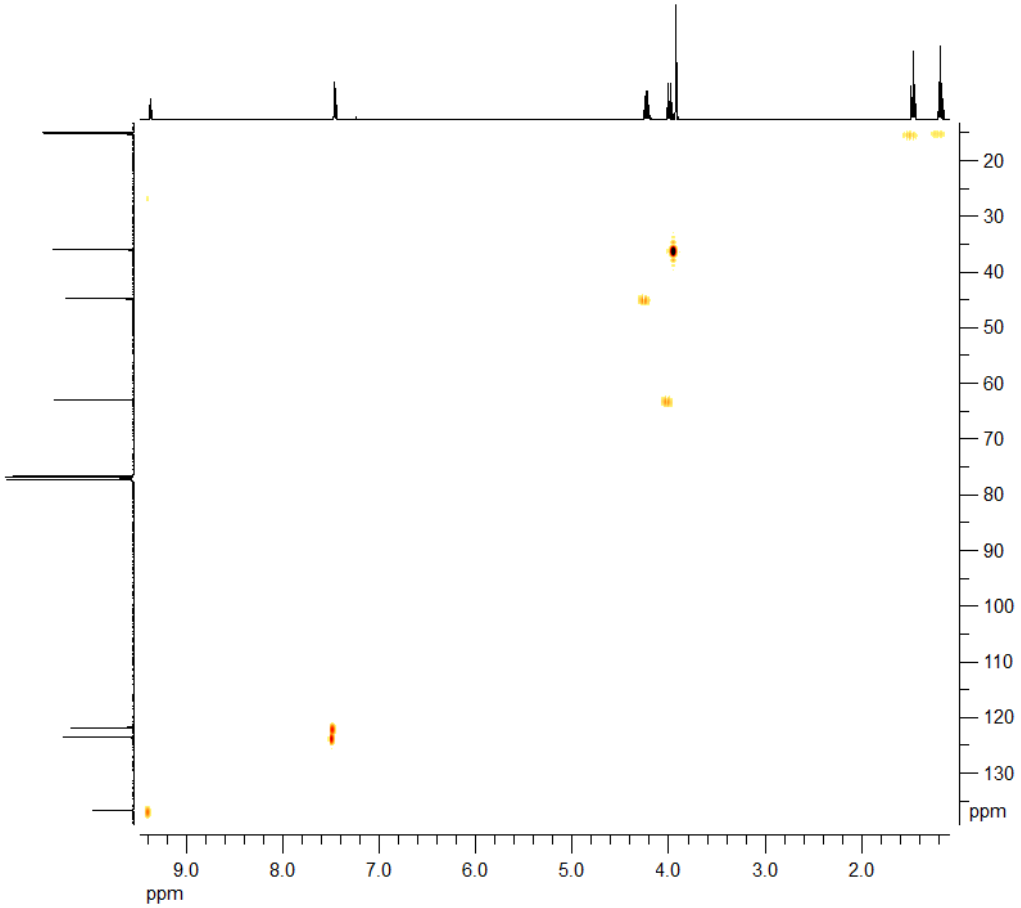

Figure S4. Two-dimensional NMR HMQC spectrum showing direct bond ^{1}H-^{13}C correlations of 1-ethyl-3-methylimidazolium ethylsulfate, $[C_2mim][EtSO_4]$, recorded at ambient temperature in $CDCl_3$.

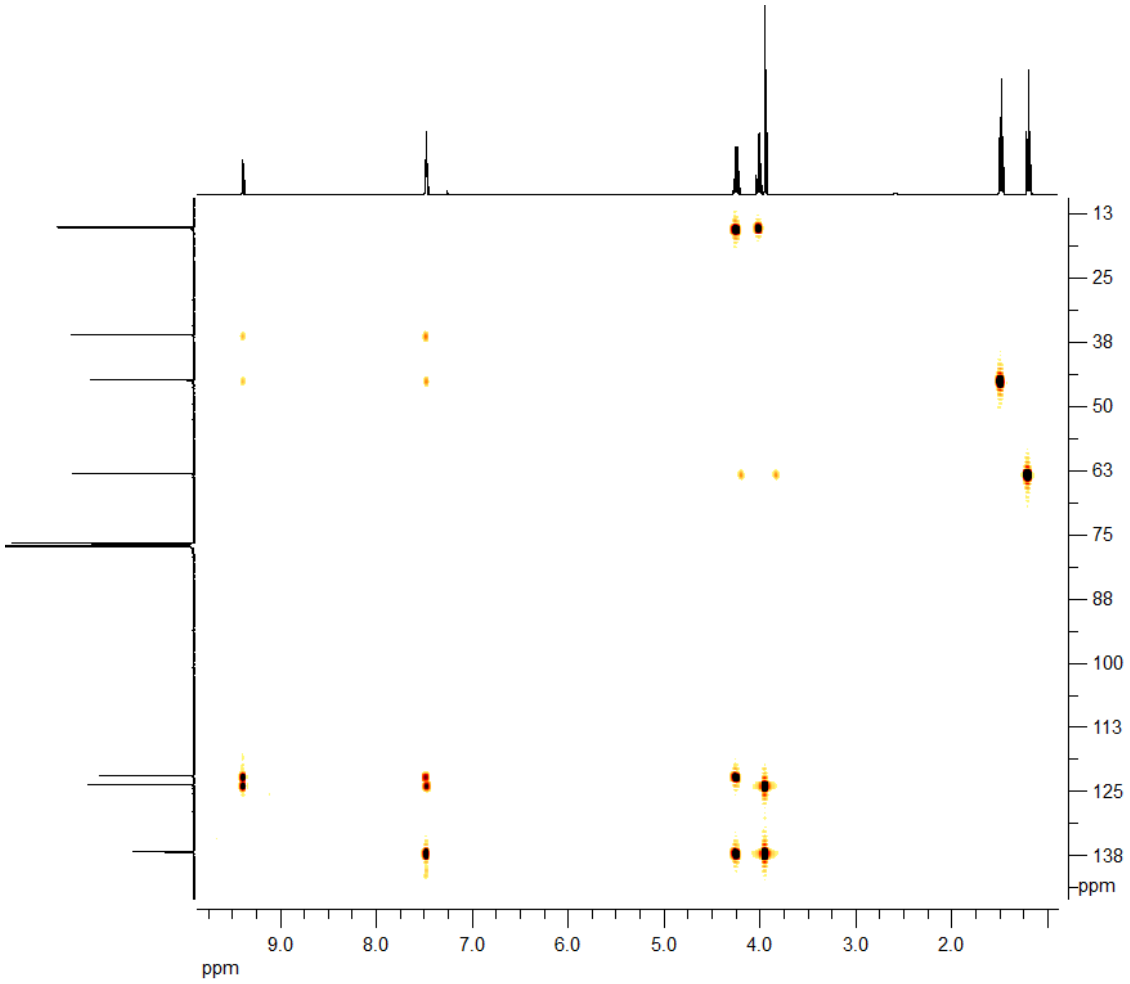

Figure S5. Two-dimensional NMR HMBC spectrum showing long range ^{1}H-^{13}C couplings of 1-ethyl-3-methylimidazolium ethylsulfate, $[C_2mim][EtSO_4]$, recorded at ambient temperature in $CDCl_3$.

Calculation of enthalpies of solution from the data reported by Ficke et al. in Reference S1

Ficke et al.[S1] reported the excess enthalpies, H^E, of H_2O + [C_2mim][$EtSO_4$] mixtures at 313.14 K, 323.12 K, 333.11 K, and 348.12 K in terms of a Redlich-Kister equation:

$$H^{\mathrm{E}} / \mathrm{J} \cdot \mathrm{mol}^{-1} = x_{\mathrm{H_2O}} x_{\mathrm{IL}} \left[A + B\left(x_{\mathrm{H_2O}} - x_{\mathrm{IL}} \right) + C(x_{\mathrm{H_2O}} - x_{\mathrm{IL}})^2 \right] \quad \text{(S1)}$$

where H^E refers to the total number of moles of the two components, x_{H_2O} and x_{IL} are the molar fractions of water and ionic-liquid, respectively, and A, B and C are the parameters listed Table S1. As shown in Figure S6 the variation of these parameters with the temperature is approximately linear. Linear least squares fits to the data led to:

$$A / \mathrm{J \cdot mol^{-1}} = -2.6679\, T - 2288.5 \quad \text{(S2)}$$

$$B / \mathrm{J \cdot mol^{-1}} = 30.8607\, T - 12401.9 \quad \text{(S3)}$$

$$C / \mathrm{J \cdot mol^{-1}} = 32.3235\, T - 12935.2 \quad \text{(S4)}$$

These equations reproduce the A, B and C values at 313.14 K, 323.12 K, 333.11 K, and 348.12 K in Table S1 with an average deviation of 1.6% and were used to derive the corresponding data at 298.15 K listed in that table.

TABLE S1: Parameters of eq S1 at 313.4 K, 323.12 K, 333.11 K and 348.11 K given in Reference S1 and Corresponding Values at 298.15 K Estimated in this Work.

T /K	$-A$ /J·mol^{-1}	$-B$ /J·mol^{-1}	$-C$ /J·mol^{-1}
298.15	3084	3201	3298
313.14	3104	2732	2828
323.12	3169	2407	2399
333.11	3193	2175	2287
348.12	3203	1635	1641

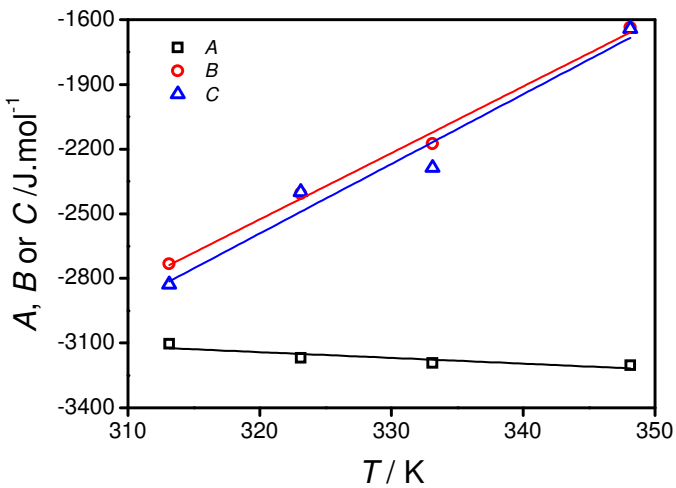

Figure S6. Variation of the *A*, *B* and *C* parameters of eq S1 (taken from reference S1) with temperature.

The enthalpy of solution of [C_2mim][$EtSO_4$] in H_2O expressed *per mole of IL* is related to the excess enthalpy in eq S1 by:

$$\Delta_{\mathrm{sol}} H_{\mathrm{m}} = \frac{H^{\mathrm{E}}}{1 - x_{\mathrm{H_2O}}} \tag{S5}$$

Substitution of eq S1 and into eq S5 leads to:

$$\Delta_{\mathrm{sol}} H_{\mathrm{m}} = \frac{x_{\mathrm{H_2O}} x_{\mathrm{IL}}}{1 - x_{\mathrm{H_2O}}} \left[A + B\left(x_{\mathrm{H_2O}} - x_{\mathrm{IL}} \right) + C(x_{\mathrm{H_2O}} - x_{\mathrm{IL}})^2 \right] \tag{S6}$$

Using eq S6 and the *A*, *B* and *C* parameters at 298.15 K given in Table S1 it was possible to calculate the enthalpies of solution in Table S2. Here *m* represents the molality of [C_2mim][$EtSO_4$], which is related to $x_{\mathrm{H_2O}}$ and x_{IL} by:

$$m = 1000 \frac{x_{\mathrm{IL}}}{x_{\mathrm{H_2O}} M_{\mathrm{H_2O}}} \tag{S7}$$

where $M_{\mathrm{H_2O}}$ = 18.0153 g·mol^{-1} is the molar mass of water.

TABLE S2: Enthalpies of Solution of [C_2mim][$EtSO_4$] in Water, at 298.15 K, Calculated from Eq S6.

x_{IL}	m /mol·kg^{-1}	-$\Delta_{sol}H_m$ /J·mol^{-1}
0.01	0.6	9294.5
0.1	6.168	6980.0
0.2	13.877	4953.5
0.3	23.789	3424.5
0.4	37.006	2313.7
0.5	55.508	1542.0
0.6	83.263	1030.3
0.7	129.520	699.4
0.8	222.033	470.1
0.9	499.575	263.4

A plot of the $\Delta_{sol}H_m$ values in Table S2 as a function of m is illustrated Figure S7. Also shown in this figure is the line corresponding to the equation:

$$\Delta_{sol}H_m / \mathrm{J \cdot mol^{-1}} = -300.541 - 7268.216 \cdot e^{-\frac{m-0.779}{14.847}} - 2391.051 \cdot e^{-\frac{m-0.779}{72.128}} \quad \text{(S8)}$$

which was obtained by using the non-linear curve fitting tool of the OriginPro 8 software package: The corresponding regression coefficient is 0.9997.

The enthalpy of a dilution process such as:

$$[C_2mim][EtSO_4]\cdot nH_2O(aq) + aH_2O(l) = [C_2mim][EtSO_4]\ (n + a)H_2O(aq) \quad \text{(S9)}$$

can be related with the enthalpy of the solution of the processes that lead to the same initial or final states:

$$[C_2mim][EtSO_4](l) + nH_2O(l) = [C_2mim][EtSO_4]\cdot nH_2O(aq) \quad \text{(S10)}$$

$$[C_2mim][EtSO_4](l) + (n + a)H_2O(l) = [C_2mim][EtSO_4]\ (n + a)H_2O(aq) \quad \text{(S11)}$$

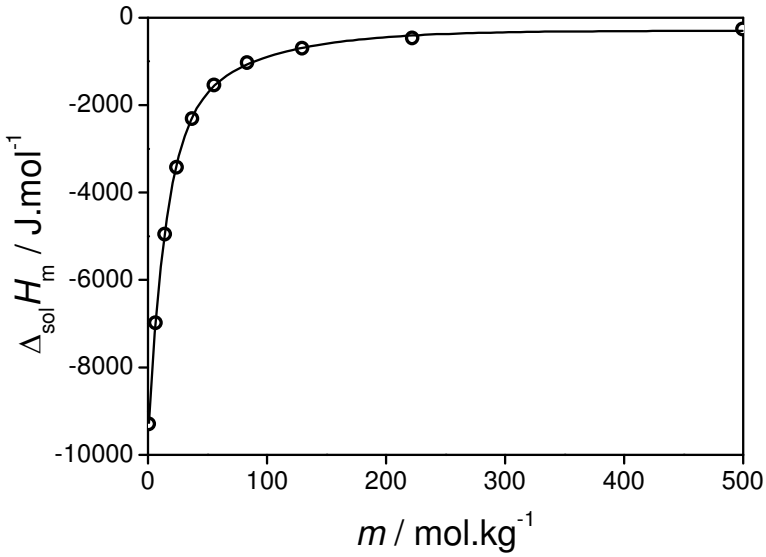

Figure S7. Variation of $\Delta_{sol}H_m$ with the molality of the [C_2mim][$EtSO_4$] solution, *m*, obtained from the data in Table S2. The line corresponds to a plot of eq S8.

by:

$$\Delta_{dil}H_m\,(\text{eq S9}) = \Delta_{sol}H_m\,(\text{eq 11}) - \Delta_{sol}H_m\,(\text{eq 10}) \qquad \text{(S12)}$$

Hence eq S12 was used in conjunction with eq S8 to derive the $\Delta_{dil}H_m$ (Lit) values included in Table 1 of the main text.

References

S1. Ficke, L. E.; Rodriguez, H.; Brennecke, J. F. *J. Chem. Eng. Data* **2008**, *53*, 2112-2119

TABLE S3: Results of the Solution Calorimetry Studies

m/mg	m/mmol.Kg^{-1}	$x(H_2O)$	ε/J.K^{-1}	$-\Delta T_{ad}$/mK	$-\Delta_{sln}H^{o}_{m}$/kJ.mol^{-1}
1108.7	46.921	0.9991554	446.363	114.921	10.932
704.9	29.832	0.9994629	446.916	74.252	11.124
348.1	14.732	0.9997347	446.082	35.279	10.682
896.2	37.928	0.9993172	448.771	94.209	11.147
984.4	41.661	0.9992500	447.820	102.250	10.991
755.0	31.952	0.9994247	449.062	74.716	10.501
687.8	29.108	0.9994759	444.407	72.909	11.131
599.1	25.355	0.9995434	447.149	62.874	11.088
492.7	20.852	0.9996245	445.421	51.761	11.057
380.0	16.082	0.9997104	446.417	39.918	11.081
248.5	10.517	0.9998106	444.475	25.938	10.962
54.4	2.302	0.9999585	446.349	5.653	10.960
1069.1	45.246	0.9991856	448.328	108.375	10.739
925.3	39.160	0.9992950	449.983	92.757	10.659
603.3	25.534	0.9995402	446.635	61.999	10.845
647.0	27.383	0.9995069	461.515	65.085	10.970
683.0	28.906	0.9994795	454.568	72.093	11.337
678.9	28.731	0.9994827	448.488	71.360	11.139

TABLE S4: Coulomb (*coul*) and van der Waals (*vdw*) Contributions to $U^{\text{IL-IL}}_{\text{conf, tot}}$ and $U^{\text{IL-H}_2\text{O}}_{\text{conf, tot}}$ Interaction Energies for Different Molar Fractions of Ionic-liquid (Data in kJ per mole of IL).

	$-U^{\text{IL-IL}}_{\text{conf, tot}}$		$-U^{\text{IL-H}_2\text{O}}_{\text{conf, tot}}$	
x_{IL}	*coul*	*vdw*	*coul*	*vdw*
0.5	362.9	91.9	440.0	90.6
0.2	329.1	72.5	607.9	63.9
0.1	294.2	52.0	864.6	22.4
0.08	280.7	45.4	989.7	3.0
0.05	253.2	34.4	1355.6	−51.8
0.03	226.6	25.5	2004.3	−146.8
0.01	158.8	12.0	5339.4	−612.7
0.004	107.3	6.3	12369.0	−1634.0

TABLE S5: Coulomb (*coul*) and van der Waals (*vdw*) Contributions to $U_{\mathrm{conf}}^{\mathrm{IL\text{-}IL}}$, $U_{\mathrm{conf}}^{\mathrm{H_2O\text{-}H_2O}}$ and $U_{\mathrm{conf}}^{\mathrm{IL\text{-}H_2O}}$ Interation energies for Different Molar Fractions of Ionic-liquid (Data in kJ per mole of IL or Water).

	$U_{\mathrm{conf}}^{\mathrm{IL\text{-}IL}}$		$U_{\mathrm{conf}}^{\mathrm{H_2O\text{-}H_2O}}$		$U_{\mathrm{conf}}^{\mathrm{IL\text{-}H_2O}}$	
x_{IL}	*coul*	*vdw*	*coul*	*vdw*	*coul*	*vdw*
0.5	–429.4	–92.3	–10.8	2.97	–66.3	–1.7
0.2	–395.6	–73.0	–25.2	6.02	–178.2	–15.4
0.1	–360.7	–52.5	–33.1	7.06	–272.3	–34.0
0.08	–347.3	–45.9	–35.1	7.18	–305.4	–40.2
0.05	–319.8	–34.9	–38.6	7.22	–368.3	–50.9
0.03	–293.2	–26.0	–41.8	7.17	–426.9	–59.7
0.01	–225.3	–12.5	–45.6	7.04	–569.5	–72.7
0.004	–173.8	–6.8	–47.1	6.99	–674.2	–78.0

TABLE S6: Coulomb (*coul*) and van der Waals (*vdw*) Contributions to $U_{\mathrm{conf,\,intra}}^{\mathrm{IL}}$ Calculated for $[C_2mim]^+$ and $[EtSO_4]^-$ Ions in the Gas Phase. Data in kJ·mol^{-1}.

	$U_{\mathrm{conf,\,intra}}^{\mathrm{IL}}$	
	vdw	*coul*
$[C_2mim]^+$	–1.04	139.83
$[EtSO_4]^-$	1.52	–73.31