

A general strategy for the experimental study of the thermochemistry of protic ionic liquids: Enthalpy of formation and vaporisation of 1-methylimidazolium ethanoate

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Supplementary Information

1. Enthalpy of vaporisation of [Hmim][O₂CCH₃] by drop-vaporisation Calvet microcalorimetry.

The standard specific enthalpy of vaporisation of [Hmim][O₂CCH₃], $\Delta_{\text{vap}}h^\circ$, at 298.15 K, was derived from:

$$\Delta_{\text{vap}}h^\circ = \frac{1}{m} \left[\frac{(A - A_b)}{\varepsilon} - \frac{m_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}} \Delta_{\text{vap}}H_m^\circ(\text{H}_2\text{O}) \right] \quad (\text{S1})$$

where m is the mass of [Hmim][O₂CCH₃] after correction for the water content; $m_{\text{H}_2\text{O}}$ is the mass of water given by Karl Fisher titration; $M_{\text{H}_2\text{O}} = 18.0153 \text{ g}\cdot\text{mol}^{-1}$ is the molar mass of water; $\Delta_{\text{vap}}H_m^\circ(\text{H}_2\text{O}) = 44.004 \pm 0.002 \text{ kJ}\cdot\text{mol}^{-1}$ is the standard molar enthalpy of vaporisation of water;¹ A is the area of the measurement curve corresponding to the over-all experiment; A_b is the area of the background contribution for the observed process due to dropping and evacuation of the cell; and ε is the energy equivalent of the calorimeter obtained by electrical calibration. The detailed results of the calorimetric experiments on samples 1 to 3 are given in Tables S1-S3 where T is the temperature of the calorimetric cell and m_s is the mass of sample ([Hmim][O₂CCH₃] + H₂O) used in the experiment.

TABLE S1: Results of the vaporisation enthalpy measurements on 1-methylimidazolium ethanoate, by drop-vaporisation Calvet microcalorimetry (Sample 1)

T/K	m_s/mg	$m_{\text{H}_2\text{O}}/\mu\text{g}$	m/mg	A	$\Delta_{\text{vap}}h^\circ/\text{J}\cdot\text{g}^{-1}$
297.96	9.72	5	9.72	521.915	830.864
297.95	10.12	5	10.12	538.315	823.320
297.93	12.23	6	12.22	638.981	810.311
297.90	9.91	5	9.91	523.286	817.053
297.89	6.66	3	6.66	355.183	822.072

Water content from Karl Fisher titration: 465 ppm

$$\langle \Delta_{\text{vap}}h^\circ \rangle = 824.01 \pm 3.46 \text{ J}\cdot\text{g}^{-1}$$

$$\langle \varepsilon \rangle = 63.805 \pm 0.138 \text{ mV}\cdot\text{W}^{-1}$$

$$A_b = 3.850 \text{ mV}\cdot\text{s}$$

$$\sigma(\text{over-all}) = 3.89 \text{ J}\cdot\text{g}^{-1}$$

$$\Delta_{\text{vap}}H_m^\circ = 117.14 \pm 1.10 \text{ kJ}\cdot\text{mol}^{-1}$$

TABLE S2: Results of the vaporisation enthalpy measurements on 1-methylimidazolium ethanoate, by drop-vaporisation Calvet microcalorimetry (Sample 2)

T/K	m_s/mg	$m_{H_2O}/\mu g$	m/mg	A	$\Delta_{vap} h^\circ / J \cdot g^{-1}$
298.11	14.00	32	13.97	735.464	812.241
298.11	14.53	33	14.50	778.122	828.345
298.07	8.50	19	8.48	450.981	817.571
298.08	11.44	26	11.41	612.997	827.958
298.08	19.32	44	19.28	1024.198	821.058
298.08	15.35	35	15.32	817.184	823.564
298.08	13.58	31	13.55	714.775	813.727

Water content from Karl Fisher titration: 2271 ppm

$$\langle \Delta_{vap} h^\circ \rangle = 820.64 \pm 2.44 \text{ J} \cdot g^{-1}$$

$$\langle \varepsilon \rangle = 63.988 \pm 0.096 \text{ mV} \cdot W^{-1}$$

$$A_b = 4.404 \text{ mV} \cdot s$$

$$\sigma(\text{over-all}) = 2.73 \text{ J} \cdot g^{-1}$$

$$\Delta_{vap} H_m^\circ = 116.66 \pm 0.78 \text{ kJ} \cdot \text{mol}^{-1}$$

TABLE S3: Results of the vaporisation enthalpy measurements on 1-methylimidazolium ethanoate, by drop-vaporisation Calvet microcalorimetry (Sample 3)

T/K	m_s/mg	$m_{H_2O}/\mu g$	m/mg	A	$\Delta_{vap} h^\circ / J \cdot g^{-1}$
298.09	12.39	27	12.36	670.089	836.327
298.09	16.20	35	16.17	877.85	838.899
298.13	13.90	30	13.87	745.148	829.344
298.12	7.34	16	7.32	398.003	834.973
298.12	17.99	39	17.95	962.823	829.136
298.12	10.65	23	10.63	578.432	838.664
298.09	6.62	14	6.61	363.318	843.419
298.09	15.39	33	15.36	809.422	813.802
298.12	12.24	27	12.21	652.894	824.652

Water content from Karl Fisher titration: 2167 ppm

$$\langle \Delta_{vap} h^\circ \rangle = 832.14 \pm 3.01 \text{ J} \cdot g^{-1}$$

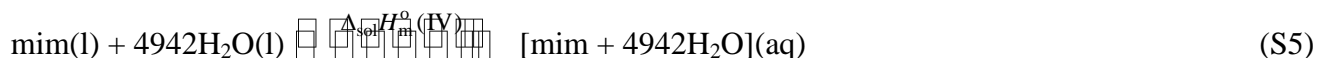
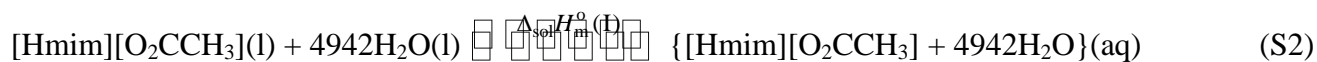
$$\langle \varepsilon \rangle = 63.988 \pm 0.096 \text{ mV} \cdot W^{-1}$$

$$A_b = 4.404 \text{ mV} \cdot s$$

$$\sigma(\text{over-all}) = 3.26 \text{ J} \cdot g^{-1}$$

$$\Delta_{vap} H_m^\circ = 118.29 \pm 0.93 \text{ kJ} \cdot \text{mol}^{-1}$$

2. Solution calorimetry. The results of the solution calorimetry determinations summarized in the thermodynamic cycle in Scheme 1 of the main text correspond to the following solution processes:



The value $\Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{II}) = -(1.25 \pm 0.80) \text{ kJ} \cdot \text{mol}^{-1}$ was taken from the NBS tables.² The remaining enthalpy of solution data were based on the results given in Tables S4 to S7. Here, m represents the mass of compound under study (ionic liquid, 1-methylimidazole or ethanoic acid) obtained from m_s the mass of sample and the corresponding water content $m_{\text{H}_2\text{O}}$ calculated from the results of Karl Fisher titration; n is the amount of substance of water per 1 mol the dissolved compound in the final calorimetric solution; ε is the energy equivalent of the calorimeter determined by electrical calibration; and ΔT_{ad} represents the adiabatic temperature change, which corresponds to the temperature variation that would have been observed in the experiments if the heat dissipation occurred under strict adiabatic conditions.

The calibration constant, ε , was obtained from:

$$\varepsilon = \frac{VIt}{\Delta T_{\text{ad}}} \quad (\text{S7})$$

where I is the current intensity that passed through the 50 Ω resistance as a result of the application of a potential difference V during the time period t . The standard molar enthalpy of the solution process, $\Delta_{\text{sol}}H_{\text{m}}^{\circ}$, was calculated from:

$$\Delta_{\text{sol}}H_{\text{m}}^{\circ} = \frac{M \varepsilon \Delta T_{\text{ad}}}{m} \quad (\text{S8})$$

where m and M are the mass and the molar mass of the compound under study, respectively.

TABLE S4: Standard molar enthalpy of solution of 1-methylimidazolium ethanoate in water, at 298.15 K

Sample	m_s/mg	$m_{\text{H}_2\text{O}}/\mu\text{g}$	m/mg	n	$\varepsilon/\text{J}\cdot\text{K}^{-1}$	$\Delta T_{\text{ad}}/\text{mK}$	$-\Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{I})/\text{kJ}\cdot\text{mol}^{-1}$
1	157.53	73	157.46	4997	447.500	69.548	28.098
	161.14	75	161.07	4885	447.410	71.075	28.066
	141.70	66	141.63	5555	447.238	62.526	28.067
	167.58	78	167.50	4697	447.484	73.996	28.102
	163.93	76	163.85	4802	446.984	72.399	28.076
	162.71	76	162.63	4837	447.734	71.851	28.119
2	161.14	366	160.77	4893	445.459	71.044	27.982
	162.02	368	161.65	4867	447.234	71.247	28.021

Water content from Karl Fisher titration: 465 ppm (sample 1); 2271 ppm (sample 2)

$$\langle n \rangle = 4942$$

$$\langle \Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{I}) \rangle = -(28.07 \pm 0.03) \text{ kJ}\cdot\text{mol}^{-1}$$

The results in Table S4 do not show any concentration dependence in the range $4697 < n < 5555$. The mean value of $\Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{I})$ was, therefore, also assigned to the mean value of n in that table, namely $n = 4942$.

TABLE S5: Standard molar enthalpy of solution of 1-methylimidazole in $\text{CH}_3\text{COOH}\cdot n\text{H}_2\text{O}$, at 298.15 K.

m_s/mg	$m_{\text{H}_2\text{O}}/\mu\text{g}$	m/mg	n	$\varepsilon/\text{J}\cdot\text{K}^{-1}$	$\Delta T_{\text{ad}}/\text{mK}$	$-\Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{III})/\text{kJ}\cdot\text{mol}^{-1}$
93.76	1	93.76	4846	446.485	101.771	39.791
92.30	1	92.30	4923	447.115	100.728	40.062
92.95	1	92.95	4889	447.567	101.179	40.001
93.42	1	93.42	4864	448.028	101.084	39.803
92.64	1	92.64	4905	447.386	101.023	40.056
84.66	1	84.66	5368	446.735	94.396	40.897
86.11	1	86.11	5277	447.822	96.136	41.049
89.90	1	89.90	5055	448.071	98.604	40.351
85.47	1	85.47	5316	447.148	95.230	40.905
89.10	1	89.10	5100	447.513	98.163	40.480

Water content from Karl Fisher titration: 12 ppm

$$\Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{III}) = -(2.297 \pm 0.175) \times 10^{-3} n - (28.73 \pm 0.88)$$

$$\langle \Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{III}) \rangle = -(40.08 \pm 0.16) \text{ kJ}\cdot\text{mol}^{-1} \text{ for } n = 4942$$

TABLE S6: Standard molar enthalpy of solution of 1-methylimidazole in water, at 298.15 K

m_s/mg	$m_{\text{H}_2\text{O}}/\mu\text{g}$	m/mg	n	$\varepsilon/\text{J}\cdot\text{K}^{-1}$	$\Delta T_{\text{ad}}/\text{mK}$	$-\Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{IV})/\text{kJ}\cdot\text{mol}^{-1}$
88.49	1	88.49	5135	447.071	24.015	9.962
87.67	1	87.67	5183	447.005	22.990	9.624
93.39	1	93.39	4865	447.828	24.542	9.662
86.14	1	86.14	5275	446.758	22.379	9.530
96.12	1	96.12	4727	447.721	25.284	9.670
90.66	1	90.66	5012	446.854	23.119	9.356

Water content from Karl Fisher titration: 12 ppm

$$\langle \Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{IV}) \rangle = -(9.63 \pm 0.16) \text{ kJ}\cdot\text{mol}^{-1}$$

The results do not show a concentration dependence in the range $4727 < n < 5275$. The mean value of $\Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{IV})$ was, therefore, also assigned to $n = 4942$.

TABLE S7: Standard molar enthalpy of solution of CH_3COOH in 1-methylimidazole- $n\text{H}_2\text{O}$, at 298.15 K

m_s/mg	$m_{\text{H}_2\text{O}}/\mu\text{g}$	m/mg	n	$\varepsilon/\text{J}\cdot\text{K}^{-1}$	$\Delta T_{\text{ad}}/\text{mK}$	$-\Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{V})/\text{kJ}\cdot\text{mol}^{-1}$
60.01	13	60.00	5539	447.035	73.703	32.978
60.53	13	60.52	5492	446.638	74.423	32.985
63.89	14	63.88	5203	447.853	77.017	32.427
95.78	21	95.76	3471	447.556	88.761	24.913
87.99	20	87.97	3778	447.142	87.025	26.563
92.53	21	92.51	3593	447.743	88.027	25.585
79.08	18	79.06	4204	447.414	85.642	29.104
71.96	16	71.94	4620	446.727	82.827	30.885
72.27	16	72.25	4600	446.109	77.884	28.877

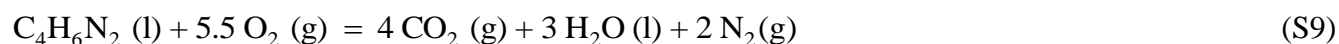
Water content from Karl Fisher titration: 223 ppm

$$\Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{V}) = -(3.892 \pm 0.304) \times 10^{-3}n - (11.86 \pm 1.39)$$

$$\langle \Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{V}) \rangle = -(31.09 \pm 1.36) \text{ kJ}\cdot\text{mol}^{-1} \text{ for } n = 4942$$

3. Enthalpies of formation and vaporisation of 1-methylimidazole.

(a) **Calculation of $\Delta_f H_m^\circ$ (mim, l) from published data.** The standard specific internal energies of combustion of 1-methylimidazole, $\Delta_c u^\circ$, calculated in this work from the results of previously reported combustion calorimetry experiments³⁻⁵ are indicated in Table S8, with the corresponding number of determinations given in parenthesis. The $\Delta_c u^\circ$ value corresponding to the first entry in Table S8 was based on the experimentally determined mass of CO₂ formed in the combustion process. The remaining values were based on the mass of ionic liquid burned after correction for the water content of the sample. These results lead to the standard molar enthalpies of combustion, $\Delta_c H_m^\circ$, that are also given in Table S8. The uncertainties assigned to $\Delta_c u^\circ$ represent standard deviations of the mean and those of $\Delta_c H_m^\circ$ represent twice the overall standard deviations of the mean, including the contributions from the calibration with benzoic acid and from the combustion of combustion aids.^{6,7} The $\Delta_c H_m^\circ$ values correspond to reaction:



and, in conjunction with $\Delta_f H_m^\circ(\text{CO}_2, \text{g}) = -393.51 \pm 0.13 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l}) = -285.830 \pm 0.040 \text{ kJ}\cdot\text{mol}^{-1}$ lead to the standard molar enthalpies of formation of liquid 1-methylimidazole indicated in Table S8. The weighted mean,⁸ of these three results, $\Delta_f H_m^\circ(\text{mim}, \text{l}) = 71.7 \pm 1.0 \text{ kJ}\cdot\text{mol}^{-1}$, was, therefore, selected in the present work.

TABLE S8: Standard molar enthalpies of combustion and formation of liquid 1-methylimidazole, at 298.15 K

$-\Delta_c u^\circ / \text{J}\cdot\text{g}^{-1}{}^a$	$-\Delta_c H_m^\circ / \text{kJ}\cdot\text{mol}^{-1}$	$\Delta_f H_m^\circ / \text{kJ}\cdot\text{mol}^{-1}$	Year ^(Reference)
30490.47±7.13 (7)	2504.62±1.50	73.09±1.59	1999 ^(3,4)
30453.60±4.02 (5)	2501.60±1.42	70.07±1.52	2011 Rostock laboratory ⁽⁵⁾
30491.27±9.29 (5)	2504.69±2.66	73.16±2.71	2011 Minsk laboratory ⁽⁵⁾

^a The number of determinations is given in parenthesis

(b) Enthalpy of vaporisation of 1-methylimidazole. The standard specific enthalpy of vaporisation of mim, $\Delta_{\text{vap}}h^{\circ}$, at 298.15 K, was obtained from two series of drop-vaporisation Calvet microcalorimetry experiments, separated by one year. Different samples (samples 1 and 2) were used in each series of runs. The $\Delta_{\text{vap}}h^{\circ}$ values were derived as described in Section 1 for [Hmim][O₂CCH₃] and the obtained results are summarized in Tables S9-S10.

TABLE S9: Results of the vaporisation enthalpy measurements on 1-methylimidazole (Sample A), by drop-vaporisation Calvet microcalorimetry

<i>T</i> /K	<i>m_s</i> /mg	<i>m_{H₂O}</i> /μg	<i>m</i> /mg	<i>A</i>	$\Delta_{\text{vap}}h^{\circ}$ /J·g ⁻¹
298.28	15.19	0.3	15.19	650.146	666.373
298.30	11.48	0.2	11.48	507.129	685.988
298.31	18.38	0.4	18.38	797.799	677.001
298.30	13.48	0.3	13.48	572.769	660.697
298.29	11.52	0.2	11.52	496.832	669.630
298.29	11.21	0.2	11.21	489.517	677.889
298.29	17.04	0.3	17.04	749.477	685.634

Water content from Karl Fisher titration: 20 ppm

$$\langle \Delta_{\text{vap}}h^{\circ} \rangle = 674.74 \pm 3.63 \text{ J} \cdot \text{g}^{-1}$$

$$\langle \varepsilon \rangle = 63.626 \pm 0.069 \text{ mV} \cdot \text{W}^{-1}$$

$$A_{\text{b}} = 6.044 \text{ mV} \cdot \text{s}$$

$$\sigma(\text{over-all}) = 3.70 \text{ J} \cdot \text{g}^{-1}$$

$$\Delta_{\text{vap}}H_{\text{m}}^{\circ} = 55.40 \pm 0.61 \text{ kJ} \cdot \text{mol}^{-1}$$

TABLE S10: Results of the vaporisation enthalpy measurements on 1-methylimidazole (Sample B), by drop-vaporisation Calvet microcalorimetry

T/K	m_s/mg	$m_{H_2O}/\mu g$	m/mg	A	$\Delta_{vap}h^\circ / J \cdot g^{-1}$
297.89	6.33	0.1	6.33	268.707	655.766
297.89	6.83	0.1	6.83	290.446	657.687
297.89	10.59	0.1	10.59	447.634	656.752
297.88	7.79	0.1	7.79	342.231	680.745
297.89	10.01	0.1	10.01	424.620	658.841
297.89	8.36	0.1	8.36	356.170	660.526
297.90	11.70	0.1	11.70	502.797	668.376
297.90	12.82	0.2	12.82	543.617	659.906

Water content from Karl Fisher titration: 12 ppm

$$\langle \Delta_{vap}h^\circ \rangle = 662.32 \pm 2.97 \text{ J} \cdot g^{-1}$$

$$\langle \varepsilon \rangle = 63.805 \pm 0.138 \text{ mV} \cdot W^{-1}$$

$$A_b = 3.850 \text{ mV} \cdot s$$

$$\sigma(\text{over-all}) = 3.30 \text{ J} \cdot g^{-1}$$

$$\Delta_{vap}H_m^\circ = 54.38 \pm 0.54 \text{ kJ} \cdot \text{mol}^{-1}$$

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