

Electronic Supplementary Information (ESI)

Structure-Property Relationships in Protic Ionic Liquids: A Thermochemical Study

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pK_a and ΔpK_a values

Aqueous pK_a values of precursor species HA and of the conjugated acid HB^+ of precursor species B, as well as their differences (ΔpK_a), are presented in Table S1.

Table S1. Values of pK_a and ΔpK_a at 298.15 K used in this work.

Species	pK_a	Species	ΔpK_a
HOAc	4.756±0.002 ^a	[HDMBuA][OAc]	5.30±0.04 ^e
[HDMBuA] ⁺	10.02; ^b 10.1 ^b	[HTMEDA][OAc]	3.94±0.44 ^e
[HTMEDA] ⁺	8.26; ^a 9.14 ^c	[HDMEtA][OAc]	4.35±0.02
[HDMEtA] ⁺	9.11±0.02 ^d		

^aReference 1; the uncertainty was assumed as two units of the last digit given in the data source. ^bReference 2. ^cReference 3. ^dCalculated from the equation: $pK_a = -(2.151 \pm 0.046) \times 10^{-2} T + 15.52 \pm 0.14$ ($r^2 = 0.9991$) obtained from a least squares linear fit to the data in reference 4 (T represents the temperature in K); the assigned uncertainty is the linear interpolation uncertainty of pK_a at $T = 298.15$ K. ^e Calculated using the mean value of the two published pK_a results given in this table; uncertainty corresponds to the mean deviation.

Calvet-drop microcalorimetry

Direct measurements of the standard molar enthalpies of vaporization of the studied PILs and their constituent amines were carried out by Calvet-drop microcalorimetry, as described in the main text. Results are summarized in Table S2.

Table S2. Standard specific enthalpy of vaporization, $\Delta_{\text{vap}}h^\circ/\text{J}\cdot\text{g}^{-1}$, of amines and PILs obtained by Calvet-drop microcalorimetry at 297.93 K.

Amines/PILs	DMBuA	TMEDA	DMEtA	[HDMBuA][OAc]	[HTMEDA][OAc]	[HDMEtA][OAc]
$M / \text{g}\cdot\text{mol}^{-1}$	101.190	116.209	89.138	161.245	176.260	149.190
$\Delta_{\text{vap}}h^\circ / \text{J}\cdot\text{g}^{-1}$	349.586	370.895	526.250	663.648	663.648	796.545
	354.331	366.870	534.395	667.617	663.599	795.269
	342.641	376.427	529.967	673.758	665.108	804.606
	343.631	368.116	528.869	688.508	660.580	796.614
$\langle\Delta_{\text{vap}}h^\circ\rangle / \text{J}\cdot\text{g}^{-1}$	347.55 ± 2.73	370.58 ± 2.12	529.87 ± 1.70	673.38 ± 5.45	663.23 ± 0.95	798.26 ± 2.14
$\langle\varepsilon\rangle / \text{mV}\cdot\text{W}^{-1}$	64.112 ± 0.034					
$\sigma(\text{over-all}) / \text{J}\cdot\text{g}^{-1}$	2.74	2.13	1.72	5.46	1.01	2.18
$\Delta_{\text{vap}}H_m^\circ / \text{kJ}\cdot\text{mol}^{-1}$	35.2 ± 0.6	43.1 ± 0.5	47.2 ± 0.3	108.6 ± 1.8	116.9 ± 0.4	119.1 ± 0.7

Solution Calorimetry

Indirect measurements of $\Delta_{\text{vap}}H_{\text{m}}^{\circ}$ were performed following an adaptation of the procedure previously described by Vitorino *et al.*^{5,6}, as described in the main text. Results of the solution calorimetry measurements are summarized in Table S3.

Table S3. Standard molar enthalpies of solution, $\Delta_{\text{sol}}H_{\text{m}}^{\circ}$ / kJ·mol⁻¹, of amines and PILs at 298.15 K.

Amines/PILs	DMBuA	TMEDA	DMEtA	[HDMBuA][OAc]	[HTMEDA][OAc]	[HDMEtA][OAc]
	Eqn 10			Eqn 8		
	60.427	79.659	55.303	46.102	59.810	31.849
	62.267	71.636	57.848	47.607	55.999	32.757
$-\Delta_{\text{sol}}H_{\text{m}}^{\circ}$ / kJ·mol ⁻¹	60.798	78.774	60.894	46.733	56.870	36.698
	57.873	79.585	57.966	47.839	61.472	35.078
	66.439	80.105	55.623	45.862	60.000	35.613
	64.712	73.882				32.400
$-\langle\Delta_{\text{sol}}H_{\text{m}}^{\circ}\rangle$ / kJ·mol ⁻¹	62.09 ± 2.53	77.27 ± 2.93	57.53 ± 2.01	46.83 ± 0.79	58.83 ± 2.06	34.07 ± 1.62

Computational Details

The individual components of the W1-F12 enthalpies are summarized in Table S4. The gas-phase standard enthalpy of formation for each of the amines under study was calculated from the respective atomization reaction using the W1-F12 enthalpies, as described in the main text (Table S5). The CCSD(T)-F12a/3C(FIX)/cc-pVDZ-F12 energies and enthalpies of acetic acid, amines, and the gaseous species resulting from combination of amines with acetic acid are given in Table S6. The corresponding entropies calculated by Statistical Mechanics,⁷ using vibration frequencies obtained by the DF-B3LYP-D3/cc-pVTZ method and scaled by 0.9889⁸ are listed in Table S7.

Table S4. Components of the W1-F12 enthalpies. All data in hartree.

	SCF	val. CCSD	val. T	core-valence	relativistic	spin-orbit	DBOC ^a	$H(\text{thermal})^b$	$H^\circ(298.15 \text{ K})^c$
C	-37.688596	-0.097659	-0.002630	-0.051452	-0.014935	-0.000135	0.001660	0.002360	-37.851387
H	-0.499967	0.000000	0.000000	0.000000	-0.000006	0.000000	0.000272	0.002360	-0.497341
O	-74.812001	-0.187544	-0.004126	-0.057770	-0.052097	-0.000355	0.002366	0.002360	-75.109167
N	-54.400727	-0.125442	-0.003085	-0.054926	-0.029194	0.000000	0.002005	0.002360	-54.609009
<i>N,N</i> -dimethylbutylamine	-290.499080	-1.451255	-0.061411	-0.375568	-0.116625	0.000000	0.015431	0.213019	-292.275488
<i>N,N,N',N'</i> -tetramethylethane-1,2-diamine	-345.527481	-1.685549	-0.072961	-0.431273	-0.145390	0.000000	0.017663	0.231307	-347.613684
<i>N,N</i> -dimethylethanol amine	-287.290688	-1.315858	-0.055392	-0.327077	-0.139012	0.000000	0.013462	0.160782	-288.953783

^a Diagonal Born-Oppenheimer correction. ^b Thermal enthalpy correction at 298.15 K. Includes the zero-point vibrational energy. ^c Enthalpy at $T = 298.15 \text{ K}$ and $p^\circ = 1 \text{ bar}$.

Table S5. Contribution of each component of the W1-F12 procedure to the gas-phase standard molar enthalpies of formation. All data in kJ mol^{-1} .

	SCF	val. CCSD	val. T	core-valence	relativistic	spin-orbit	DBOC ^a	$H(\text{thermal})^b$	$\Delta_{\text{at}}H_{\text{m}}^\circ{}^c$	$\Delta_{\text{f}}H_{\text{m}}^\circ{}^d$
<i>N,N</i> -dimethylbutylamine	6477.8	1942.5	111.7	31.3	-6.0	-2.1	1.6	-423.0	8133.9	-91.2 ± 2.7
<i>N,N,N',N'</i> -tetramethylethane-1,2-diamine	6813.1	2228.3	133.9	33.4	-7.1	-2.1	1.7	-458.6	8742.6	-9.2 ± 2.8
<i>N,N</i> -dimethylethanol amine	4788.8	1607.4	98.9	22.5	-5.5	-2.3	1.4	-316.8	6194.4	-207.8 ± 1.8

^a Diagonal Born-Oppenheimer correction. ^b Thermal enthalpy correction at 298.15 K. Includes the zero-point vibrational energy. ^c Enthalpy of atomization at $T = 298.15 \text{ K}$ and $p^\circ = 1 \text{ bar}$. ^d Enthalpy of formation at $T = 298.15 \text{ K}$ and $p^\circ = 1 \text{ bar}$.

Table S6. CCSD(T)-F12a/3C(FIX)/cc-pVDZ-F12 energies and enthalpies. All data in hartree.

	energy ^a	<i>H</i> (thermal) ^b	<i>H</i>
HOAc	-228.830891	0.066283	-228.764608
DMEtA	-288.629110	0.160782	-288.468328
TMEDA	-347.251050	0.231307	-347.019743
DMBuA	-291.983365	0.213019	-291.770346
[DMEtA][HOAc]	-517.479781	0.229099	-517.250682
[TMEDA][HOAc]	-576.104836	0.300036	-575.804800
[DMBuA][HOAc]	-520.836438	0.282415	-520.554023

^a CCSD(T)-F12a/3C(FIX)/cc-pVTZ-F12 energy. ^b Thermal enthalpy correction at 298.15 K. Includes the zero-point vibrational energy. ^c Enthalpy at *T* = 298.15 K.

Table S7. Standard (*p*^o = 1 bar) molar entropies at 298.15 K.

	<i>S</i> _m ^o /J·K ⁻¹ ·mol ⁻¹
HOAc	288.8
DMEtA	349.2
TMEDA	401.7
DMBuA	375.4
[DMEtA][HOAc]	443.7
[TMEDA][HOAc]	488.3
[DMBuA][HOAc]	491.0

Standard Molar Enthalpies of Formation of Gaseous [HDMBuA]⁺, [HTMEDA]⁺, and [HDMEtA]⁺

The standard molar enthalpies of formation of gaseous [HDMBuA]⁺, [HTMEDA]⁺, and [HDMEtA]⁺ (Table S6) were obtained from:

$$\Delta_f H_m^\circ([\text{HB}]^+, \text{g}) = \Delta_f H_m^\circ(\text{B}, \text{g}) + \Delta_f H_m^\circ(\text{H}^+, \text{g}) - PA(\text{B}) \quad (\text{S1})$$

where $\Delta_f H_m^\circ(\text{B}, \text{g})$ and $PA(\text{B})$ represent the standard molar enthalpies of formation and the proton affinities of the corresponding neutral amines, respectively (Table S6), and $\Delta_f H_m^\circ(\text{H}^+, \text{g}) = 1536.202 \pm 0.080 \text{ kJ}\cdot\text{mol}^{-1}$.⁹

Table S8. Standard molar enthalpies of formation and proton affinities of amines at 298.15 K.

Species	$-\Delta_f H_m^\circ(\text{B}, \text{g}) / \text{kJ}\cdot\text{mol}^{-1}$ ^a	$PA(\text{B}) / \text{kJ}\cdot\text{mol}^{-1}$	$\Delta_f H_m^\circ([\text{HB}]^+, \text{g})$
DMBuA	91.2±2.7	969.2±8.0 ^b	475.8±8.4
TMEDA	9.2±2.8	1012.8±8.0 ^b	514.2±8.5
DMEtA	207.8±1.8	943.3±16.1 ^c	385.1±16.2

^a This work, see Table 1 of main text. ^b From reference 10. ^c Mean value of the B3LYP/6-311+G** and MP2/6-311+G**//B3LYP/6-311+G** values given in reference 11 and corresponding mean deviation.

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