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Experimental and Theoretical Enthalpies of Formation of Glycine-Based Sulfate/Bisulfate Amino Acid Ionic Liquids

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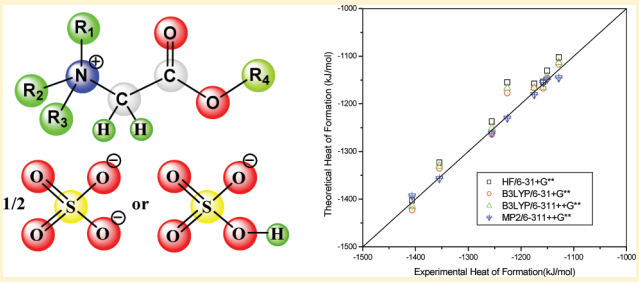
ABSTRACT: The experimental and theoretical enthalpies of formation of several structural-similar glycine-based sulfate/bisulfate amino acid ionic liquids including glycine sulfate (Gly_2SO_4, **1**), glycine bisulfate ($GlyHSO_4$, **2**), *N,N*-dimethylglycine sulfate ($[DMGly]_2SO_4$, **3**), *N,N*-dimethylglycine bisulfate ($[DMGly]HSO_4$, **4**), *N,N*-dimethylglycine methyl ester sulfate ($[DMGlyC_1]_2SO_4$, **5**), *N,N*-dimethylglycine methyl ester bisulfate ($[DMGlyC_1]HSO_4$, **6**), *N,N,N*-trimethylglycine methyl ester sulfate ($[TMGlyC_1]_2SO_4$, **7**), and *N,N,N*-trimethylglycine methyl ester bisulfate ($[TMGlyC_1]HSO_4$, **8**) were studied. Their experimental enthalpies of formation were obtained from the corresponding energies of combustion determined by the bomb calorimetry method. The enthalpies of formation of these amino acid ionic liquids are in the range from -1406 kJ mol^{-1} to -1128 kJ mol^{-1}. Systematic theoretical study on these amino acid ionic liquids were performed by quantum chemistry calculation using the Gaussian03 suite of programs. The geometric optimization and the frequency analyses are carried out using the B3LYP method with the 6-31+G** basis set. Their calculated enthalpies of formation were derived from the single point energies carried out with the HF/6-31+G**, B3LYP/6-31+G**, B3LYP/6-311++G**, and MP2/6-311++G** level of theory, respectively. The relevance of experimental and calculated enthalpies of formation was studied. The calculated enthalpies of formation are in good agreement with their experimental data in less than 3% error.



INTRODUCTION

In recent years, ionic liquids attract considerable interest to serve as interesting modifiable solvents and soft materials including solvents,[1−5] catalysts,[6−12] electrolytes,[13−15] lubricants,[16,17] propellants,[18−23] magnetic fluids,[24−26] and optical fluids.[27−29] Ionic liquids are a class of low-melting salts comprised entirely of ions with melting points below 100 °C.[30] Typical formulations of ionic liquids rely mostly on quaternary nitrogen cations (alkylammonium, dialkylimidazolium, alkylpyridinium, etc.) and inorganic anions (Cl^-, $AlCl_4^-$, PF_6^-, BF_4^-, $N(CF_3SO_2)_2^-$, $CF_3CO_2^-$, $CF_3SO_3^-$, etc.). These novel liquid materials may have some unique physical properties such as high thermal stability, large liquidus range, negligible vapor pressure, and wide electrochemical window.[31−33]

For the preparation of ionic liquids in a cost-saving and clean way, many natural materials, including carboxylate salts,[34,35] amino acids,[36−39] and sugars or sugar derivatives[40−43] are employed as precursors. Among these natural materials, amino acids and their derivatives are the most abundant natural source containing quarternary nitrogens. Bao's group is first successful to obtain ionic liquids from natural amino acids in 2003.[36] Mauduit and Guillemin et al. have also tried to synthesize ionic liquids using L-valine as the starting material.[37] In 2005, amino acid ionic liquids, which can keep the amino acid framework in anions ([emim][AA])[38] or cations ([AA]X and [AAE]X),[39] were reported by Ohno's and Kou's group separately. Amino acid ionic liquids are fascinating for chemists in view of their close association with chirality and biomolecules.[44,45] Some interesting research have found amino acid ionic liquids may be useful to be potential chiral solvent, catalyst, and absorbent for carbon dioxide.[46−50]

In order to design a task-specific/functionalized ionic liquid, it is necessary to know or predict its certain key physiochemical properties.[51] The standard enthalpy of formation, $\Delta_f H°$, is an intrinsic characteristic of a substance and also important information of the thermochemical properties. Some former work have studied the viscosity, density, chirality, melting point, conductivity, binding energy, hydrogen bonding interaction, refractive index, and surface tension of amino acid ionic liquids.[52−57] However, the thermochemical properties especially enthalpies of formation of amino acid ionic liquids are still of lack. Furthermore, the prediction of the unknown physiochemical properties of amino acid ionic liquids by theoretical calculation is also of considerable interest.

Herein, eight glycine-based sulfate/bisulfate amino acid ionic liquids were selected to be model compounds. For ready comparison of the effect disturbed by the cations, both sulfate and bisulfate anions were chosen as the common anion. In order

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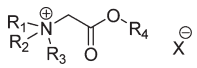
Scheme 1. Structures of Glycine-Based Sulfate/Bisulfate Amino Acid Ionic Liquids 1−8



1: $R_1 = R_2 = R_3 = R_4 = H$, $X = 1/2SO_4$;
2: $R_1 = R_2 = R_3 = R_4 = H$, $X = HSO_4$;
3: $R_1 = R_2 = CH_3$, $R_3 = R_4 = H$, $X = 1/2SO_4$;
4: $R_1 = R_2 = CH_3$, $R_3 = R_4 = H$, $X = HSO_4$;
5: $R_1 = R_2 = R_4 = CH_3$, $R_3 = H$, $X = 1/2SO_4$;
6: $R_1 = R_2 = R_4 = CH_3$, $R_3 = H$, $X = HSO_4$;
7: $R_1 = R_2 = R_3 = R_4 = CH_3$, $X = 1/2SO_4$;
8: $R_1 = R_2 = R_3 = R_4 = CH_3$, $X = HSO_4$.

to establish a general rule in predicting the impact on the enthalpies of formation of the amino acid ionic liquids, theoretical enthalpies of formation were systematically investigated by various theoretical levels (HF, B3LYP, MP2) and different basis sets. Meanwhile, the experimental enthalpies of formation have been determined by bomb calorimetry. The relevance of experimental and calculated enthalpies of formation was also studied.

RESULTS AND DISCUSSION

Eight structurally similar glycine-based sulfate/bisulfate amino acid ionic liquids including glycine sulfate (Gly_2SO_4, **1**), glycine bisulfate ($GlyHSO_4$, **2**), *N,N*-dimethylglycine sulfate ($[DMGly]_2SO_4$, **3**), *N,N*-dimethylglycine bisulfate ($[DMGly]HSO_4$, **4**), *N,N*-dimethylglycine methyl ester sulfate ($[DMGlyC_1]_2SO_4$, **5**), *N,N*-dimethylglycine methyl ester bisulfate ($[DMGlyC_1]HSO_4$, **6**), *N,N,N*-trimethylglycine methyl ester sulfate ($[TMGlyC_1]_2SO_4$, **7**), and *N,N,N*-trimethylglycine methyl ester bisulfate ($[TMGlyC_1]HSO_4$, **8**) were studied (Scheme 1). Both Gly_2SO_4 and $GlyHSO_4$ are white solids at room temperature. The other six amino acid ionic liquids are colorless liquids at ambient conditions.

The standard enthalpy (or heat) of formation of a substance, $\Delta_f H°$, is the standard reaction enthalpy for the formation of the compound from its elements in their reference states.[58] $\Delta_f H°$ is dependent on the chemical structure and chemical bond energy of comprising molecules. The molecular structure including the framework and their thermochemical group govern its enthalpy of formation. In this work, the experimental enthalpy of formation is calculated from the enthalpy of combustion ($\Delta_c H°_{298}$), which is derived from the constant volume energy of combustion ($\Delta_c U$) and a correction for change in gas volume during combustion. The $\Delta_c U$ was determined experimentally using oxygen bomb calorimetry and summarized in Table 1. The acidic correction was performed for all the amino acid ionic liquids.

The standard enthalpies of formation ($\Delta_f H°_{298}$) were back calculated from the designed Hess thermochemical cycle: the enthalpies of combustion on the basis of the combustion equations, a−h of Scheme 2, Hess's Law as applied in the thermochemical equations, 1−8 of Scheme 2, and known standard enthalpies of formation of CO_2 (−393.51 kJ mol^{-1}), H_2O (−285.83 kJ mol^{-1}) and H_2SO_4 (−909.3 kJ mol^{-1}).[59] The enthalpies of formation of the two elementary substances, O_2 and N_2, are 0 kJ mol^{-1}. Thus, they did not appear in the thermochemical equations. After every combustion experiment, the liquid remain in the oxygen bomb was checked and found to be strongly acidic. Combined with the primary structures of amino acid ionic liquids, the residual liquid should be sulfuric acid aqueous solution. Therefore, the molar enthalpy of formation of the sulfuric acid aqueous system at 298.15 K not the molar enthalpy of formation of pure sulfuric acid was used in the combustion equations.

Table 1. Experimental Thermochemical Data of the Amino Acid Ionic Liquids 1−8[a]

compound	formula	$-\Delta_c U$[b] (kJ mol^{-1})	$-\Delta_c H°_{298}$[c] kJ mol^{-1})	$\Delta_f H°_{298}$[d] (kJ mol^{-1})
1	$C_4H_{12}N_2O_8S$	2475.91	2474.68	−1406.38
2	$C_2H_7NO_6S$	1264.38	1263.76	−1157.90
3	$C_8H_{20}N_2O_8S$	5367.88	5371.60	−1354.64
4	$C_4H_{11}NO_6S$	2608.83	2610.69	−1174.78
5	$C_{10}H_{24}N_2O_8S$	6759.09	6765.29	−1255.26
6	$C_5H_{13}NO_6S$	3320.19	3323.26	−1150.17
7	$C_{12}H_{28}N_2O_8S$	8173.91	8182.59	−1225.91
8	$C_6H_{15}NO_6S$	3995.32	3999.66	−1128.34

[a] The standard enthalpy of formation (298.15 K): CO_2, −393.51 kJ mol^{-1}; H_2O, −285.83 kJ mol^{-1}; N_2, 0 kJ mol^{-1}; O_2, 0 kJ mol^{-1}; H_2SO_4 aqueous system, 909.3 kJ mol^{-1}; see ref 59. [b] Experimental (constant volume) energy of combustion. [c] Experimental molar enthalpy of combustion. [d] Experimental molar enthalpy of formation.

All the amino acid ionic liquids exhibit negative enthalpies of formation. The molar standard enthalpies of formation of amino acid ionic liquids **1**−**8** ($\Delta_f H°_{298}$) were obtained from −1406 kJ mol^{-1} to −1128 kJ mol^{-1}. The negative values show these ionic liquids are very thermally stable. Among these amino acid ionic liquids, the highest enthalpy of formation value is −1128.34 kJ mol^{-1}, which belongs to the amino acid ionic liquid **8**. The enthalpy of formation of **1**, −1406.38 kJ mol^{-1}, is the lowest one. The molecular structures of the amino acid ionic liquids may affect their enthalpies of formation. The four sulfate amino acid ionic liquids have lower enthalpies of formation than the four corresponding bisulfate amino acid ionic liquids. The enthalpy of formation of **1** is about 250 kJ mol^{-1} lower than that of **2**. However, the differences of the enthalpy of formation between the sulfate-based and bisulfate-based amino acid ionic liquids were decreased when methyl groups were introduced into the structures. The energy difference of **3** to **4** is about 180 kJ mol^{-1}. When the ester group substitutes the carboxyl group, the energy difference is only 100 kJ mol^{-1} between **5** and **6**. The same energy difference was also found between **7** and **8**. Normally, alkyl groups including a methyl group may increase enthalpy of formation than a sole hydrogen atom, while this hypothesis is only significant in the sulfate-based amino acid ionic liquids. For those bisulfate-based amino acid ionic liquids, the enthalpies of formation did not clearly increase with more methyl groups, showing the enthalpies of formation were also affected by other structural effects. An ester group has higher enthalpy of formation than carboxylic group. The enthalpy of formation of **5** with the *N,N*-dimethylglycine methyl ester cation is 100 kJ mol^{-1} higher than that of **3** with the *N,N*-dimethylglycine cation. The big energy difference shows the methyl in the ester group is different with the one directly attached to the nitrogen atom.

The theoretical enthalpies of formation of **1**−**8** were studied to verify whether it is possible to predict the enthalpies of formation of amino acid ionic liquids by theoretical calculation method. Computations were performed by using the Gaussian03 suite of programs.[60] The geometric optimization and the frequency analyses were carried out using the popular Becke three-parameter hybrid functional Lee−Yang−Parr (B3LYP) analyses up to the 6-31+G** basis set, which included the polarizable and

Scheme 2. Hess Thermochemical Cycle for the Amino Acid Ionic Liquids 1−8

1: $C_4H_{12}N_2O_8S(s) + 9/2O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l) + N_2(g) + H_2SO_4(aq)$ (a)

$\Delta_f H^o_{298}$ (**1**, s) = $4\Delta_f H^o_{298}$ (CO_2, g) + $5\Delta_f H^o_{298}$ (H_2O, l) + $\Delta_f H^o_{298}$ (H_2SO_4, aq) − $\Delta_c H^o_{298}$ (**1**, s) (1)

2: $C_2H_7NO_6S(s) + 9/4O_2(g) \rightarrow 2CO_2(g) + 5/2H_2O(l) + 1/2N_2(g) + H_2SO_4$ (aq) (b)

$\Delta_f H^o_{298}$ (**2**, s) = $2\Delta_f H^o_{298}$ (CO_2, g) + $5/2\Delta_f H^o_{298}$ (H_2O, l) + $\Delta_f H^o_{298}$ (H_2SO_4, aq) − $\Delta_c H^o_{298}$ (**2**, s) (2)

3: $C_8H_{20}N_2O_8S(l) + 21/2O_2(g) \rightarrow 8CO_2(g) + 9H_2O(l) + N_2(g) + H_2SO_4(aq)$ (c)

$\Delta_f H^o_{298}$ (**3**, l) = $8\Delta_f H^o_{298}$ (CO_2, g) + $9\Delta_f H^o_{298}$ (H_2O, l) + $\Delta_f H^o_{298}$ (H_2SO_4, aq) − $\Delta_c H^o_{298}$ (**3**, l) (3)

4: $C_4H_{11}NO_6S(l) + 21/4O_2(g) \rightarrow 4CO_2(g) + 9/2H_2O(l) + 1/2N_2(g) + H_2SO_4$ (aq) (d)

$\Delta_f H^o_{298}$ (**4**, l) = $4\Delta_f H^o_{298}$ (CO_2, g) + $9/2\Delta_f H^o_{298}$ (H_2O, l) + $\Delta_f H^o_{298}$ (H_2SO_4, aq) − $\Delta_c H^o_{298}$ (**4**, l) (4)

5: $C_{10}H_{24}N_2O_8S(l) + 27/2O_2(g) \rightarrow 10CO_2(g) + 11H_2O(l) + N_2(g) + H_2SO_4(aq)$ (e)

$\Delta_f H^o_{298}$ (**5**, l) = $10\Delta_f H^o_{298}$ (CO_2, g) + $11\Delta_f H^o_{298}$ (H_2O, l) + $\Delta_f H^o_{298}$ (H_2SO_4, aq) − $\Delta_c H^o_{298}$ (**5**, l) (5)

6: $C_5H_{13}NO_6S(l) + 27/4O_2(g) \rightarrow 5CO_2(g) + 11/2H_2O(l) + 1/2N_2(g) + H_2SO_4$ (aq) (f)

$\Delta_f H^o_{298}$ (**6**, l) = $5\Delta_f H^o_{298}$ (CO_2, g) + $11/2\Delta_f H^o_{298}$ (H_2O, l) + $\Delta_f H^o_{298}$ (H_2SO_4, aq) − $\Delta_c H^o_{298}$ (**6**, l) (6)

7: $C_{12}H_{28}N_2O_8S(l) + 33/2O_2(g) \rightarrow 12CO_2(g) + 13H_2O(l) + N_2(g) + H_2SO_4(aq)$ (g)

$\Delta_f H^o_{298}$ (**7**, l) = $12\Delta_f H^o_{298}$ (CO_2, g) + $13\Delta_f H^o_{298}$ (H_2O, l) + $\Delta_f H^o_{298}$ (H_2SO_4, aq) − $\Delta_c H^o_{298}$ (**7**, l) (7)

8: $C_6H_{15}NO_6S(l) + 33/4O_2(g) \rightarrow 6CO_2(g) + 13/2H_2O(l) + 1/2N_2(g) + H_2SO_4$ (aq) (h)

$\Delta_f H^o_{298}$ (**8**, l) = $6\Delta_f H^o_{298}$ (CO_2, g) + $13/2\Delta_f H^o_{298}$ (H_2O, l) + $\Delta_f H^o_{298}$ (H_2SO_4, aq) − $\Delta_c H^o_{298}$ (**8**, l) (8)

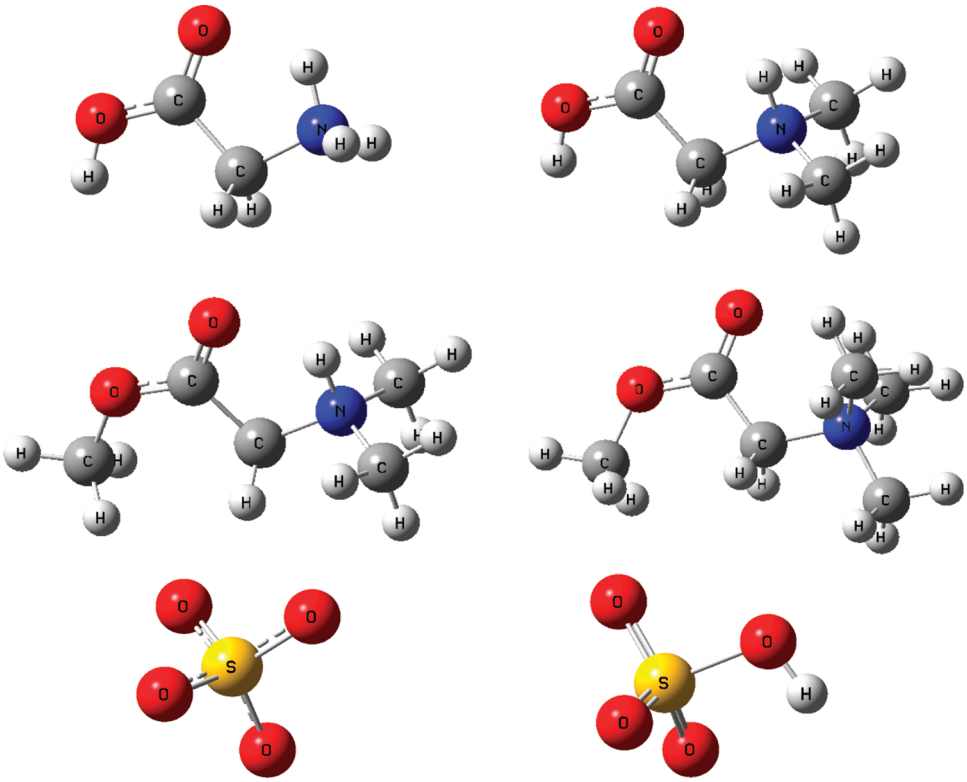


Figure 1. Optimal geometries of four glycine-based cations along with sulfate and bisulfate anions.

diffuse functions for the H atom for the descriptions of hydrogen-bonded interactions.[61−63] All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies. The optimal geometries of four glycine-based cations along with sulfate and bisulfate anions are shown in Figure 1. Single point energies

Scheme 3. Isodesmic Reactions of Glycine-Based Cations in the Amino Acid Ionic Liquids 1−8

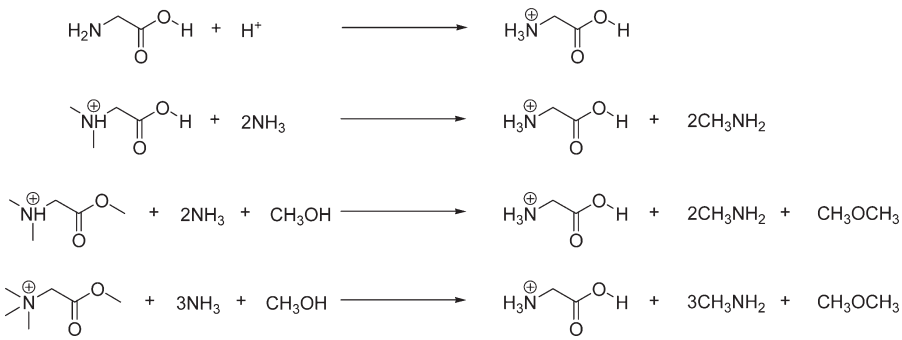


Table 2. Computational Results of the Cations and Anions by Four Levels[a]

			HF/6-31+G*		B3LYP/6-31+G**		B3LYP/6-311++G**		MP2/6-311++G**	
	ZPE_{corr}[b] (a.u.)	ΔH_{corr}[c] (a.u.)	ΔH (a.u.)	$\Delta_f H°$ (kJ mol^{-1})	ΔH (a.u.)	$\Delta_f H°$ (kJ mol^{-1})	ΔH (a.u.)	$\Delta_f H°$, (kJ mol^{-1})	ΔH (a.u.)	$\Delta_f H°$ (kJ mol^{-1})
Gly^+	0.093740	0.100294	−283.190774	261.07	−284.7932783	264.15	−284.8649946	267.51	−284.1238475	266.96
$DMGly^+$	0.150483	0.159583	−361.2711605	225.89	−363.4316069	233.23	−363.5164826	235.12	−362.5189423	210.52
$DMGlyC_1^+$	0.178357	0.188224	−400.2967352	242.37	−402.7390493	245.55	−402.8293805	248.03	−401.698311	223.27
$TMGlyC_1^+$	0.206521	0.218325	−439.3242303	259.33	−442.0455103	264.66	−442.1427061	265.66	−440.8887304	214.99
HSO_4^-	0.026001	0.032053	−697.5430493	−886.32	−699.7301161	−902.40	−699.836491	−904.19	−698.5996712	−893.48
SO_4^{2-}	0.014408	0.019546	−696.8193191	−545.87	−699.0103889	−572.46	−699.1158092	−571.74	−697.8743545	−548.86
H_2SO_4	0.038195	0.044442	−698.0522838		−700.233226		−700.3389185		−699.1061768	
glycine	0.079370	0.086045	−282.8438639		−284.4475392		−284.5205373		−283.7791779	

[a] The standard enthalpy of formation $\Delta_f H°_{298}$ (H^+, g) = −1528.08 kJ mol^{-1}; see ref 71. [b] Zero-point correction in the B3LYP/6-31+G** level. [c] Thermal correction to the enthalpy in the B3LYP/6-31+G** level.

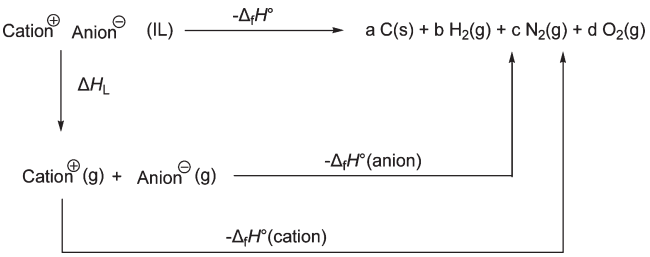
(on gas-phase geometries) were calculated at four different levels, which are the level of Hatree−Fock (HF) up to the 6-31+G** basis sets,[64−66] the level of Becke three Lee−Yang−Parr (B3LYP) up to the 6-31+G** basis sets,[61−63] the level of Becke three Lee−Yang−Parr (B3LYP) up to the 6-311++G** basis sets,[61−63] and the level of Møller−Plesset second order perturbation theory truncated at the second-order (MP2) up to the 6-311++G** basis sets.[67,68] The theoretical enthalpies of formation of the cations of **1**−**8** were computed by using the method of isodesmic reactions (Scheme 3).[69−71] The enthalpies of reaction ($\Delta_r H°_{298}$) were obtained by combining the HF/6-31+G**, the B3LYP/6-31+G**, the B3LYP/6-311++G**, and the MP2/6-311++G** energy differences for the reaction separately, the scaled zero point energies, and other thermal factors. The calculated data including the zero-point correction, the thermal correction to enthalpy, the single point energies, and the theoretical enthalpies of formation of the cations and anions by four levels are summarized in Table 2.

The theoretical enthalpies of formation of amino acid ionic liquids at T = 298.15 K were calculated based on the Born−Haber energy cycle (Scheme 4). In a Born−Haber energy cycle, enthalpies of formation of ionic liquids can be simplified by the expression

$$\Delta_f H^\circ_{298}\ (\text{ionic liquid}) = \sum \Delta_f H^\circ_{298}\ (\text{cation}) + \sum \Delta_f H^\circ_{298}\ (\text{anion}) - \Delta H_L \quad (1)$$

where ΔH_L is the lattice energy of the ionic liquid. For ionic liquid, ΔH_L (kJ mol^{-1}) can be predicted by the formula suggested by

Scheme 4. Born−Haber Cycle for the Formation of Ionic Liquids



Jenkins et al.[72] as

$$\Delta H_L = U_{POT} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT \quad (2)$$

where n_M and n_X depend on the nature of the ions M^{p+} and X^{q-}, respectively, and have a value of 6 for nonlinear polyatomic ions. The equation for lattice potential energy U_{POT} (eq 2) has the form

$$U_{POT} = \gamma(\rho_m/M_m)^{1/3 + \delta} \quad (3)$$

where ρ_m is density in g cm^{-3}, and M_m is the chemical formula mass of the ionic liquid.For M_2X (1:2) salt, γ is 8375.6, and δ is −178.8. Therefore, the U_{POT} of the glycine-based sulfate amino acid ionic liquids (**1**, **3**, **5**, and **7**) can be predicted as

$$U_{POT} = 8375.6(\rho_m/M_m)^{1/3 - 178.8} \quad (4)$$

Table 3. Experimental and Theoretical Enthalpies of Formation of Amino Acid Ionic Liquids 1−8

	$\Delta_f H^\circ_{298}$ (kJ mol^{-1})				
ILs	HF/ 6-31+G**[a]	B3LYP/ 6-31+G**[b]	B3LYP/ 6-311++G**[c]	MP2/ 6-311++G**[d]	exptl[e]
1	−1402.12	−1422.56	−1415.12	−1393.35	−1406.38
2	−1154.02	−1167.03	−1165.46	−1155.31	−1157.90
3	−1323.11	−1335.02	−1330.53	−1356.84	−1354.64
4	−1157.92	−1166.67	−1166.57	−1180.45	−1174.78
5	−1233.46	−1253.68	−1248.01	−1274.66	−1255.26
6	−1128.60	−1141.50	−1140.81	−1154.86	−1150.17
7	−1151.18	−1167.11	−1164.41	−1242.88	−1225.91
8	−1100.49	−1111.24	−1112.04	−1152.00	−1128.34

[a] Calculated molar enthalpy of formation by HF/6-31+G**. [b] Calculated molar enthalpy of formation by B3LPY/6-31+G**. [c] Calculated molar enthalpy of formation by B3LYP/6-311++G**. [d] Calculated molar enthalpy of formation by MP2/6-311++G**. [e] Experimental molar enthalpy of formation.

While for MX (1:1) salt, γ is 1981.2, and δ is 103.8. Thus, the U_{POT} of the glycine-based bisulfate amino acid ionic liquids (**2**, **4**, **6**, and **8**) is given by

$$U_{POT} = 1981.2(\rho_m/M_m)^{1/3 + 103.8} \quad (5)$$

The physiochemical characteristics of molecules are governed by their molecular structures. The theoretical enthalpies of formation of amino acid ionic liquids are related to not only the enthalpies of formation of separated cations and anions but also the lattice energies of amino acid ionic liquids. In the MP2/6-311++G** basis set, the enthalpy of formation of the bisulfate anion is −893.48 kJ mol^{-1}, and that of the sulfate anion is −548.86 kJ mol^{-1}. However, the four sulfate amino acid ionic liquids have lower enthalpies of formation than the four corresponding bisulfate amino acid ionic liquids. From the Born−Haber energy cycle, this result shows that the lattice energy in sulfate amino acid ionic liquids are much higher than that in bisulfate amino acid ionic liquids. The reason is that the sulfate amino acid ionic liquids have two cations, while the bisulfate amino acid ionic liquids have only one. It has been verified by the calculated data based on Jenkins' equation.[72] In a simplified model, the large volumes of the amino acid ionic liquids result in low Coulomb interactions between anions and cations and thus low lattice energies. The sulfate ionic liquid molecule is much bigger than the bisulfate amino acid ionic liquid molecule. So the lattice energy decreases more in sulfate amino acid ionic liquid. This is the origin that when the two cations are same, the energy difference between two sulfate ionic liquids is larger than that of two bisulfate ionic liquids. From Table 2, the enthalpy of formation of the glycine cation are 30−50 kJ mol^{-1} higher than that of the *N*,*N*-dimethylglycine cation. This difference is lower than the lattice energy difference between **1** and **3** but higher than the lattice energy difference between **2** and **4**. So, the enthalpy of formation of **3** is higher than that of **1**, but the enthalpy of formation of **4** is lower than that of **2**.

The calculated enthalpies of formation by four different levels and the experimental enthalpies of formation are summarized in Table 3. Compared with the experimental data, the energy differences of the theoretical enthalpies of formation are in the range from −23.66 kJ mol^{-1} to 74.73 kJ mol^{-1}. For the eight enthalpies of formation in the HF/6-31+G** test set, the mean absolute deviation of the HF method is 25.31 kJ mol^{-1}. The data obtained by the B3LYP method is better. The mean absolute deviation is just 17.40 kJ mol^{-1} in the B3LYP/6-31+G** test set. The mean absolute deviation is 17.88 kJ mol^{-1} in the B3LYP/6-311++G** test set. The calculated enthalpies of formation by the MP2 method are the closest to the experimental data. For the eight enthalpies of formation in the MP2/6-311++G** test set, the mean absolute deviation is 11.03 kJ mol^{-1}. The deviation is nearly half of that of the HF method. The fractional error of each theoretical level in this article relative to experimental enthalpy of formation is less than 3%. The theoretical enthalpies of formation of the amino acid ionic liquids **1**−**8**, especially the data by the MP2/6-311++G** test set, are in great agreement with the experimental data obtained from oxygen bomb calorimetry (Figure 2). The eight amino acid ionic liquids all consisted of carbon, hydrogen, nitrogen, sulfur, and oxygen elements. Each calculated cation or anion only includes 5 to 9 heavy atoms, which belong to small-sized systems for theoretical simulation. So, high level correlation methods MP2 in combination with the large basis sets 6-311++G** did not occupy much larger computer resources than the HF/6-31+G**, B3LYP/6-31+G**, and B3LYP/6-311++G** test sets. Therefore, enough accurate predictions of the enthalpy of formation in the MP2/6-311++G** test set are reliable for amino acid ionic liquids. By the same method, it is possible to predict enthalpies of formation of novel amino acid ionic liquids, which have not been synthesized.

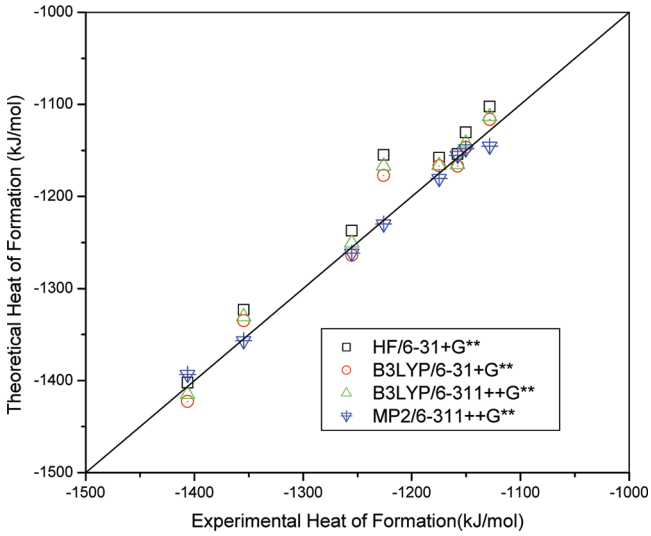


Figure 2. Relevance of experimental and calculated enthalpies of formation.

CONCLUSIONS

The enthalpies of formation of eight glycine-based sulfate/bisulfate amino acid ionic liquids including Gly_2SO_4, $GlyHSO_4$, $[DMGly]_2SO_4$, $[DMGly]HSO_4$, $[DMGlyC_1]_2SO_4$, $[DMGlyC_1]HSO_4$, $[TMGlyC_1]_2SO_4$, and $[TMGlyC_1]HSO_4$ were determined by experimental method and theoretical calculation. The enthalpies of formation of these amino acid ionic liquids are in the range from −1406 kJ mol^{-1} to −1128 kJ mol^{-1}. They own negative enthalpies of formation showing their very stable thermodynamics status. Gly_2SO_4 is the most stable structure in these

amino acid ionic liquids. For these amino acid ionic liquids, the enthalpies of formation of the bisulfate ionic liquids are higher than the corresponding sulfate ionic liquids. Furthermore, the calculated results well agree with the available experimental data. The MP2/6-311++G** level of theory is the best simulation method in all of the four used levels to predict the enthalpies of formation of amino acid ionic liquids. It will be help to reveal further physiochemical properties of amino acid ionic liquids and make for designing and development of novel amino acid ionic liquids in the near future.

EXPERIMENTAL SECTION

Glycine-based sulfate/bisulfate amino acid ionic liquids, glycine sulfate (Gly_2SO_4), glycine bisulfate ($GlyHSO_4$), *N,N*-dimethylglycine sulfate ($[DMGly]_2SO_4$), *N,N*-dimethylglycine bisulfate ($[DMGly]HSO_4$), *N,N*-dimethylglycine methyl ester sulfate ($[DMGlyC_1]_2SO_4$), *N,N*-dimethylglycine methyl ester bisulfate ($[DMGlyC_1]HSO_4$), *N,N,N*-trimethylglycine methyl ester sulfate ($[TMGlyC_1]_2SO_4$), and *N,N,N*-trimethylglycine methyl ester bisulfate ($[TMGlyC_1]HSO_4$) were prepared using the literature method[39] and confirmed by NMR and IR analysis.

Bomb Calorimetry. For the calorimetric measurements, a Parr 6725 bomb calorimeter (static jacket) equipped with a Parr 207A oxygen bomb for the combustion of samples was used. The samples were placed in a platinum pan burned in a 3.2 MPa atmosphere of pure oxygen. The acidic correction was performed for all amino acid ionic liquids. The sulfur value and sulfur multiplier was input into the program for the fixed sulfur correction. The sulfur value is entered as its weight percent sulfur. The sulfur multiplier is the default number (0.6238) when the sulfur value is used as weight percent. Small pellets of benzoic acid were added to ignite the samples, and the values were deducted from the final data. A Parr 1755 printer was furnished with the 6725 calorimeter to produce a record of the activity in the calorimeter. Typical experimental results of the constant volume combustion energy ($\Delta_c U$) of the salts are summarized in Table 1. The standard molar enthalpy of combustion ($\Delta_c H^\circ_{298}$) was derived from $\Delta_c H^\circ_{298} = \Delta_c U + \Delta nRT$ ($\Delta n = \Sigma n_i$ (products, g) $- \Sigma n_i$ (reactants, g); Σn_i is the total molar amount of gases in the products or reactants). The enthalpy of formation, $\Delta_f H^\circ_{298}$, for each of the corresponding amino acid ionic liquid was calculated at 298.15 K using designed Hess thermochemical cycles.

Computational Method. Computations were performed by the Gaussian03 suites of programs.[60] The geometric optimizations were carried out using the B3LYP method with the 6-31+G** basis set.[61−63] The frequency analyses was also performed at the same level of theory. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies. Single point energies were calculated at the HF/6-31+G**,[64−66] the B3LYP/6-31+G**,[61−63] the B3LYP/6-311++G**,[61−63] and the MP2/6-311++G** level.[67,68] Every enthalpy of formation value of studied amino acid ionic liquid at $T = 298.15$ K was calculated based on a Born−Haber energy cycle.

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