Enthalpy of dissolution of the complex
Zn(Leu)SO₄·1/2H₂O(s)

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Molar enthalpies of dissolution of [ZnSO₄·7H₂O (s) and Leu (s)] mixture [n (ZnSO₄·7H₂O) : n (Leu) = 1 : 1] and the complex Zn(Leu)SO₄·1/2H₂O (s) in 100 cm³ of 2 mol·dm⁻³ HCl at (298.15 ± 0.001) K have been determined to be \( \Delta_{f}H_{m}^{s} = -(84.943 ± 0.090) \text{kJ·mol}^{-1} \) and \( \Delta_{f}H_{m}^{e} = (55.967 ± 0.060) \text{kJ·mol}^{-1} \), respectively, using an isoperibol solution-reaction calorimeter. The standard molar entropy of formation of the complex Zn(Leu)SO₄·1/2H₂O (s) has been found to be \( \Delta_{f}S_{m}^{s} = -(1998.155 ± 0.965) \text{J·mol}^{-1} \cdot \text{K}^{-1} \), on the basis of experimental values of enthalpies of dissolution with some auxiliary thermodynamic data through a designed Hess thermochemical cycle. The constant-volume combustion energy of the complex Zn(Leu)SO₄·1/2H₂O (s) has been measured to be \( \Delta_{c}H_{m}^{c} = -(8971.85 ± 11.27) \text{kJ·mol}^{-1} \) by a precision rotating bomb combustion calorimeter at 298.15 K. The standard molar enthalpy of combustion and formation of the compound have been calculated to be \( \Delta_{f}H_{m}^{c} = -(3007.889 ± 3.399) \text{kJ·mol}^{-1} \) and \( \Delta_{f}H_{m}^{e} = -(2001.25 ± 3.503) \text{kJ·mol}^{-1} \). The relative deviation of results obtained from the two calorimetric methods agree with each other and is within ±0.2%.

The complexes of zinc with L-α-amino acids are considered to be one of the best zinc tonics due to a higher absorption ratio in the human body than other inorganic and organic weak-acid zinc tonics. These coordination compounds have vast application prospects in medicines, foodstuffs and cosmetics as nutrient additives. Sheng-Li Gao et al. have investigated the coordination behavior between zinc sulphate and L-α-leucine (abbreviated as Leu) by adopting the semi-micro phase equilibrium, and have successfully synthesized the coordination compound, Zn(Leu)SO₄·1/2H₂O(s), from a mixture of water and acetone under the guidance of the ternary equilibrium phase diagram. However, till date, the data on standard molar enthalpy of formation of the complex have not been reported. The present note throws light on the enthalpy of dissolution of the complex Zn(Leu)SO₄·1/2H₂O(s) in thin acid, investigated by an isoperibol solution calorimeter designed in our laboratory. The constant-volume combustion energy of the complex has been measured by a precision rotating bomb combustion calorimeter at 298.15 K. Furthermore, the standard molar enthalpy of formation of the complex has been derived through a specially designed thermochemical cycle based on experimental results of two calorimetric methods.

Experimental

The sample, Zn(Leu)SO₄·1/2H₂O(s), a white crystalline solid, was prepared by semi-micro phase equilibrium method, and the solid complex obtained was kept in a desiccator containing P₂O₅ until the weight of the complex became constant. The data on chemical and elemental analysis, IR spectra, TG-DTG and X-ray diffraction showed that the composition of the complex was Zn(Leu)SO₄·1/2H₂O(s), as reported in the literature. The purity of the complex determined by chemical analysis was higher than 0.995 mass fractions showed (analytical error, ±0.002 mass fraction).

Isoperibol solution and reaction calorimetry

The isoperibol solution calorimeter comprised a precision temperature controlling system, an electric energy calibration system, an electric stirring system, a thermostatic bath made by transparent silicate glass and a data processing system. The principle and structure of the calorimeter have been described in detail elsewhere.

The precision of controlling and measuring the temperature can reach ± 1·10⁻³ K and ± 1·10⁻⁴ K, respectively. The amount of sample used for the calorimetric measurement was 0.2-0.8 g for each time. During each electric calibration, the electric current through the heater was set at \( I = 10.115 \text{mA} \) and the resistance of the electric heater at \( R = 1017.2 \Omega \) at \( T = 298.15 \text{K} \).

Dickinson’s method (the equal area method) was applied in the processing of all the original data so as
to correct stirring heat and heat transfer between the calorimetric chamber and its surroundings. The before period was about 5 min, the main period about 6-15 min, and the after period about 5 min. When the temperature during the after period became stable, an electrical calibration was done at approximately the same energy as the reaction.

The reliability of the calorimeter was verified by measuring the dissolution enthalpy of KCl (calorimetrically primary standard) in doubly distilled water at $T = 298.15$ K. The mean dissolution enthalpy was $(17.597 \pm 1.7) \text{ J} \cdot \text{mol}^{-1}$ for KCl, which agreed with corresponding published data, $(17.536 \pm 3.4) \text{ J} \cdot \text{mol}^{-1}$ for KCl.

**Rotating-bomb combustion calorimetry**

The constant-volume combustion energy of the compound was measured by a precision rotating-bomb combustion calorimeter (model RBC-type II, China). The structure and principle of the calorimeter has been described in detail elsewhere.

The temperature rise was corrected on the basis of the heat exchange between the calorimetric tube and its surroundings. The correction value ($\xi / K$) of the heat exchange was calculated by the following equation (Eq. 1).

$$
\xi = \left( \frac{V_n - V_0}{\theta_n - \theta_0} \right) \left( \frac{T_0 + T_n}{2} + \sum_{i=1}^{n-1} T_i - n \theta_n \right) + nV_n \quad ... (1)
$$

where $V_n$ and $V_0$ (in K·min$^{-1}$) denote the temperature drift rates in the final and initial stages, respectively ($V$ is positive when the temperature decreases); $\theta_n$ and $\theta_0$ (in K), the average temperatures of the calorimeter during the final and initial stages, respectively; $T_0$ (in K), the last reading of the initial stage; $T_n$ (in K), the first reading of the final stage; $\sum_{i=1}^{n-1} T_i$ (in K), the sum of all the temperature readings, except for the last one, of the main stage; $(V_n - V_0)/(\theta_n - \theta_0)$ (in min), a constant related to the calorimeter performance; $n$, the number of readings for the main (or reaction) stage.

At the end of the experiment, the final products of the combustion reaction were analyzed. The nitrogen oxides (NO$_x$) mainly existed in the form of NO$_2$ due to excess of oxygen in the bomb. No NO$_2$ appeared in the gas phase because it was readily dissolved in the water poured into the bottom of the bomb to form the aqueous nitric acid. The amount of sulfuric dioxide was determined through TCM-pararosaniline colorimetric analysis.

The total amount of nitric acid was obtained by titrating the solution to a phenolphthalein end-point with a standard solution of NaOH. Since the crucible in the rotating bomb was attached to the support, the final solid products remained in the crucible at the end of the experiment. The results of the IR spectra and chemical analyses have proved that the final solid product was only zinc oxide. The analyses of the combustion products indicate that the compound was combusted to ZnO(s), CO$_2$ (g), SO$_2$ (g), N$_2$(g), and H$_2$O (l) under excessive oxygen. The amount of NO and CO in the final gas phase was negligible.

The energy equivalent of the RBC-type II calorimeter was determined from six combustion experiments using $= 0.8 \text{ g}$ of NIST 39I benzoic acid with a certified molar energy of combustion $\Delta_c U = - (26434 \pm 3) \text{ J} \cdot \text{g}^{-1}$ under the same experimental conditions to be $\varepsilon_{\text{calor}} = (18007.71 \pm 8.42) \text{ J} \cdot \text{K}^{-1}$ (Eq. 2).

$$
\varepsilon_{\text{calor}} = (\Delta_c U \cdot a + G \cdot b + 59.8 \cdot V \cdot N) / \Delta T \quad ... (2)
$$

where $\varepsilon_{\text{calor}}$ (in J·K$^{-1}$) is the energy equivalent of the calorimeter; $\Delta_c U$ (in J·g$^{-1}$), the molar energy of combustion of benzoic acid; $a$ (in g), the mass of a pellet of benzoic acid; $G$ (in cm$^3$), the combustion enthalpy of Ni-Cr wire for ignition ($G = 0.9 \text{ J} \cdot \text{cm}^{-1}$); $b$ (in cm), the length of the actual Ni-Cr wire consumed in ignition. The energy of formation of aqueous nitric acid was found to be $\Delta_f H^\circ_m = 59.8 \text{ kJ} \cdot \text{mol}^{-1}$ (ref. 9), based on the molar energy of formation of HNO$_3$(aq) from N$_2$(g), O$_2$(g) and H$_2$O(l) for 0.1 mol·dm$^{-3}$ of HNO$_3$(aq); $V$ (in cm$^3$), the volume of the sodium hydroxide solution consumed; $N$ (in mol·dm$^{-3}$), the molar concentration of the sodium hydroxide solution used in the neutral titration of the nitric acid ($N = 0.1000 \text{ mol} \cdot \text{dm}^{-3}$) and $\Delta T$, the corrected temperature rise of the combustion or reaction, $\Delta T = (T_n - T_0) + \xi$.

**Results and discussion**

**Enthalpy of dissolution**

The complex, Zn(Leu)SO$_4$·1/2H$_2$O(s) was formed as follows:

$$
\text{ZnSO}_4 \cdot 7\text{H}_2\text{O (s)} + \text{Leu(s)} = \text{Zn (Leu)SO}_4 \cdot 1/2\text{H}_2\text{O (s)} + 6.5\text{H}_2\text{O (l)} \quad ... (3)
$$

A thermochemical cycle using the experimental data of isoperibol solution calorimetry was designed...
on the basis of the above reaction, and a reaction scheme was used to derive the standard molar enthalpy of formation of the complex Zn(Leu)SO₄·1/2H₂O(s) according to the cycle. In all these measurements, 2 mol·dm⁻³ HCl was chosen as the calorimetric solvents for measuring the dissolution enthalpies of the reactants and products except for water in the above reaction (Eq. 3). The ZnSO₄·7H₂O(s) and Leu(s) were ground with an agate mortar into fine powder. About 0.001 mol of ZnSO₄·7H₂O(s) + Leu(s) mixture at a mole ratio of n (ZnSO₄·7H₂O) : n (Leu) = 1 : 1 was dissolved in 100 cm³ of 2 mol·dm⁻³ HCl at T = 298.15 K. The results obtained from six tests have been listed in Table 1. In this case, “s” = calorimetric solvent of 100 cm³ of 2 mol·dm⁻³ HCl, then,

\[
\text{ZnSO}_4\cdot7\text{H}_2\text{O (s) + Leu (s) + “s” = solution A}
\]

The dissolution of 6.5H₂O(l) for one of reactants of the reaction (3) in solution A may be given as:

\[
\text{solution A + 6.5H}_2\text{O (l) = solution A’}
\]

The enthalpy change of the process \(\Delta H_{m,2}^\circ\) was within the scope of experimental error, which could not be detected, and may be omitted since the amount of \(\text{H}_2\text{O (l)}\) was very small according to the stoichiometric number of \(\text{H}_2\text{O (l)}\) in Eq. 3.

\[
\text{ZnSO}_4\cdot7\text{H}_2\text{O (s) + Leu (s) + “s” = solution A}
\]

The method for determining the combustion energy of the sample was same as the calibration method of the calorimeter with benzoic acid. The sample weights were adjusted to a vacuum state, and the combustion energy was calculated using the following Eq. 4

\[
\Delta_c U = (W\cdot AT\cdot G \cdot b - 59.83 \cdot N \cdot y) / a
\]

where \(\Delta_c U\) (in J·g⁻¹) denotes the constant-volume combustion energy of the sample and \(a\) is the mass (in g) of the sample adjusted to vacuum. The other symbols have their meaning as in Eq. 1. The results of the six measurements for \(\Delta_c U\) (J·g⁻¹) are listed in Table 3.

The standard molar enthalpy of combustion, \(\Delta_c H_m^\circ\), is the combustion enthalpy change of the following reaction (Eq. 5) at \(T = 298.15\) K and \(p^o = 100\) kPa on the basis of the definition of the combustion enthalpy:

\[
\text{Zn(Leu)SO}_4\cdot1/2\text{H}_2\text{O (s) + “s” = solution A’}
\]

\[
\text{Constant-volume combustion energy and standard molar enthalpy of combustion}
\]

The results obtained from six tests have been listed in Table 2. In this case, Zn(Leu)SO₄·1/2H₂O(s) + “s” = solution A’.

<table>
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<th>No</th>
<th>(W_{\text{Leu}}) (g)</th>
<th>(W_{\text{ZnSO}_4\cdot7\text{H}_2\text{O}}) (g)</th>
<th>(\Delta E_c) (mV)</th>
<th>(\Delta E_s) (mV)</th>
<th>(t) (s)</th>
<th>(Q_s) (J)</th>
<th>(\Delta_c H_{m,2}^\circ) (kJ·mol⁻¹)</th>
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</table>

\(W, W_{\text{ZnSO}_4\cdot7\text{H}_2\text{O}}\) = mass of the sample, \(\Delta E_c\) = voltage change during electric calibration, \(\Delta E_s\) = voltage change during dissolution of the sample, \(t\) = heating time during electric calibration, \(Q_s\) = heat effect during dissolution of the sample and \(\Delta_c H_{m,2}^\circ\) = molar enthalpy of dissolution

\[\Delta_c H_{m,2}^\circ = (\Delta E_s / \Delta E_s \cdot 1017.2 \cdot (W/M))\]

\(W_{\text{ZnSO}_4\cdot7\text{H}_2\text{O}}\) = mass of the sample, \(\Delta E_s\) = voltage change during dissolution of the sample, \(Q_s\) = heat effect during dissolution of the sample, \(R\) = resistance of the heater in the reaction chamber, \(W\) = mass of the sample, \(M\) = molar weight of the sample

<table>
<thead>
<tr>
<th>No</th>
<th>(W_{\text{Zn(Leu)SO}_4\cdot1/2\text{H}_2\text{O}}) (g)</th>
<th>(\Delta E_c) (mV)</th>
<th>(\Delta E_s) (mV)</th>
<th>(t) (s)</th>
<th>(Q_s) (J)</th>
<th>(\Delta_c H_{m,3}^\circ) (kJ·mol⁻¹)</th>
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</tbody>
</table>
Zn(Leu)SO₄·1/2H₂O + \( \frac{31}{2} \) O₂ = ZnO(s) + 6CO₂(g)  
+ SO₃(g) + \( \frac{1}{2} \) N₂(g) + 7H₂O(l) \ldots (5)

The standard molar enthalpy of combustion of the complex was calculated to be,  
\[ \Delta_r H'_m^{\circ} [\text{Zn(Leu)SO}_4 \cdot 1/2\text{H}_2\text{O}, \text{s}] = -(3007.889 ± 3.399) \text{kJ·mol}^{-1} \]  
\[ \Delta_r H'_m^{\circ} [\text{H}_2\text{O}, \text{l}] = -(285.830 ± 0.042) \text{kJ·mol}^{-1} \]  
\[ \Delta_r H'_m^{\circ} [\text{N}_2, \text{g}] = -(3077.75 \text{kJ·mol}^{-1} \]  
\[ \Delta_r H'_m^{\circ} [\text{CO}_2, \text{g}] = -(637.39 ± 0.92) \text{kJ·mol}^{-1} \]  
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The standard molar enthalpy of formation of the complex Zn(Leu)SO₄·1/2H₂O(s) was calculated at T = 298.15 K from dissolution enthalpies of (ZnSO₄·7H₂O(s) + Leu(s)) in accordance with Hess’s law and the above designed thermochemical cycle by means of the following equation:

\[ \Delta_f H'_m^{\circ} = \Delta_f H'_m^{\circ} + (\Delta_f H'_m^{\circ} - \Delta_f H'_m^{\circ}) + \Delta_f H'_m^{\circ} = -(140.91 ± 0.108) \text{kJ·mol}^{-1} \ldots (6) \]

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A reaction scheme applied to derive standard molar enthalpy of formation of the complex Zn(Leu)SO₄·1/2H₂O(s) has been given in Table 3. Enthalpy change of Eq. 3 was combined with some auxiliary thermodynamic data from literature, Zn(s) + SO₂(g) + \( \frac{1}{2} \) N₂(g) + 7H₂O(l) = ZnSO₄·7H₂O(s)

\[ \Delta_f H'_m^{\circ} = \Delta_f H'_m^{\circ} + (\Delta_f H'_m^{\circ} - \Delta_f H'_m^{\circ}) + \Delta_f H'_m^{\circ} = -(140.91 ± 0.108) \text{kJ·mol}^{-1} \ldots (6) \]

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where $\Delta H_m^\circ [\text{ZnO, s}] = -(350.46 \pm 0.27) \text{kJ·mol}^{-1}$, 
$\Delta H_m^\circ [\text{CO}_2, \text{g}] = -(393.51 \pm 0.13) \text{kJ·mol}^{-1}$, 
$\Delta H_m^\circ [\text{SO}_2, \text{g}] = -(296.81 \pm 0.20) \text{kJ·mol}^{-1}$ (ref. 10).

The present data indicate that solution A from dissolution of reactants in the Eq. 3 is in thermodynamically equivalent states to solution A' from dissolution of products in the reaction, which has been confirmed by UV-vis spectroscopy and the refractive indices of two solutions (A and A'). The UV-vis Spectrum and the value of the refractive index of solution A agree with those of solution A'. These results demonstrated that chemical components and physical-chemistry properties of solutions are consistent with those of solution A'. As a result, the designed thermochemical cycle is reasonable and reliable, and can be used to calculate the standard molar enthalpy of formation of the complex, Zn(Leu)SO$_4$·1/2H$_2$O(s).

The standard molar enthalpy of formation, 
$\Delta_f H_m^\circ [\text{Zn(Leu)SO}_4\cdot1/2\text{H}_2\text{O, s}] = -(1998.155 \pm 0.965) \text{J·mol}^{-1}$, obtained from the isoperibol solution-reaction calorimeter is identical with that, 
$\Delta_f H_m^\circ [\text{Zn(Leu)SO}_4\cdot1/2\text{H}_2\text{O, s}] = -(2001.251 \pm 3.503) \text{J·mol}^{-1}$, from the precision rotating-bomb combustion calorimeter. The relative deviation of results between the two calorimetry is within ±0.2%.

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References