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Short communication

Thermochemistry of $Zn(AA)SO_4{\cdot}H_2O(s)$ (AA = L-α-valine and methionine)

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Abstract

The standard molar enthalpies of dissolution of $\{ZnSO_4{\cdot}7H_2O(s) + Val(s)\}$, $\{ZnSO_4{\cdot}7H_2O(s) + Met(s)\}$, $Zn(Val)SO_4{\cdot}H_2O(s)$ and $Zn(Met)SO_4{\cdot}H_2O(s)$ (where Val is L-α-valine and Met is L-α-methionine) in 2 mol dm^{-3} HCl at $T = 298.15 \pm 0.001$ K have been measured to be $\Delta_d H^\circ_{m,1} = 94.588 \pm 0.025\,kJ\,mol^{-1}$, $\Delta_d H^\circ_{m,3} = -46.118 \pm 0.055\,kJ\,mol^{-1}$, $\Delta_d H^\circ_{m,4} = -70.619 \pm 0.051\,kJ\,mol^{-1}$, $\Delta_d H^\circ_{m,5} = 58.415 \pm 0.046\,kJ\,mol^{-1}$, respectively. The derived molar enthalpies of formation of the complexes $Zn(Val)SO_4{\cdot}H_2O(s)$ and $Zn(Met)SO_4{\cdot}H_2O(s)$ are $\Delta_f H^\circ_m[Zn(Val)SO_4 \cdot H_2O,\ s] = -1851 \pm 2\,kJ\,mol^{-1}$ and $\Delta_f H^\circ_m[Zn(Met)SO_4 \cdot H_2O,\ s] = -2069 \pm 0.7\,J\,mol^{-1}$.

Keywords: Isoperibol temperature-rise calorimetry; Valine and methionine complexs of Zn(II); Molar enthalpy of dissolution; Molar enthalpy of formation

1. Introduction

Zinc coordination compounds have application in medicines, foodstuffs and cosmetics [1,2]. Gao and co-workers [3,4] investigated the coordination of zinc sulphate to L-α-valine and L-α-methionine and successfully synthesized two coordination compounds, $Zn(Val)SO_4{\cdot}H_2O(s)$ and $Zn(Met)SO_4{\cdot}H_2O(s)$. This paper reports the enthalpies of dissolution of these complexes in acid solution and their standard molar enthalpies of formation from a thermochemical cycle.

2. Experimental

2.1. Sample

KCl (A.R.) for calibration of the calorimeter was obtained from the U.S. National Institute of Standards and Technology, Standard Reference Material 1655. It was dried at 620–720 K for 16 h before the measurements were carried out.

$Zn(Val)SO_4{\cdot}H_2O(s)$ and $Zn(Met)SO_4{\cdot}H_2O(s)$ are white crystals prepared by a semi-micro phase equilibrium method [3,4]. The solid complexes were stored in a desiccator over P_4O_{10} until the weight of the complexes became constant. Chemical and elemental analysis, IR spectra, TG-DTG and X-ray diffraction prove that the complexes were $Zn(Val)SO_4{\cdot}H_2O(s)$ and $Zn(Met)SO_4{\cdot}H_2O(s)$, as shown in the literature [3,4]. The purities of the complexes were higher than 0.999 ± 0.002 mass fractions.

2.2. Isoperibol temperature-rise calorimetry

The isoperibol solution calorimeter was described in detail elsewhere [5–7].

The amount of sample used for the calorimetric measurement was 0.2–0.8 g per experiment.

Dickinson's method [8] (the equal area method) was applied in the processing of all the original data so as to correct stirring and heat transfer between the calorimetric chamber and its surroundings.

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Table 1
Reaction scheme used to determine the standard molar enthalpy of formation of the complex $Zn(Val)SO_4{\cdot}H_2O(s)$ at $T = 298.15$ K

No.	Reaction scheme	$\Delta_f H_m^\circ$ or $\Delta_d H_m^\circ \pm \sigma_a$ (kJ mol^{-1})
1	$\{ZnSO_4{\cdot}7H_2O(s)$ and $Val(s)\}$ + 's' = solution A	94.588 ± 0.025 ($\Delta_d H_{m,1}^\circ$) ($n = 6$)
2	$\{Zn\ (Val)\ SO_4{\cdot}H_2O(s)\}$ + 's' = solution A′	-69.875 ± 0.055 ($\Delta_d H_{m,3}^\circ$) ($n = 6$)
3	Solution A + $\{6H_2O(l)\}$ = solution A′	0 ($\Delta_d H_{m,2}^\circ$)
4	$Zn(s) + S(s) + 11/2O_2(g) + 7H_2(g) = ZnSO_4{\cdot}7H_2O(s)$	-3077.75
5	$5C(s) + 1/2N_2(g) + O_2(g) + 11/2H_2(g) = Val(s)$	-629 ± 2
6	$1/2O_2(g) + H_2(g) = H_2O(l)$	-285.83 ± 0.04
7	$Zn(s) + S(s) + 7/2O_2(g) + 5C(s) + 11/2H_2(g) = Zn(Val)SO_4{\cdot}H_2O(s)$	-1851 ± 2

In which 's' is the solvent, 2 mol dm^{-3} hydrochloric acid; σ_a is standard deviation of the mean; n is the number of experiments.

The fore 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 the dissolution enthalpy of KCl in double distilled water at 298.15 K. The mean dissolution enthalpy was $17\,597 \pm 17$ J mol^{-1}, compared with published data [9], $17\,536 \pm 3.4$ J mol^{-1} for KCl.

In all the measurements, 2 mol dm^{-3} HCl was chosen as the calorimetric solvent for measuring the dissolution enthalpies of the reactants and products. The $ZnSO_4{\cdot}7H_2O(s)$ and AA(s) or $Zn(AA)\ SO_4{\cdot}H_2O(s)$ were ground within an agate mortar into fine powder. About 0.001 mol of $ZnSO_4{\cdot}7H_2O(s)$ and AA(s) mixture at a mole ratio of n $(ZnSO_4{\cdot}7H_2O)$:n (AA) = 1:1 and about 0.001 mol of $Zn(AA)SO_4{\cdot}H_2O(s)$ were dissolved in 100 dm^3 of 2 mol dm^{-3} HCl at 298.15 K, respectively. The results of six determinations are listed in Tables 1 and 2, respectively.

Table 2
Reaction scheme used to determine the standard molar formation enthalpy of the $Zn(Met)SO_4{\cdot}H_2O(s)$ at 298.15 K

No.	Reaction scheme	$\Delta_f H_m^\circ$ or $\Delta_d H_m^\circ$ $\pm \sigma_a$ (kJ mol^{-1})
1	$\{ZnSO_4{\cdot}7H_2O(s)$ and $Met(s)\}$ + 's' = solution A	-70.619 ± 0.051 ($\Delta_d H_{m,4}^\circ$) ($n = 6$)
2	$\{Zn\ (Met)\ SO_4{\cdot}H_2O(s)\}$ + 's' = solution A′	58.415 ± 0.046 ($\Delta_d H_{m,5}^\circ$) ($n = 6$)
3	Solution A + $\{6H_2O(l)\}$ = solution A′	0 ($\Delta_d H_{m,2}^\circ$)
4	$Zn(s) + S(s) + 11/2O_2(g) + 7H_2(g) = ZnSO_4{\cdot}7H_2O(s)$	-3077.75
5	$5C(s) + 1/2N_2(g) + O_2(g) + 11/2H_2(g) + S(s) = Met(s)$	-577.5 ± 0.7
6	$1/2O_2(g) + H_2(g) = H_2O(l)$	-285.83 ± 0.04
7	$Zn(s) + 2S(s) + 7/2O_2(g) + 5C(s) + 13/2H_2(g) + 1/2N_2(g) = Zn(Met)SO_4{\cdot}H_2O(s)$	-2069.3 ± 0.7

σ_a: standard deviation of the mean.

The resistance of the heater in the reaction chamber R is 1017.2 Ω at $T = 298.15$ K, the current I through heater is 10.115 mA during electric calibration.

3. Results and discussion

3.1. Enthalpies of dissolution of $\{ZnSO_4{\cdot}7H_2O(s) + \text{L-}Val(s)\}$, $\{ZnSO_4{\cdot}7H_2O(s) + \text{L-}Met(s)\}$ and $Zn(AA)SO_4{\cdot}H_2O(s)$ in 2 mol dm^{-3} HCl

A thermochemical cycle using the calorimetric data was designed on the basis of the reaction,

$$ZnSO_4{\cdot}7H_2O(s) + AA(s) = Zn(AA)SO_4{\cdot}H_2O(s) + 6H_2O(l) \qquad (1)$$

and used to derive the standard molar enthalpy of formation of the complexes.

If "s" = calorimetric solvent of 100 cm^3 of 2 mol dm^{-3} HCl, then,

$$\{ZnSO_4{\cdot}7H_2O(s) + AA(s)\} \text{ or } Zn(AA)SO_4{\cdot}H_2O(s) + \text{“s''} = \text{solution A or solution B}$$

The solutions obtained from the dissolution of the $\{ZnSO_4{\cdot}7H_2O(s) + \text{L-}Val(s)\}$ and the $\{ZnSO_4{\cdot}7H_2O(s) + \text{L-}Met(s)\}$ in 100 dm^3 of 2 mol dm^{-3} HCl were represented as solution A and solution B, respectively.

The dissolution of $\{6H_2O(l)\}$ for one of reactants of the reaction (1) in solution A or solution B can be shown as

$$\text{solution A or solution B} + \{6H_2O(l)\} = \text{solution A}' \text{ or solution B}'$$

The enthalpy change of the process ($\Delta_d H_{m,2}^\circ$) may be omitted because the amount of $H_2O(l)$ was very small according to the stoichiometric amount of $H_2O(l)$ in the reaction (1).

3.2. Standard molar enthalpies of formation of the complexes $\{Zn(Val)SO_4{\cdot}H_2O(s)\}$ and $\{Zn(Met)SO_4{\cdot}H_2O(s)\}$

Enthalpy change ($\Delta_r H_{m,1}$ or $\Delta_r H_{m,2}$) of reaction (1) can be calculated from dissolution enthalpies of $\{ZnSO_4{\cdot}7H_2O(s) + AA(s)\}$ ($\Delta_d H_{m,1}^\circ$ and $\Delta_d H_{m,4}^\circ$) and $\{Zn(AA)SO_4{\cdot}H_2O(s)\}$($\Delta_d H_{m,3}^\circ$ and $\Delta_d H_{m,5}^\circ$) by the equations:

$$\Delta_r H_{m,1} = \Delta_d H_{m,1}^\circ - (\Delta_d H_{m,2}^\circ + \Delta_d H_{m,3}^\circ) = (140.71 \pm 0.06)\ \text{kJ mol}^{-1}$$

$$\Delta_r H_{m,2} = \Delta_d H_{m,4}^\circ - (\Delta_d H_{m,2}^\circ + \Delta_d H_{m,5}^\circ) = -(129.03 \pm 0.07)\ \text{kJ mol}^{-1}$$

Two reaction schemes were applied to derive standard molar enthalpies of formation of the complexes, respectively. The derived molar enthalpies of formation of the complexes $Zn(Val)SO_4{\cdot}H_2O(s)$ and $Zn(Met)SO_4{\cdot}H_2O(s)$ are $\Delta_f H_m^\circ[Zn(Val)SO_4 \cdot H_2O, s] = 1851 \pm 2\,kJ\,mol^{-1}$ and $\Delta_f H_m^\circ[Zn(Met)SO_4 \cdot H_2O, s] = 2069 \pm 0.7\,J\,mol^{-1}$, as shown in Tables 1 and 2.

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