Journal of Thermal Analysis and Calorimetry, Vol. 65 (2001) 301–304

THE ENTHALPY OF SOLUTION IN WATER OF COMPLEXES OF ZINC WITH METHIONINE

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(Received March 2, 2001)

Abstract

The enthalpies of solution in water of *L*-α-methionine and its zinc complexes $Zn(Met)Cl_2$, $Zn(Met)_2Cl_2 \cdot 2H_2O$, $Zn(Met)(NO_3)_2 \cdot 1/2H_2O$, $Zn(Met)_3(NO_3)_2 \cdot H_2O$ and $Zn(Met)SO_4 \cdot H_2O$ have been measured at 298.15 K. The standard enthalpy of formation of met(aq) has been calculated. The experimental results have been discussed.

Keywords: complexes, enthalpy of solution, *L*-α-methionine, zinc salts

Introduction

The complexes of zinc salts with *L*-α-methionine as additives have a wide application in medicine, foodstuff and cosmetics. Using phase equilibrium method, Gao Shengli and Hou Yudong *et al.* [1, 2] studied the coordination behavior of zinc salts with *L*-α-methionine. According to the results of phase equilibrium, they prepared a series of complexes of zinc salts with *L*-α-methionine.

In this paper, the enthalpies of solution in water of *L*-α-methionine and its five zinc complexes have been determined at 298.15 K using a heat conduction microcalorimeter. The standard enthalpy of formation of met(*aq*) has been calculated. The experimental results have been discussed.

Experimental

Preparation and composition of the compounds

Referred to literature [3], *L*-α-methionine (B. R., purity >99.9%, made in Shanghai Kanda) was recrystallized and analyzed. Its purity, density and melting point were 99.99%, 1.3514 g cm^{-3} and 282–283°C, respectively.

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1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Five solid complexes of zinc salts with *L*-α-methionine shown in Table 1 were prepared and analyzed according to the methods reported in literature [1, 2]. Zn^{2+} was determined complexometrically with EDTA. *L*-α-methionine was analyzed by the iodometry method. Carbon, hydrogen and nitrogen analyses were performed on 1106 type elemental analyzer. The analytical results are summarized in Table 1. The conductivity of the deionized water used in the experiments was $5.48 \cdot 10^{-8}$ S cm^{-1}.

Table 1 Analytical results on chemical composition of the complexes/%

Complex	Zn^{2+}	Met	C	H	N
$Zn(Met)Cl_2$	22.91 (22.90)*	51.94 (52.21)	21.11 (21.04)	3.92 (3.88)	4.96 (4.91)
$Zn(Met)_2Cl_2 \cdot 2H_2O$	14.01 (14.90)	63.27 (63.39)	25.58 (25.52)	4.47 (4.71)	6.01 (5.95)
$Zn(Met)(NO_3)_2 \cdot 1/2H_2O$	18.83 (18.81)	42.83 (42.90)	17.29 (17.28)	3.58 (3.48)	12.06 (12.09)
$Zn(Met)_3(NO_3)_2 \cdot H_2O$	9.88 (9.98)	68.24 (68.34)	27.75 (27.50)	5.77 (5.39)	10.37 (10.69)
$Zn(Met)SO_4 \cdot H_2O$	20.23 (19.90)	45.27 (45.40)	18.35 (18.27)	3.41 (3.37)	4.29 (4.26)

*The data in brackets are calculated values

Experimental equipment and conditions

All measurements were made using a heat conduction microcalorimeter, type RD496-III from Southwest Electronic Engineering Institute of China, which was equipped with two 15 mL calorimetric vessels, and operated at 298.15±0.005 K. The microcalorimeter was calibrated by the Joule effect and its sensitivity was 63.994±0.042 μV mW^{-1}. The experimental precision and accuracy were checked by the measurement of the enthalpy of solution of special purity crystalline KCl in deionized water at 298.15 K. The experimental value of $\Delta_{sol}H_m^{\theta}$ of 17.238± 0.048 kJ mol^{-1} is excellent agreement with that of $\Delta_{sol}H_m^{\theta}$ of 17.241±0.018 kJ mol^{-1} reported in the literature [4]. This indicates that the device for the enthalpy of solution measurements used in this work is reliable.

Results

Results for the enthalpies of solution of *L*-α-methionine and its five complexes with zinc salts in deionized water at 298.15 K are given in Table 2. Where *r* is the molar ratio $n(H_2O)/n$(compound). The values of $\Delta_{sol}H_m^{\theta}$ in Table 2 can be considered of a value at infinite dilution.

Table 2 Enthalpies of solution in water of *L*-α-methionine and its zinc complexes at 298.15 K

Compound	Number of experiments	*r*	$\Delta_{sol}H_m^\theta$/kJ mol^{-1}
L-α-methionine	6	3987–7445	9.308±0.091
$Zn(Met)Cl_2$	6	5152–12859	–24.638±0.169
$Zn(Met)_2Cl_2·2H_2O$	6	7479–16900	–15.742±0.115
$Zn(Met)(NO_3)_2·1/2H_2O$	6	7556–14508	–14.568±0.120
$Zn(Met)_3(NO_3)_2·H_2O$	6	18376–25765	–27.649±0.111
$Zn(Met)SO_4·H_2O$	6	6548–16972	–12.867±0.121

Discussion

1. At 298.15 K, the process of solution in water of *L*-α-methionine is an endothermic reaction:

$$L\text{-}\alpha\text{-met}(s) \rightarrow L\text{-}\alpha\text{-met}(aq)$$

According to the process, the standard enthalpy of formation of *L*-α-methionine(*aq*), $\Delta_{fL\text{-}\alpha\text{-met(aq)}}H_m^\theta$, can be calculated as follows:

$$\begin{aligned}\Delta_{fL\text{-}\alpha\text{-met(aq)}}H_m^\theta &= \Delta_{sol}H_m^\theta + \Delta_{fL\text{-}\alpha\text{-met(s)}}H_m^\theta \\ &= [(9.31\pm0.09)+(-588.43\pm2.98)] \\ &= -579.12\pm2.98 \text{ kJ mol}^{-1}\end{aligned}$$

where $\Delta_{sol}H_m^\theta$ is enthalpy of solution of *L*-α-met(*s*) in water, $\Delta_{fL\text{-}\alpha\text{-met(s)}}H_m^\theta$ is enthalpy of formation of *L*-α-met(*s*) and its value derives from the literature [3].

2. For the complexes with mole ratio 1:1, the values of of the complexes decrease in the order:

$$\Delta_{sol,Zn(met)Cl_2}H_m^\theta > \Delta_{sol,Zn(met)(NO_3)_2\cdot 1/2H_2O}H_m^\theta > \Delta_{sol,Zn(met)SO_4\cdot H_2O}H_m^\theta$$

An attempt at calculating the standard enthalpy of formation of $Zn(Met)_{aq}^{2+}$ was not successful. Maybe, because of the different structures of the complexes, $Zn(Met)_{aq}^{2+}$ was not always formed after the solution process.

3. For the complexes of with the same anion, the larger the molar ratio of zinc with *L*-α-methionine is, the smaller the exothermic effect of dissolution is. The process of solution even in water of $Zn(Met)_3(NO_3)_2·H_2O$ is an endothermic reaction. As the value of enthalpy is connected with the bond enthalpy in the crystal structure of the solid complex and the hydration enthalpy of the products, it is necessary for further study of the crystal structures of the solid complexes.

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We thank the National Natural Science Foundation of China for financial support.

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