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Enthalpies of Dissolution of $[Mn(SCZ)_3](PA)_2 \cdot H_2O$ in DMF

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Abstract: The molar enthalpies of dissolution of $[Mn(SCZ)_3](PA)_2 \cdot H_2O$ in N,N-dimethylformamide (DMF) at 298.15 K were measured by means of a SETARAM C80 Ⅱ calorimeter. The standard molar enthalpy of dissolution was determined to be $\Delta_{diss}H_m^\theta = -43.607\ kJ \cdot mol^{-1}$. The empirical formulae for calculating the enthalpies of dissolution ($\Delta_{diss}H = -43.607 - 454.98b + 9378.2b^{1/2}$) of the title coordination complex at different concentrations b ($mol \cdot kg^{-1}$) was obtained. Relative apparent molar enthalpy (ΦL_i), relative partial molar enthalpy (L_i) and enthalpy of dilution ($\Delta_{dil}H_{1,2}$) were obtained respectively from the experimental data of the enthalpies of dissolution of the coordination compound: $\Phi L_i = -454.98b + 9378.2b^{1/2}$, $L_i = -909.96b + 14067.3b^{1/2}$ and $\Delta_{dil}H_{1,2} = -454.98(b_2^{1/2} - b_1^{1/2}) + 9378.2(b_2 - b_1)$.

Key words: physical chemistry; coordination complex; $[Mn(SCZ)_3](PA)_2 \cdot H_2O$; enthalpy of dissolution; microcalorimetry

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1 Introduction

Picric acid (PA) and Semicarbazide (SCZ) have been used widely as energetic materials with good performance [1,2]. Recently, considerable attention has been paid to its coordination compounds[3-5]. The preparation, molecular structure, thermal decomposition mechanism of $[Mn(SCZ)_3](PA)_2 \cdot H_2O$ has been studied by using DSC, TG-DTG, FTIR techniques[6]. Thermochemical properties are of great importance to understand thermal activity of energetic materials, but relatively little study has been carried out.

In this paper, a SETARAM C80 Ⅱ calorimeter is introduced to study the enthalpies of dissolution of the coordination complex in N,N-dimethylformamide (DMF) at different concentrations at 298.15 K. Values of the standard molar enthalpy of dissolution, relative apparent molar enthalpy, relative partial molar enthalpy and enthalpy of dilution are determined.

2 Experimental

2.1 Preparation of reagents and the complex

N,N-dimethylformamide (DMF), absolute ethanol, chloroform, acetic acid are of A. R. grade. The electrical conductivity of deionized water is $6.25 \times 10^{-8}\ S \cdot cm^{-1}$. The coordination complex is prepared as described in literature[6]. The obtained fulvous crystal is purified, dried, sifted through a 160 mesh sifter and then kept in vacuum 24 h prior to use. Its stoichiometric formula is $MnC_{21}N_{15}O_{18}H_{23}$.

2.2 Equipment and conditions

The calorimetric measurements were carried out in a SETARAM C80 Ⅱ calorimeter and a reaction calorimeter using mixing with membrane vessels made from stainless steel, and each mixing with membrane vessel was in the form of an 60 mm high vertical cylinder with 10 mm outside diameter and two compartments. The smaller, lower recipient (2.5 cm^3) of each cell was used to contain the reagent (about 2.6 g) and was closed by membrane made of PTFE (0.05 mm thick). The larger, upper container (3.5 cm^3) of the measuring cell contained the known amount of $[Mn(SCZ)_3](PA)_2 \cdot H_2O$ (0.88 – 7.36 mg). The measuring and reference cells were placed inside a metallic block of the Calvet-type calorimeter. The temperature was measured by means of a 100 Ω platinum resistance thermometer located between the two vessels, and was held constant to within ±0.01 K during each measurement.

The working temperature was constant, and when thermal equilibrium was reached , the components in the

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vessels were mixed by piercing the membrane using a rod. The differential heat-flux was then recorded, and integrated as a function of time to give the heat changes during mixing.

The microcalorimeter was calibrated by Joule effect before experiment, and the sensitivity was 30.50 $\mu V \cdot mW^{-1}$ at 298.15 K. The accuracy of the calorimeter was checked by measurement of the enthalpies of dissolution of KCl (special purity) in deionized water at 298.15 K. The results were shown in Table 1. The molar masses M and the densities ρ used throughout this study are as follows: $M_{KCl} = 74.551$ g $\cdot$ mol^{-3}; $M_{H_2O} = 18.015$ g $\cdot$ mol^{-3}, $\rho_{H_2O} = 1.000$ g $\cdot$ cm^{-3}; $M_{[Mn(SCZ)_3](PA)_2 \cdot H_2O} = 754.410$ g $\cdot$ mol^{-3}; $\rho_{DMF} = 0.948$ g $\cdot$ cm^{-3}.

Table 1　Calorimetric results for the enthalpy of dissolution of KCl in water at 298.15 K

m/mg	$10^3\ b$/mol $\cdot$ kg^{-1}	$\Delta_{diss}H_m^\theta$/kJ $\cdot$ mol^{-1}
3.81	18.79	17.251
4.18	20.61	17.138
4.35	21.45	17.094
8.18	40.34	17.150
8.89	43.84	17.424
9.20	45.36	17.151
		mean 17.201 ± 0.058[1)]

Note: m represents mass of sample; b represents molality of sample in the dissolution; $\Delta_{diss}H_m^\theta$ represents the integral molar enthalpies of dissolution of sample at 298.15 K, same as that in Table 2.

1) Uncertainties are twice the standard deviation of the mean.

The experimental value of $\Delta_{diss}H_m^\theta = 17.201 \pm 0.058$ kJ $\cdot$ mol^{-1} is in good agreement with that of $\Delta_{diss}H_m^\theta = 17.241 \pm 0.018$ kJ $\cdot$ mol^{-1} reported in the literature[7]. The accuracy is within 0.23%, which indicated that the device used in this work was reliable.

3　Results and discussion

The title coordination complex $[Mn(SCZ)_3](PA)_2 \cdot H_2O$ is soluble-easily in DMF, soluble-hardly in absolute ethanol, is insoluble in deionized water, chloroform and acetic acid.

The experimental and calculated values of enthalpy of dissolution in DMF for $[Mn(SCZ)_3](PA)_2 \cdot H_2O$ are given in Table 2, and the relative apparent molar enthalpy (ΦL_i, calculated) and relative partial molar enthalpy (L_i, calculated) of the coordination complex are also given. The typical heat flow curve at 298.15 K is shown in Fig. 1. It can be seen from Fig. 1 that the reaction is exothermic. And the curves at other different concentrations are similar in tendency.

Table 2　Enthalpy of dissolution of the coordination complex in DMF at 298.15 K

m/mg	$10^3\ b$ /mol $\cdot$ kg^{-1}	$\Delta_{diss}H$/kJ $\cdot$ mol^{-1} found	$\Delta_{diss}H$/kJ $\cdot$ mol^{-1} calculated	ΦL_i /kJ $\cdot$ mol^{-1}	L_i /kJ $\cdot$ mol^{-1}
0.00	0.00	–	−43.61	0.00	0.00
0.88	0.45	−49.47	−49.04	199.25	298.77
1.21	0.62	−48.82	−49.12	233.60	350.26
1.35	0.69	−49.23	−49.08	246.73	369.93
2.52	1.30	−47.03	−47.83	336.93	505.11
2.62	1.35	−46.91	−47.67	343.54	515.01
3.25	1.67	−46.89	−46.54	382.55	573.44
3.84	1.97	−46.25	−45.31	415.75	623.18
4.21	2.16	−45.12	−44.48	435.28	652.42
5.35	2.75	−41.33	−41.68	490.54	735.19
6.56	3.37	−38.91	−38.40	543.04	813.79
7.55	3.88	−37.93	−35.55	582.46	872.80

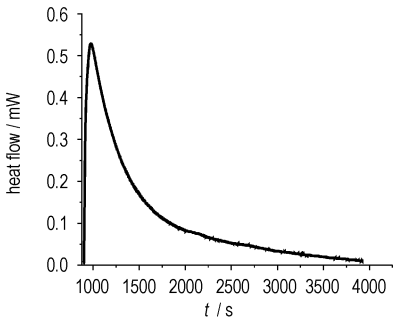

Fig. 1　Heat flow curve of the dissolution process of the coordination complex in DMF at 298.15 K

By substituting the values of b in Table 2 into Equation (1)[8],

$$\Delta_{diss}H = A + Bb + Cb^{1/2} \quad (1)$$

The empirical formula of enthalpy $\Delta_{diss}H$ of dissolution in DMF (Fig. 2) and the values of the standard enthalpies of dissolution $\Delta_{diss}H_m^\theta$, which also means the enthalpies of dissolution in pure solvent, for the coordination complex $[Mn(SCZ)_3](PA)_2 \cdot H_2O$ are obtained:

$$\Delta H = -43.607 - 454.98b + 9378.2b^{1/2}$$

$$\Delta_{diss}H_m^\theta = -43.607 \text{ kJ} \cdot \text{mol}^{-1}$$

According to the relationship shown in Equation (2)[8]

$$\Phi L_i = \Delta_{diss}H - \Delta_{diss}H_m^\theta \quad (2)$$

The empirical formula of relative apparent molar enthalpy in the two ingredients ΦL_i for the coordination

complex is obtained: $\Phi L_i = -454.98b + 9378.2b^{1/2}$

According to the empirical formula presented in Equation (3)[8]

$$L_i = b\left[\frac{\partial \Delta_{diss}H}{\partial b}\right] + \Phi L_i \quad (3)$$

From Equations (1) and (2), the following empirical formula of the relative partial molar enthalpy in the two ingredients L_i for the title coordination complex is obtained:

$$L_i = -909.96b + 14067.3b^{1/2}$$

According to the empirical formula described in Equation (4)[8], the following empirical formula of dilution enthalpy $\Delta_{dil}H_{1,2}$ for the complex is obtained:

$$\Delta_{dil}H_{1,2} = \sum_{1}^{2} A_i[(b_2^{1/2})^i - (b_1^{1/2})^i] \quad (4)$$

Where $A_1 = -454.98$, $A_2 = 9378.2$; b_1 represents molality of solvent, b_2 represents molality of solute.

Then $\Delta_{dil}H_{1,2} = -454.98(b_2^{1/2} - b_1^{1/2}) + 9378.2(b_2 - b_1)$

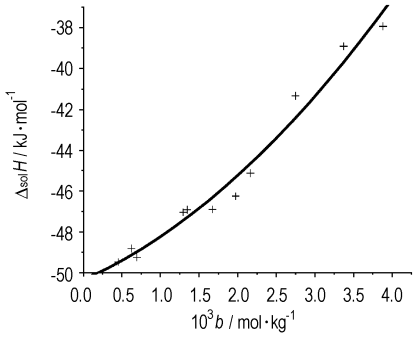

Fig. 2 Measured $\Delta_{diss}H$ for $[Mn(SCZ)_3](PA)_2 \cdot H_2O$ as a function of molality b at 298.15 K

4 Conclusions

The enthalpies of dissolution in DMF of the $[Mn(SCZ)_3](PA)_2 \cdot H_2O$ coordination complex were measured by means of a Calvet microcalorimeter. Empirical formulae for calculating the enthalpies of dissolution ($\Delta_{diss}H$), relative apparent molar enthalpies (ΦL_i), relative partial molar enthalpies (L_i) and enthalpies of dilution ($\Delta_{dil}H_{1,2}$) were obtained from the experimental data of the enthalpies of dissolution of the title coordination complex. It can provide new content to the thermochemical properties and function mechanism of the title coordination complex.

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$[Mn(SCZ)_3](PA)_2 \cdot H_2O$ 在 DMF 中的溶解焓

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摘要: 用微热量仪对配合物$[Mn(SCZ)_3](PA)_2 \cdot H_2O$在溶剂 N,N-二甲基甲酰胺(DMF)中不同浓度(b)时的溶解焓进行了测定,用计算机拟合的方法求得该配合物的标准摩尔溶解焓($\Delta_{diss}H_m^\theta = -43.607$ kJ·mol^{-1})及溶解焓($\Delta_{diss}H$)的经验公式($\Delta_{diss}H = -43.607 - 454.98b + 9378.2b^{1/2}$)。由此得到配合物的相对表观摩尔焓($\Phi L_i$)、相对偏摩尔焓($L_i$)以及配合物的稀释焓($\Delta_{dil}H_{1,2}$)的经验公式: $\Phi L_i = -454.98b + 9378.2b^{1/2}$, $L_i = -909.96b + 14067.3b^{1/2}$和 $\Delta_{dil}H_{1,2} = -454.98(b_2^{1/2} - b_1^{1/2}) + 9378.2(b_2 - b_1)$。

关键词: 物理化学; 配合物; $[Mn(SCZ)_3](PA)_2 \cdot H_2O$; 溶解焓; 微量热法

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