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LOW-TEMPERATURE HEAT CAPACITIES AND STANDARD MOLAR ENTHALPY OF FORMATION OF THE COMPLEX $Zn(Val)SO_4{\cdot}H_2O(s)$ (Val=*L*-α-valine)

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Low-temperature heat capacities of a solid complex $Zn(Val)SO_4{\cdot}H_2O(s)$ were measured by a precision automated adiabatic calorimeter over the temperature range between 78 and 373 K. The initial dehydration temperature of the coordination compound was determined to be, T_D=327.05 K, by analysis of the heat-capacity curve. The experimental values of molar heat capacities were fitted to a polynomial equation of heat capacities ($C_{p,m}$) with the reduced temperatures (x), [$x=f(T)$], by least square method. The polynomial fitted values of the molar heat capacities and fundamental thermodynamic functions of the complex relative to the standard reference temperature 298.15 K were given with the interval of 5 K.

Enthalpies of dissolution of the [$ZnSO_4{\cdot}7H_2O(s)$+Val(s)] ($\Delta_{sol}H^0_{m,1}$) and the $Zn(Val)SO_4{\cdot}H_2O(s)$ ($\Delta_{sol}H^0_{m,2}$) in 100.00 mL of 2 mol dm^{-3} HCl(aq) at T=298.15 K were determined to be, $\Delta_{sol}H^0_{m,1}=(94.588\pm0.025)$ kJ mol^{-1} and $\Delta_{sol}H^0_{m,2}=-(46.118\pm0.055)$ kJ mol^{-1}, by means of a homemade isoperibol solution–reaction calorimeter. The standard molar enthalpy of formation of the compound was determined as: $\Delta_f H^0_m(Zn(Val)SO_4{\cdot}H_2O(s)$, 298.15 K)=$-(1850.97\pm1.92)$ kJ mol^{-1}, from the enthalpies of dissolution and other auxiliary thermodynamic data through a Hess thermochemical cycle. Furthermore, the reliability of the Hess thermochemical cycle was verified by comparing UV/Vis spectra and the refractive indexes of solution A (from dissolution of the [$ZnSO_4{\cdot}7H_2O(s)$+Val(s)] mixture in 2 mol dm^{-3} hydrochloric acid) and solution A' (from dissolution of the complex $Zn(Val)SO_4{\cdot}H_2O(s)$ in 2 mol dm^{-3} hydrochloric acid).

Keywords: *adiabatic calorimetry, isoperibol solution–reaction calorimetry, standard molar enthalpy of formation, UV/Vis spectroscopy, $Zn(Val)SO_4{\cdot}H_2O(s)$*

Introduction

It is well known that zinc is one of the trace elements necessitated for the human body. It plays an important role in human's physical growth, especially intelligence development. Many diseases result from the shortage of the zinc as one of bioelements in the human body. The *L*-α-amino acids are indispensable nutrients in the organism and the basic units that constitute the proteins demanded for life activity. The complexes of zinc with *L*-α-amino acid have been considered to be one of the most efficient zinc-tonics because it has been verified experimentally that this kind of complex has a higher absorption ratio in the human body than that of traditionally inorganic and organic weak-acid zinc-tonics. It is well established that this kind of coordination compound has found wide application in medicines, foodstuffs, forages and cosmetics as nutrient additives [1–3]. Gao *et al*. [4] have investigated phase chemistry of coordination behavior of zinc salts with *L*-α-valine by the method of semi-micro phase equilibrium, the corresponding equilibrium phase diagram and refractive index diagram have been constructed from the compositions of saturated solutions and the data of refractive indexes in ternary systems, and finally synthesized the coordination compound $Zn(Val)SO_4{\cdot}H_2O(s)$ in the mixed solution of water and acetone under the guidance of equilibrium phase diagram. They have characterized the structure and other properties of the complex by means of FTIR, XRD, TG and DTA, and pointed out that the initial decomposition temperature of the solid complex is T_D=323.15 K according to the result of thermogravimetry.

However, up to now, various thermodynamic properties of the complex have not been reported in the literature. As one project of the research program about the complexes of zinc with *L*-α-amino acid, the low-temperature heat capacities over the temperature range between T=78 and 373 K and the standard molar enthalpies of formation at T=298.15 K were measured by adiabatic calorimetry and isoperibol solution-reaction calorimetry, respectively. The experimental values of molar heat capacities were fitted to a polynomial equation of heat capacities ($C_{p,m}$) as a function of reduced temperatures (x), [$x=f(T)$], by a least square method so as to calculate various thermodynamic properties of the coordination compound.

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Reagents and sample

$ZnSO_4 \cdot 7H_2O(s)$, valine(s), α-$Al_2O_3(s)$ and HCl(aq)) used were the reagents of analytical grade and obtained from the Shanghai Reagent Factory, P.R. China. KCl(s) was provided from the National Institute of Standards and Technology, Standard Reference Material 1655. THAM(s) was a NBS-742a standard substance and provided from the formerly National Bureau of Standardisation.

The solid complex $Zn(Val)SO_4 \cdot H_2O(s)$ was a white crystal with a lumpy shape. The sample used for the measurements was prepared by a semi-micro phase equilibrium method [4, 5]. The solid complex obtained was put into a desiccator containing P_4O_{10} until the mass of the complex became constant. The results of chemical and elemental analysis, IR spectra, TG-DTG and XRD indicated that the composition of the complex was $Zn(Val)SO_4 \cdot H_2O(s)$ [4]. The purity of the complex determined by chemical and elementary analysis was higher than 99.90% mass fraction (analytical uncertainty in mass fraction ≤0.2).

Methods

Adiabatic calorimetry

A high-precision automatic adiabatic calorimeter was used to measure the heat capacities over the temperature range $78 \le T \le 373$ K. The calorimeter was established in the Thermochemistry Laboratory of Dalian Institute of Chemical Physics, Chinese Academy of Sciences in P. R. China. The principle and structure of the adiabatic calorimeter were described in detail elsewhere [6, 7]. Briefly, the calorimeter mainly comprised a sample cell, a platinum resistance thermometer, an electric heater, inner and outer adiabatic shields, two sets of six-junctions chromel-constantan thermopiles installed between the calorimetric cell and the inner shield and between the inner and outer shields, respectively, and a high vacuum can. The miniature platinum resistance thermometer (IPRT No. 2, produced by Shanghai Institute of Industrial Automatic Meters, 16 mm in length, 1.6 mm in diameter and a nominal resistance of 100 Ω) was applied to measure the temperature of the sample. The thermometer was calibrated on the basis of ITS-90 by the Station of Low-Temperature Metrology and Measurements, Academia Sinica. The electrical energy introduced into the sample cell and the equilibrium temperature of the cell after the energy input were automatically recorded by use of the Data Acquisition/ Switch Unit (Model 34970A, Agilent, USA), and processed on line by a computer.

To verify the accuracy of the calorimeter, the heat capacity measurements of the reference standard material, α-Al_2O_3, were made over the temperature range $78 \le T \le 373$ K. The sample mass used was 1.6382 g, which was equivalent to 0.0161 mol based on its molar mass, M (Al_2O_3)=101.9613 g mol^{-1}. Deviations of the experimental results from those of the smoothed curve lie within ±0.2%, while the uncertainty is within ±0.3%, as compared with the values given by the former National Bureau of Standards [8] over the whole temperature range.

Heat capacity measurements were continuously and automatically carried out by means of the standard method of intermittently heating the sample and alternately measuring the temperature. The heating rate and temperature increments were generally controlled at 0.1 to 0.4 K min^{-1} and 1 to 3 K. The heating duration was 10 min, and the temperature drift rates of the sample cell measured in an equilibrium period were always kept within 10^{-3} to 10^{-4} K min^{-1} during the acquisition of all heat capacity data. The data of heat capacities and corresponding equilibrium temperature have been corrected for heat exchange of the sample cell with its surroundings [6, 7]. The sample mass used for calorimetric measurements was 2.0433 g, which was equivalent to 0.0069 mol in terms of its molar mass, M=296.618 g mol^{-1}.

Isoperibol solution–reaction calorimetry

The isoperibol solution–reaction calorimeter consisted primarily of a precision temperature controlling system, an electric energy calibration system, the calorimetric body, the electric stirring system, the thermostatic bath made by transparent silicate glass, the precision temperature measuring system and the data acquisition system. The principle and structure of the calorimeter were described in detail elsewhere [9, 10].

The reliability of the calorimeter was verified previously [10] by measuring the dissolution enthalpies of THAM (NBS 742a, USA) in 0.1 mol dm^{-3} hydrochloric acid and KCl (calorimetrically primary standard) in double distilled water at T=298.15 K.

In all dissolution experiments of the sample, 2 mol dm^{-3} HCl was chosen as the calorimetric solvent for measuring the dissolution enthalpies of the [Val(s) and $ZnSO_4 \cdot 7H_2O(s)$] mixture and the complex $Zn(Val)SO_4 \cdot H_2O(s)$, respectively.

The solid $ZnSO_4 \cdot 7H_2O(s)$ was ground within an agate mortar into fine powder. The mixture of about 0.001 mol of Val(s) and about 0.001 mol of $ZnSO_4 \cdot 7H_2O(s)$ at mole ratio of $n(ZnSO_4 \cdot 7H_2O):n(Val)$= 1:1 was dissolved in 100 mL of 2 mol dm^{-3} HCl at T=298.15 K. The final solution obtained was designated as solution A.

The solid complex Zn(Val)SO_4·H_2O(*s*) was dried in a vacuum desiccator in order to take off some additional adsorbing water. Then, it was ground into fine powder. The dissolution enthalpy of about 0.001 mol of Zn(Val)SO_4·H_2O(*s*) in 100 mL of 2 mol dm^{-3} hydrochloric acid was determined under the same condition as the above. The final solution obtained was named as solution A'.

Finally, UV/Vis spectroscopy and the data of the refractive indexes were used to confirm whether solution A was in the same thermodynamic state as that of solution A'. These results have indicated that chemical components and physical-chemistry properties of solution A were consistent with those of solution A'.

Results and discussion

Low-temperature heat capacities

All experimental results, listed in Table 1 and plotted in Fig. 1, showed that the structure of the coordination compound was stable over the temperature range between *T*=78 and 327 K, no phase change, association nor thermal decomposition occurred. However, at temperatures above 327 K, the heat capacity curve began to rise steeply. The phenomenon was associated with the dehydration or thermal decomposition of the

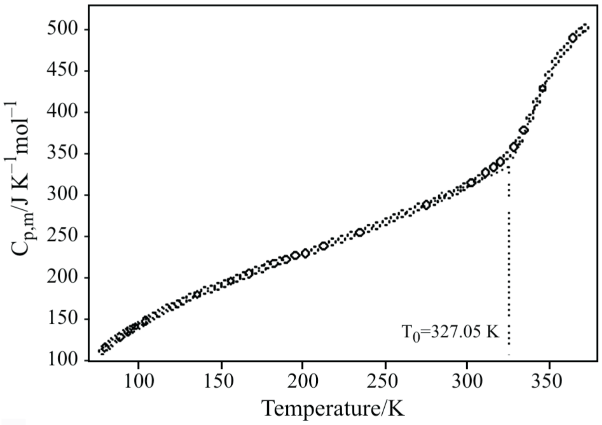

Fig. 1 The curve of the experimental molar heat capacities of the complex Zn(Val) SO_4·H_2O(*s*) *vs.* the temperature (*T*)

Table 1 The experimental molar heat capacities of the complex Zn(Val)SO_4·H_2O (M=296.6182 g mol^{-1})

Temperature/K	$C_{p,m}$/J K^{-1} mol^{-1}	Temperature/K	$C_{p,m}$/J K^{-1} mol^{-1}	Temperature/K	$C_{p,m}$/J K^{-1} mol^{-1}
78.099	114.03	152.514	194.39	275.730	289.06
80.164	117.75	156.434	197.91	280.499	293.91
82.008	120.77	160.354	200.40	285.138	298.62
84.295	124.94	164.173	204.51	289.711	301.83
86.582	127.83	167.998	206.72	294.285	306.39
89.016	130.72	171.787	210.24	298.792	311.24
91.450	134.06	175.446	212.54	303.235	315.37
93.810	137.28	179.235	216.67	307.678	320.87
96.023	140.29	182.828	218.50	311.989	327.76
98.295	142.86	186.422	222.17	316.367	334.59
100.508	145.17	190.080	223.74	320.679	341.17
102.691	147.29	195.960	227.98	324.991	348.40
104.801	150.06	201.709	231.04	329.172	358.66
107.235	152.88	207.458	235.34	331.916	365.49
109.669	155.96	213.076	240.21	335.248	377.33
112.398	158.79	218.695	244.19	338.710	392.45
115.128	161.81	224.183	248.11	342.630	409.81
117.709	164.89	229.671	252.91	346.550	425.85
120.807	168.87	235.094	255.30	350.339	439.79
123.834	170.31	240.386	260.58	354.194	457.68
127.427	173.83	245.678	264.59	357.983	469.64
131.804	178.39	250.904	269.11	361.642	481.21
136.051	181.91	256.012	273.21	365.235	493.05
140.297	185.87	261.096	277.68	368.828	503.57
144.413	188.81	266.061	280.73	372.161	511.46
148.464	190.57	270.896	286.09		

compound, as shown by TG analysis [3]. In addition, the initial dehydration temperature (T_D) has been obtained by means of the analysis of heat capacity curve. Two sections of the heat capacity curves for 78 to 326 and 328 to 371 K were extrapolated linearly. The intersection point of these two straight lines was the initial decomposition temperature, T_D=327.05 K (Fig. 1). TG analysis had given the initial dehydration temperature (323.15 K), the final dehydration temperature (470.15 K) and the mass loss% (6.10) of the compound. The mass loss% was identical with the percentage of the water molecule in the coordination compound (the theoretical mass loss of the dehydration was 6.07%). The initial dehydration temperature obtained from TG analysis was in agreement with that from the heat capacity curve.

Because dehydration of the sample started at 327.05 K, the section of the heat capacity curve in the temperature range $328 \le T \le 373$ K corresponded to the thermal anomaly of the compound on the basis of the above analysis. Therefore, the useful and real section of the heat capacity curve of the compound itself was in the temperature region $78 \le T \le 327$ K. The 107 experimental points in the temperature region between 78 and 327 K were fitted by means of the least square method and a polynomial equation of experimental molar heat-capacities ($C_{p,m}$) *vs.* reduced temperature (x), $x=f(T)$, has been obtained:

$$C_{p,m}/\mathrm{J\ K^{-1}\ mol^{-1}}=232.026+92.139x+4.619x^2+6.701x^3-19.032x^4+20.597x^5+15.045x^6$$

where $x=(T/\mathrm{K}-202)/124$. The standard deviations of experimental molar heat capacities from the smoothed heat capacities calculated by the polynomial equation were within ±0.3% except for several points around the lower and upper temperature limits. The plot of the relative deviations of the experimental molar heat capacities $C_{p,m}$ (exp.) of the coordination compound from the smoothed heat capacities $C_{p,m}$(cal.) against the experimental temperature T were given in Fig. 2.

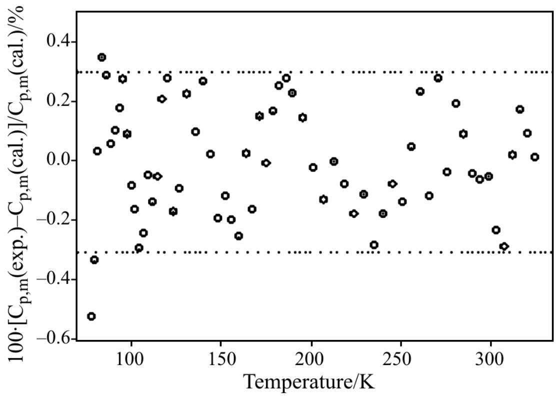

Fig. 2 The relative deviations of experimental molar heat capacities $C_{p,m}$(exp.) from smoothed heat capacities $C_{p,m}$(cal.)

Thermodynamic functions of the complex Zn(Val)SO$_4$·H$_2$O(s)

The smoothed molar heat capacities and thermodynamic functions of the complex Zn(Val)SO$_4$·H$_2$O(*s*) were calculated based on the fitted polynomial of the heat capacities as a function of the reduced temperature (x) according to the following thermodynamic equations:

$$H_T - H_{298.15\,\mathrm{K}} = \int_{298.15\,\mathrm{K}}^{T} C_{p,m}\,\mathrm{d}T$$

$$S_T - S_{298.15\,\mathrm{K}} = \int_{298.15\,\mathrm{K}}^{T} C_{p,m}T^{-1}\,\mathrm{d}T$$

The polynomial fitted values of the molar heat capacities and fundamental thermodynamic functions of the sample relative to the standard reference temperature 298.15 K were tabulated in Table 2 with the interval of 5 K.

The standard molar enthalpy of formation of the complex Zn(Val)SO$_4$·H$_2$O(s)

The complex Zn(Val)SO$_4$·H$_2$O(*s*) was one of the products in the following reaction:

$$\mathrm{ZnSO_4{\cdot}7H_2O}(s)+\mathrm{Val}(s)= \mathrm{Zn(Val)SO_4{\cdot}H_2O}(s)+6\mathrm{H_2O}(l) \quad (1)$$

The enthalpy change of the above supposed reaction and standard molar enthalpy of formation of the complex Zn(Val)SO$_4$·H$_2$O(*s*) were determined through a designed Hess thermochemical cycle using the experimental data of isoperibol calorimetry and other auxiliary thermodynamic data.

If '*s*'=calorimetric solvent, 2 mol dm^{-3} HCl(*aq*), the dissolution process of the mixture of reactants in the reaction (1) was expressed into:

$$\{\mathrm{ZnSO_4{\cdot}7H_2O}(s) \text{ and } \mathrm{Val}(s)\}+\text{'}s\text{'}=\text{solution A}$$

The experimental results of the process were listed in Table 3.

The dissolution process of the product, Zn(Val)SO$_4$·H$_2$O(*s*), in the reaction (1) may be expressed as follows:

$$\mathrm{Zn(Val)SO_4{\cdot}H_2O}(s)+\text{'}s\text{'}=\text{solution A'}$$

The results of the dissolution experiments were shown in Table 4.

The dissolution enthalpy of 6H$_2$O(*l*) ($\Delta_{\mathrm{sol}}H^0_{\mathrm{m,3}}$) as one of the products in the reaction (1) in the solvent was within the range of experimental error, which cannot be detected and may be omitted because the amount of H$_2$O(*l*) was very small according to the stoichiometric number of H$_2$O(*l*) in the reaction, namely, $\Delta_{\mathrm{sol}}H^0_{\mathrm{m,3}}$/kJ mol^{-1}=0.

Table 2 Thermodynamic functions of the complex $Zn(Val)SO_4{\cdot}H_2O$

Temperature/K	$C_{P,\,m}$/J K^{-1} mol^{-1}	$[H_T–H_{298.15\,K}]$/J mol^{-1}	$[S_T–S_{298.15\,K}]$/J K^{-1} mol^{-1}
80	117.762	–48125.3	–264.7
85	125.047	–47518.3	–257.3
90	131.981	–46875.6	–250.0
95	138.571	–46199.2	–242.7
100	144.827	–45490.7	–235.4
105	150.764	–44751.6	–228.3
110	156.401	–43983.6	–221.2
115	161.756	–43188.2	–214.1
120	166.851	–42366.6	–207.2
125	171.710	–41520.1	–200.3
130	176.354	–40649.9	–193.5
135	180.809	–39756.9	–186.7
140	185.098	–38842.1	–180.1
145	189.242	–37906.2	–173.5
150	193.264	–36949.9	–167.0
155	197.186	–35973.7	–160.5
160	201.025	–34978.2	–154.2
165	204.801	–33963.6	–147.9
170	208.529	–32930.3	–141.7
175	212.222	–31878.4	–135.6
180	215.895	–30808.1	–129.5
185	219.556	–29719.4	–123.6
190	223.216	–28612.5	–117.6
195	226.879	–27487.3	–111.8
200	230.553	–26343.7	–106.0
205	234.240	–25181.7	–100.2
210	237.943	–24001.3	–94.56
215	241.664	–22802.3	–88.93
220	245.403	–21584.6	–83.35
225	249.161	–20348.2	–77.81
230	252.938	–19093.0	–72.32
235	256.735	–17818.8	–66.87
240	260.554	–16525.6	–61.46
245	264.399	–15213.2	–56.07
250	268.274	–13881.5	–50.72
255	272.189	–12530.4	–45.39
260	276.153	–11159.6	–40.09
265	280.184	–9768.77	–34.80
270	284.300	–8357.60	–29.53
275	288.527	–6925.57	–24.27
280	292.899	–5472.06	–19.03
285	297.453	–3996.25	–13.78
290	302.238	–2497.10	–8.542
295	307.309	–973.330	–3.302
298.15	310.682	0	0
300	312.735	576.675	1.940
305	318.593	2154.87	7.187
310	324.974	3763.65	12.44
315	331.981	5405.88	17.70
320	339.732	7084.99	22.98
325	348.363	8805.05	28.27

Table 3 Dissolution enthalpy of [$ZnSO_4\cdot 7H_2O(s)$ and Val(s)] mixture [$n(ZnSO_4\cdot 7H_2O):n(Val)=1:1$] in 100 mL 2 mol dm^{-3} HCl at 298.15 K (I=10.115 mA, R=1017.2 Ω)

No.	W_{Val}/g	$W_{ZnSO_4\cdot 7H_2O}$/g	ΔE_s/mV	ΔE_e/mV	Time/s	Q_s/J	$\Delta_d H^0_{m,1}$/kJ mol^{-1}
1	0.1175	0.2886	2.5546	2.5915	923.9	94.780	94.495
2	0.1178	0.2892	2.7599	2.7694	917.5	95.152	94.625
3	0.1180	0.2897	2.5095	2.5770	939.7	95.229	94.541
4	0.1174	0.2882	2.6943	2.7282	923.0	94.864	94.659
5	0.1176	0.2888	2.7284	2.7681	926.1	94.999	94.633
6	0.1179	0.2894	2.7087	2.7559	930.5	95.183	94.575
							Avg. $\Delta_d H^0_{m,1}$/kJ mol^{-1}=(94.588±0.025)

m – mass of sample; ΔE_e – the voltage change during the electrical calibration; ΔE_s – the voltage change during the sample dissolution; t – heating duration of electrical calibration; Q_s – heat effect of sample dissolution; $\Delta_{sol}H^0_m$ – dissolution enthalpy, $\Delta_{sol}H^0_m=(\Delta E_s/\Delta E_e)\cdot I^2RT\cdot(M/W)$, where R is the electrical resistance of the heater in the reaction vessel (R=1017.2 Ω at T=298.15 K);

Table 4 Dissolution enthalpy of the $Zn(Val)SO_4\cdot H_2O(s)$ in 100 mL of 2 mol dm^{-3} HCl at 298.15 K

No.	$W_{Zn(Val)SO_4\cdot H_2O}$/g	ΔE_s/mV	ΔE_e/mV	Time/s	Q_s/J	$\Delta_d H^0_{m,2}$/kJ mol^{-1}
1	0.2967	–3.5603	3.3702	419.0	–46.076	–46.064
2	0.2966	–3.5703	3.3734	417.4	–45.975	–45.978
3	0.2969	–3.5783	3.4013	421.6	–46.202	–46.158
4	0.2965	–3.5855	3.3309	412.3	–46.172	–46.191
5	0.2970	–3.6404	3.3744	411.6	–46.275	–46.215
6	0.2964	–3.5818	3.3251	411.2	–46.067	–46.101
						Avg. $\Delta_d H^0_{m,2}$/kJ mol^{-1}=–(46.118±0.055)

The enthalpy change of the reaction (1), $\Delta_r H_m(1)$, can be calculated in accordance with the above designed Hess thermochemical cycle and experimental results listed in Tables 3 and 4 by means of the following equation as follows:

$$\Delta_r H_m(l)=\Delta_{sol}H^0_{m,1}-(\Delta_{sol}H^0_{m,2}+\Delta_{sol}H^0_{m,3})=$$
$$-(140.706\pm0.060)\ \mathrm{kJ\ mol^{-1}}$$

A reaction scheme used to derive the standard molar enthalpy of formation of the complex $Zn(Val)SO_4\cdot H_2O(s)$ has given in Table 5. The enthalpy change of the reaction (1) obtained from experimental values of the dissolution enthalpies of the [Val(s)+$ZnSO_4\cdot 7H_2O(s)$] mixture and the complex $Zn(Val)SO_4\cdot H_2O(s)$ in 100 cm^3 of 2 mol dm^{-3} HCl were combined with some auxiliary thermodynamic data, $\Delta_f H^0_m$ [$ZnSO_4\cdot 7H_2O(s)$, 298.15 K]=–3077.75 kJ mol^{-1} [11], $\Delta_f H^0_m$ [Val(s)]=–(628.90±1.90) kJ mol^{-1} [12] and $\Delta_f H^0_m$ [$H_2O(l)$, 298.15 K]=–(285.83±0.04) kJ mol^{-1} [13], to calculate the standard molar enthalpy of formation of the complex $Zn(Val)SO_4\cdot H_2O(s)$ as follows:

$$\Delta_f H^0_m[Zn(Val)SO_4\cdot H_2O(s)]=\Delta H_7=\Delta H_1-(\Delta H_2+\Delta H_3)$$
$$+(\Delta H_4+\Delta H_5-6\Delta H_6)=\Delta_r H_m(l)+(\Delta_f H^0_m[ZnSO_4\cdot 7H_2O(s)]$$
$$+\Delta_f H^0_m[L\text{-}Val(s)]-6\Delta_f H^0_m[H_2O(l)])=$$
$$-(1850.97\pm1.92)\ \mathrm{kJ\ mol^{-1}}$$

where ΔH_1, ΔH_2,...ΔH_7 are the molar enthalpy changes of the corresponding reactions in Table 5.

The results of UV-Vis spectra and refrangibility (refractive index) were two important information for detecting the differences of the structure and composition between two kinds of solutions. In this paper, all of the reactants and products of the reaction (1) can be easily dissolved in the selected solvent. The measured values of the refractive indexes of solution A and solution A' were (1.3883±0.0007) and (1.3878±0.0008), respectively. The results of UV-Vis spectroscopy were shown in Fig. 3. UV/Vis spectrum and the data of the refractive indexes of solution A obtained agreed with those of solution A', no differ-

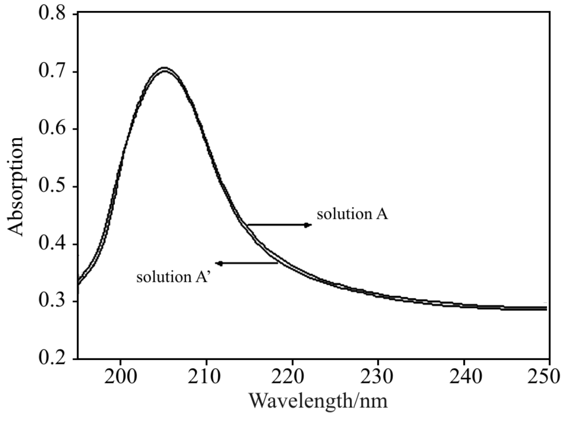

Fig. 3 UV/Vis spectra of solution A and solution A' obtained from the dissolution of the [$ZnSO_4\cdot 7H_2O(s)$ and Val(s)] mixture and the $Zn(Val)SO_4\cdot H_2O(s)$ in the supposed reaction (1) in 100 cm^3 of 2 mol dm^{-3} HCl (diluted into 1:20)

Table 5 Reaction scheme used to determine the standard molar enthalpy of formation of the complex Zn(Val)SO_4·H_2O (*s*) at 298.15 K

No.	Reaction scheme	$\Delta_f H_m^0 \Delta_d H_m^0 \pm \sigma_a$/kJ mol^{-1}
1	{$ZnSO_4$·$7H_2O(s)$ and Val(*s*)}+'*s*'^{a}=solution A	(94.588±0.025) (ΔH_1)
2	{Zn(Val)SO_4·$H_2O(s)$}+'*s*'^{a}=solution A'	–(69.875±0.055)(ΔH_2)
3	solution A'+$6H_2O(l)$=solution A	0 (ΔH_3)
4	$Zn(s)+S(s)+11/2O_2(g)+7H_2(g)=ZnSO_4\cdot 7H_2O(s)$	–3077.75 (ΔH_4)
5	$5C(s)+1/2N_2(g)+O_2(g)+11/2H_2(g)$=Val(*s*)	–(628.90±1.90) (ΔH_5)
6	$1/2O_2(g)+H_2(g)=H_2O(l)$	–(285.83±0.04) (ΔH_6)
7	$Zn(s)+S(s)+7/2O_2(g)+5C(s)+11/2H_2(g)$=Zn(Val)$SO_4$·$H_2O(s)$	–(1850.97±1.92) (ΔH_7)

^{a}'*s*' – calorimetric solvent, 2 mol dm^{-3} hydrochloric acid; $\sigma_a=\sqrt{\sum_{i=1}^{n}(x_i-\bar{x})^2/n(n-1)}$, where *n* – experimental number, x_i – a single value in a set of dissolution measurements; $\bar{x}$ – the mean value of a set of measurement results

ence in the structure and chemical composition existed between the two solutions. These results have demonstrated that the solutions A and A' were same, the designed Hess thermochemical cycle was reasonable and reliable, and can be used to derive the standard molar enthalpy of formation of the coordination compound Zn(Val)SO_4·$H_2O(s)$.

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