J. Chem. Eng. Data **2010,** *55,* 2451–2454

Phase Equilibrium System of Cadmium Chloride + DL-Alanine + Water at 298.15 K and Standard Molar Enthalpy of Formation of $Cd_3(Ala)_2Cl_6 \cdot 4H_2O$

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The equilibrium solubility of the ternary system cadmium chloride + DL-alanine (Ala) + water was determined at 298.15 K, and the corresponding equilibrium diagram was constructed. The ternary system is complicated with three equilibrium solid phases, $CdCl_2 \cdot 2.5H_2O$, $Cd_3(Ala)_2Cl_6 \cdot 4H_2O$, and Ala, of which a new compound of $Cd_3(Ala)_2Cl_6 \cdot 4H_2O$ was found to be congruently soluble in the system. The new compound obtained was identified and characterized by the methods of IR, elementary analysis, X-ray diffraction, X-ray diffraction single crystal structure analysis, thermogravimetry, and differential thermogravimetry. It belongs to the monoclinic system, with space group P2(1)/*n*, $a = 0.70393(16)$ nm, $b = 0.9074(2)$ nm, $c = 1.6982(4)$ nm, $\beta = 92.529(4)°$, $V = 1.0837(4)\ \mathrm{nm}^3$, $Dc = 2.434\ \mathrm{g \cdot cm^{-3}}$, $Z = 2$. The dissolution enthalpies of Ala, $CdCl_2$, and $Cd_3(Ala)_2Cl_6 \cdot 4H_2O$ in 2 $\mathrm{mol \cdot dm^{-3}}$ H_2SO_4 were measured by heat conduction microcalorimetry. By designing a thermochemical cycle according to Hess' Law and through calculation, we obtained the reaction enthalpy of Ala with cadmium chloride, $\Delta_r H_m^{\Theta}(298.15\ \mathrm{K}) = -(50.86 \pm 0.77)\ \mathrm{kJ \cdot mol^{-1}}$, and the standard molar enthalpy of formation of $Cd_3(Ala)_2Cl_6 \cdot 4H_2O$, $\Delta_f H_m^{\Theta} = -(3499.9 \pm 1.1)\ \mathrm{kJ \cdot mol^{-1}}$.

Introduction

Phase diagrams of ternary systems of zinc chloride + amino acids (valine (Val), leucine (Leu), threonine (Thr), methionine (Met), phenylalanine (Phe), histidine (His), tryptophane (Try)) + water at 298.15 K have been investigated. The corresponding solubilities were determined in previous studies.[1−4] It is highly valuable and important for us to understand the phase relations and interactions of zinc chloride and amino acids in aqueous media. We can estimate whether new solid-phase compounds are formed and if they are congruently or incongruently soluble in aqueous systems. These can provide the fundamental basis and serve as a guide for the preparation of new solid phase compounds. For the zinc chloride + amino acid (AA) (Leu, Try, His) + water systems,[1,4] three equilibrium solid-phase regions $ZnCl_2$, $Zn(AA)Cl_2 \cdot nH_2O$ (1:1 type) ($n = 0, 0.5$), and AA were observed. In these ternary systems, the new compound $Zn(Try)Cl_2 \cdot 0.5H_2O$ is incongruently soluble, whereas $Zn(Leu)Cl_2$ and $Zn(His)Cl_2 \cdot 0.5H_2O$ are congruently soluble in the aqueous systems. These results showed that phase chemical reactions of the three ternary systems are similar (they all have a 1:1 type compound). Li et al. and Gao et al. re-examined the zinc chloride + AA (Val, Thr, Phe, Met) + water systems[1−3] and confirmed the presence of four stable complexes $ZnCl_2$, $Zn(AA)Cl_2 \cdot nH_2O$ (1:1 type), $Zn(AA)_2Cl_2 \cdot nH_2O$ (1:2 type) ($n = 0, 0.5, 1, 2$) and AA, and the new compounds of the 1:1 and 1:2 types are incongruently soluble in the aqueous systems. Comparing the four ternary systems,[1−3] we find that the phase chemical behavior of the four ternary systems is very similar because they all have 1:1 type and 1:2 type compounds and are incongruently soluble in the aqueous systems.

Cadmium and zinc are in the same subgroup B. To find out interactions of cadmium chloride with amino acid, contrast the difference of the phase chemical relationship of cadmium chloride and zinc chloride with amino acid in aqueous salt systems, and provide equilibrium data in the aqueous ternary systems of cadmium chloride and amino acid to scientists and engineers using corresponding phase diagrams, it is necessary for us to further study the phase equilibria systematically. The present paper is concerned with the solubility and phase equilibrium relations of the cadmium chloride + Ala + water system at 298.15 K and related measurement of properties of a new solid-phase compound established in the system.

Experimental Section

Reagents. $CdCl_2$ (mass fraction $\geqslant 0.996$), DL-alanine (mass fraction $\geqslant 0.998$), KCl (mass fraction $\geqslant 0.9999$), and sulfuric acid (mass fraction $\geqslant 0.995$) were used.

Investigations on the System at 298.15 K and Analysis Methods. The method of investigation of the solubility of the cadmium chloride + Ala + water ternary system has been previously reported.[5] All sealed samples were put in a big water tank with a thermostat fixed at 298.15 K and an electrical stirrer. The precision of the temperature was 0.1 K. The solid−liquid phase equilibrium was established for these samples after (22 to 25) days.

The saturated solutions and the corresponding wet solid phases (wet residues) of the samples were separated, taken out, and analyzed. The analysis methods were as follows: (1) The concentration of Cd^{2+} by titration with a normal solution of EDTA. (2) The concentration of Cl^- was analyzed by titration with a normal solution of silver nitrate. (3) The concentration of formic acid in formaldehyde solution was first determined by the titration with a solution of sodium hydroxide as the blank experiment. Then, the concentration of DL-alanine was titrated with sodium hydroxide, and the termination was determined by a pH potentiometer after the amidogen of DL-alanine was blanketed with formaldehyde solution and Cd^{2+} was blanketed with a screening agent of 1,10-phenanthroline. The composition of the new compound in the system was determined by the well-

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10.1021/je900845g

Table 1. Solubility Data of the Ternary System Cadmium Chloride + Ala + Water at 298.15 K

	composition of saturated solution (%)[a]		composition of wet residue (%)		
no.	Ala	$CdCl_2$	Ala	$CdCl_2$	solid phase[b]
1	0.00	55.60	-----	-----	A
2	1.87	55.49	0.63	74.40	A
3	2.71	55.47	0.48	76.08	A
4	2.92	55.01	0.59	75.56	A
5	3.03	55.00	6.50	67.49	A + B
6	3.22	49.69	16.78	63.57	B
7	4.41	44.86	16.95	61.33	B
8	4.81	41.34	16.52	59.59	B
9	7.44	36.37	17.75	59.27	B
10	10.63	32.23	18.43	56.72	B
11	12.06	30.94	19.19	58.10	B
12	14.94	30.63	20.52	59.96	B
13	18.98	29.03	21.59	57.87	B
14	20.63	28.83	27.62	56.50	B + C
15	20.74	28.46	35.18	51.52	B + C
16	20.75	27.61	60.40	13.46	C
17	19.55	20.69	65.28	8.77	C
18	17.99	13.39	73.16	4.25	C
19	16.61	6.64	79.99	2.07	C
20	14.30	0.00	-----	-----	C

[a] Double saturation point (average): E_1: $CdCl_2$, 55.00 %; Ala, 3.03 %. E_2: $CdCl_2$, 28.64 %; Ala, 20.68 %. [b] Compounds: A, $CdCl_2 \cdot 2.5H_2O$; B, $Cd_3(Ala)_2Cl_6 \cdot 4H_2O$; C, Ala.

known wet residue method of Schreinemaker[6] and checked by chemical analysis.

Equipment and Conditions. C, H, N, and O analyses were carried out with a Vario EL III CHNOS element analysis instrument. The IR analysis was conducted on a Nicolet 5700 spectrometer (KBr discs). Thermal characterization of the new compound was undertaken with a SDT Q600 V8.0 thermal analysis apparatus (TG-DTG) that worked with a heating rate of 10 $K \cdot min^{-1}$ under a N_2 atmosphere with a flow rate of 100 $cm^3 \cdot min^{-1}$. X-ray diffraction (XRD) measurements were performed by a D/Max-3C diffractometer using Cu Kα radiation, 50 kV and 80 mA, at room temperature, in air. The diffraction data of the structure analysis were collected by a Bruker Smart Apex-II CCD diffractometer using graphite monochromatized Mo Kα radition ($\lambda = 0.071\,073$ nm), at room temperature.

An RD496-III-2000 heat conduction microcalorimeter (Southwest Institute of Electron Engineering, China) was used at 298.15 K and was described in detail previously.[7,8]

The enthalpy of solution of KCl in deionized water was measured to verify microcalorimeter calibration. The mean value (17.31 ± 0.06) $kJ \cdot mol^{-1}$ of $\Delta_{sol}H_m$ agrees with the literature value of 17.234 $kJ \cdot mol^{-1}$ reported in ref 9.

Each calorimetric experiment was performed five times. The temperature of the calorimetric experiment was (298.15 ± 0.01) K. The sulfuric acid solution (2 $mol \cdot dm^{-3}$) was put in the 15 cm^3 Teflon sample cell and reference cell of the calorimeter. After thermal equilibration for at least 1.5 h, the solid sample was pressed into the solvent by a rod. The thermal effect was then recorded automatically on a computer. The total time required for complete dissolution was about 25 min. There were no solid residues observed after the dissolutions.

Results and Discussion

Cadmium Chloride + Ala + Water System at 298.15 K. The solubility data of the cadmium chloride + Ala + water system at 298.15 K are listed in Table 1. Figure 1 depicts the corresponding phase equilibrium diagram.

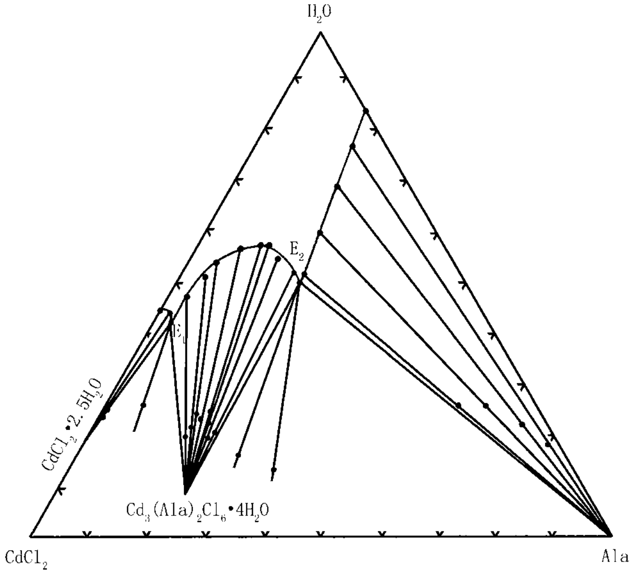


Figure 1. Isothermal solubility diagram of the system cadmium chloride + Ala + water at 298.15 K.

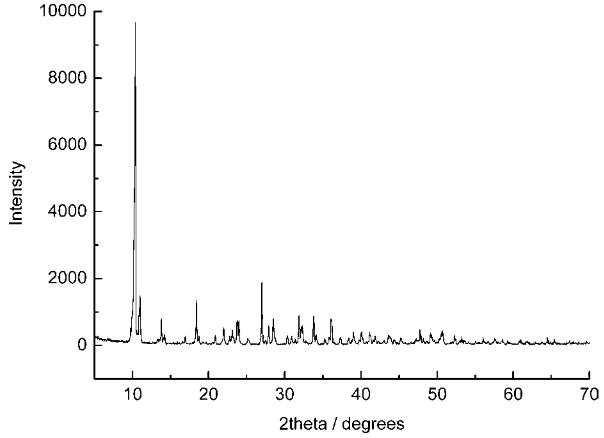


Figure 2. X-ray powder diffraction spectrum of $Cd_3(Ala)_2Cl_6 \cdot 4H_2O$.

As can be seen in Figure 1, the curves of solubility in the ternary system consist of three branches of cadmium chloride + Ala + water, which correspond to the equilibrium solid phases of $CdCl_2 \cdot 2.5H_2O$ (A), $Cd_3(Ala)_2Cl_6 \cdot 4H_2O$ (3:2 type) (B), and Ala (C), respectively. It indicates that a new phase region of the $Cd_3(Ala)_2Cl_6 \cdot 4H_2O$ (B) compound was formed in the system except for initial compounds A and C, and the compound $Cd_3(Ala)_2Cl_6 \cdot 4H_2O$ is congruently soluble in the aqueous and has not been reported in the literature so far. $Cd_3(Ala)_2Cl_6 \cdot 4H_2O$ obtained from the system was analyzed by a titration method. Its composition by mass was analyzed as follows: Cd (42.10 %), Ala (22.20 %), and Cl (26.62 %) in agreement with theoretical data (42.14 % Cd, 22.27 % Ala, and 26.58 % Cl). The compound $Cd_3(Ala)_2Cl_6 \cdot 4H_2O$ was analyzed by a Vario EL III CHNOS element analysis instrument. The contents of C, N, H, and O are 9.09 %, 3.42 %, 2.56 %, and 16.21 %, respectively. These values are also in agreement with theoretical data (9.00 % C, 3.50 % N, 2.75 % H, and 15.99 % O).

Characterization of $Cd_3(Ala)_2Cl_6 \cdot 4H_2O$. The X-ray powder diffraction pattern of the $Cd_3(Ala)_2Cl_6 \cdot 4H_2O$ compound obtained is shown in Figure 2. It is neither the same as $CdCl_2$ nor Ala, nor the simple superposition of $CdCl_2$ and Ala. This demonstrates that $Cd_3(Ala)_2Cl_6 \cdot 4H_2O$ is formed from a reaction between $CdCl_2$ and Ala.

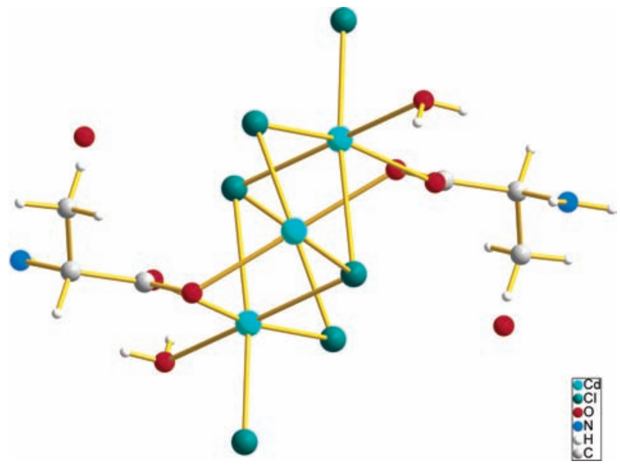


Figure 3. Asymmetric unit structure of $Cd_3(Ala)_2Cl_6 \cdot 4H_2O$.

The FT-IR spectra of Ala and the complex $Cd_3(Ala)_2Cl_6 \cdot 4H_2O$ were recorded from the KBr tablet in the region of (4000 to 100) cm^{-1}. Compared with that of Ala, the spectrum of the as-formed complex displays several significant differences: (1) The adsorption peaks at (3086 and 2958) cm^{-1} result from the asymmetrical stretching vibration and the symmetrical stretching vibration of NH_3^+; however, as for the complex, these adsorption bands become broadened and are shifted to 3130 cm^{-1}, which reveals the existence of strong hydrogen bonds between amino groups and H_2O. (2) For the spectrum of the complex, the adsorption bonds at (1624 and 1410) cm^{-1}, assigned to the asymmetrical and symmetrical stretching vibrations of COO^- in Ala, are shifted to (1619 and 1464) cm^{-1}, respectively. The results indicate that these carboxyl groups of the complexes are doubly coordinated. (3) The band around 3444 cm^{-1} is attributed to the stretching vibration of −OH in the H_2O molecule. The band observed near 531 cm^{-1} is the wagging vibration of H_2O, which indicates that the H_2O molecule takes part in coordination. (4) The complexes also exhibit some bands in the low wavelength range. For example, the bands around 369 cm^{-1} and 357 cm^{-1} are assigned to the symmetrical stretching vibration of Cd−O, and the peaks around 283 cm^{-1}, 266 cm^{-1}, and 260 cm^{-1} are ascribed to the symmetrical stretching vibration of Cd−Cl, which suggests that the oxygen atoms and chlorine atoms also take part in coordination.

A single crystal of $Cd_3(Ala)_2Cl_6 \cdot 4H_2O$ with approximate dimension of 0.12 mm × 0.10 mm × 0.08 mm was selected for structure analysis. The compound $Cd_3(Ala)_2Cl_6 \cdot 4H_2O$ belongs to a monoclinic system, with space group P2(1)/*n*, $a = 0.70393(16)$ nm, $b = 0.9074(2)$ nm, $c = 1.6982(4)$ nm, $\beta = 92.529(4)°$, $V = 1.0837(4)$ nm^3, Dc = 2.434 $g \cdot cm^{-3}$, $Z = 2$. The asymmetric unit structure of the compound is shown in Figure 3. As shown in Figure 3, there are two H_2O molecules taking part in coordination, and the other two H_2O molecules form crystalloid water in $Cd_3(Ala)_2Cl_6 \cdot 4H_2O$.

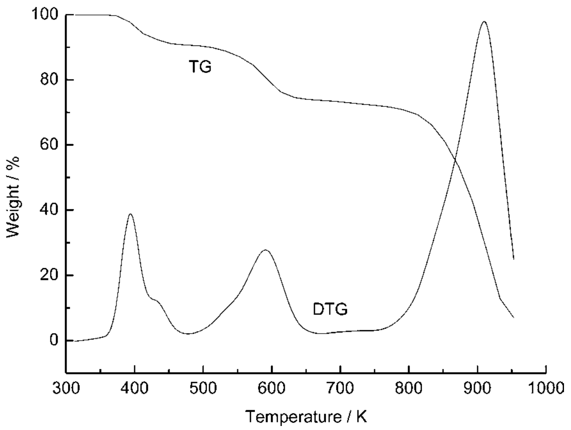
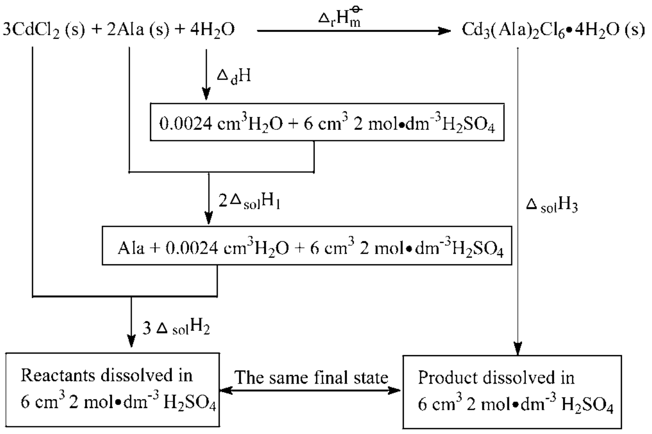


Figure 4. Thermogravimetric curve of $Cd_3(Ala)_2Cl_6 \cdot 4H_2O$.

TG−DTG curves for the compound are presented in Figure 4. It can be seen clearly from the TG curve that there exist three steps in the process of the thermal decomposition of $Cd_3(Ala)_2Cl_6 \cdot 4H_2O$. The solid complex was stable below 360 K and started decomposition at this point. The first mass loss, 9.19 %, took place in the range of (360 to 475) K, which was associated with the loss of water and can be compared with the calculated value of 9.00 %. The second mass loss, 17.12 %, occurred in the temperature range (508 to 643) K, which corresponded to the decomposition of Ala. The third mass loss arose at 782 K, which represented the sublimation of cadmium chloride. It should be noted that the first mass loss value was in accordance with data of water determined by the Schreinemaker method and analyzed by a titration method.

Enthalpy of Reaction. H_2SO_4(aq) (2 $mol \cdot dm^{-3}$) rapidly dissolves all components of the reaction. According to Hess's law, the reaction enthalpy of Ala and cadmium chloride, $\Delta_r H_m^{\Theta}(s)$, can be calculated on the basis of the thermochemical cycle.



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The molar enthalpy of dilution of 2.4 mg of water in 6.00 cm^3 of [2 $mol \cdot dm^{-3}$ H_2SO_4(aq)] at 298.15 K, $\Delta_d H$, was very small, in the range of measurement error, and can be ignored.[9,10] The molar enthalpy of solution of 5.94 mg of Ala in 6.00 cm^3 of [0.0024 cm^3 H_2O + 2 $mol \cdot dm^{-3}$ H_2SO_4(aq)] at 298.15 K, $\Delta_{sol}H_1$, was (3.60 ± 0.094) $kJ \cdot mol^{-1}$. The molar enthalpy of solution of 18.34 mg of $CdCl_2$ in 6.00 cm^3 of [5.94 mg of Ala + 0.0024 cm^3 of H_2O + 2 $mol \cdot dm^{-3}$ H_2SO_4(aq)] at 298.15 K, $\Delta_{sol}H_2$, was −(4.39 ± 0.22) $kJ \cdot mol^{-1}$. The molar enthalpy of solution of 26.68 mg of $Cd_3(Ala)_2Cl_6 \cdot 4H_2O$ in 6.00 cm^3 of [2 $mol \cdot dm^{-3}$ H_2SO_4(aq)] at 298.15 K, $\Delta_{sol}H_3$, was (44.89 ± 0.36) $kJ \cdot mol^{-1}$. The values of $\Delta_{sol}H_1$, $\Delta_{sol}H_2$, and $\Delta_{sol}H_3$ are listed in Table 2, in which *m* was the mass of sample. The uncertainty was estimated as twice the standard deviation of the mean.

The reaction enthalpy of Ala and cadmium chloride at 298.15 K can be calculated as

$$\Delta_r H_m^{\Theta}(s) = 2\Delta_{sol}H_1 + 3\Delta_{sol}H_2 - \Delta_{sol}H_3 = [2(3.60 \pm 0.094) + 3(-4.39 \pm 0.22) - (44.89 \pm 0.36)]\ kJ \cdot mol^{-1} = -(50.86 \pm 0.77)\ kJ \cdot mol^{-1}$$

The validity of the thermochemical cycle was proven as follows: The refractive index of the reactants and product in

Table 2. Molar Enthalpies of Solution of $\Delta_{sol}H_1$, $\Delta_{sol}H_2$, and $\Delta_{sol}H_3$ at 298.15 K[a]

no.	M mg	Q_s mJ	$\Delta_{sol}H_1$ kJ·mol^{-1}	M mg	Q_s mJ	$\Delta_{sol}H_2$ kJ·mol^{-1}	M mg	Q_s mJ	$\Delta_{sol}H_3$ kJ·mol^{-1}
1	5.93	243.2	3.654	18.33	−436.7	−4.367	26.67	1497.0	44.915
2	5.93	246.1	3.697	18.34	−424.1	−4.239	26.68	1501.5	45.034
3	5.94	245.8	3.686	18.33	−441.9	−4.419	26.67	1515.4	45.467
4	5.94	233.5	3.502	18.34	−444.2	−4.440	26.66	1486.0	44.602
5	5.94	231.8	3.477	18.35	−451.9	−4.514	26.68	1481.7	44.440
mean[b]			3.60 ± 0.094			−4.39 ±0.22			44.89 ± 0.36

[a] $\Delta_{sol}H_1$, 6.00 cm^3 of [0.0024 cm^3 of H_2O + 2 mol·dm^{-3} H_2SO_4(aq)]; $\Delta_{sol}H_2$, 6.00 cm^3 of [5.94 mg of Ala + 0.0024 cm^3 of H_2O + 2 mol·dm^{-3} H_2SO_4(aq)]; $\Delta_{sol}H_3$, 6.00 cm^3 of [2 mol·dm^{-3} H_2SO_4(aq)]. [b] Uncertainty was twice the standard deviation of the mean.

6.00 cm^3 of [2 mol·dm^{-3} H_2SO_4(aq)] was measured, namely, 1.3540 and 1.3539, respectively. The values of the refractive index were the same. This suggests that the final thermodynamic state of reactants and product was the same, and the proposed thermochemical cycle is correct.

Standard Molar Enthalpy of Formation. The molar enthalpy of formation of $Cd_3(Ala)_2Cl_6\cdot 4H_2O$ can be calculated as shown in following equation:

$$\Delta_r H_m^\Theta(s) = \Delta_f H_m^\Theta[Cd_3(Ala)_2Cl_6\cdot 4H_2O](s) - 3\Delta_f H_m^\Theta(CdCl_2)(s) - 2\Delta_f H_m^\Theta(Ala)(s) - 4\Delta_f H_m^\Theta(H_2O)(l)$$

The standard molar enthalpies of formation of $CdCl_2$ were taken from the NBS table,[11] namely, −(391.50 ± 0.10) kJ·mol^{-1}. The standard molar enthalpy of formation of Ala(s) was taken from the CRC Handbook,[9] −(565.64 ± 0.32) kJ·mol^{-1}. The standard molar enthalpy of H_2O(l) was taken from the CODATA Key Values,[12] −(285.830 ± 0.042) kJ·mol^{-1}. Using these schemes and data, the standard molar enthalpy of formation of $Cd_3(Ala)_2Cl_6\cdot 4H_2O$ was calculated to be −(3499.9 ± 1.1) kJ·mol^{-1}.

Conclusion

The solubility of the ternary system of cadmium chloride + Ala + water at 298.15 K was measured, and the corresponding phase diagram was prepared to search for new compounds and obtain equilibrium data for cadmium chloride/Ala in aqueous solution. One new solid phase was found to exist in the system, and the composition of the new solid phase compound $Cd_3(Ala)_2Cl_6\cdot 4H_2O$ was determined by the Schrienemaker method and confirmed by chemical analysis. The compound $Cd_3(Ala)_2Cl_6\cdot 4H_2O$ is congruently soluble. By designing a thermochemical cycle according to Hess' Law and through measuring the enthalpy of solution at 298.15 K, the reaction enthalpy of Ala with cadmium chloride at 298.15 K, and the standard molar enthalpy of formation of the new compound, $Cd_3(Ala)_2Cl_6\cdot 4H_2O$ was obtained.

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Received for review October 16, 2009. Accepted December 24, 2009.

JE900845G