Study on Determination of Standard Molar Enthalpy of Formation for Complex of Europium Chloride with Glycine and Alanine by Calorimetry

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Abstract: The ternary complex of $Eu(Gly)_2(Ala)_3Cl_3\cdot 2H_2O$(Gly = Glycine and Ala = Alanine) was synthesized and characterized by comparison of elementary analysis, chemical analysis, thermogravimetric analysis, and data with corresponding. The dissolution enthalpies of the $EuCl_3\cdot 6H_2O(s)$, 2Gly(s) + 3Ala(s) and $Eu(Gly)_2(Ala)_3Cl_3\cdot 2H_2O(s)$ in 2 mol/L HCl solution have been measured at 298.15K by isoperibol calorimeter. Based on the results, by designing a thermochemical cycle in terms of Hess' Law and through calculation, The standard molar reaction enthalpy of Europium chloride six-hydrate with Glycine and Alanine has been determined: $\Delta_r H_m^\theta$ (298.15K) = - 51.780 kJ/mol, and the standard enthalpy of formation of $Eu(Gly)_2(Ala)_3Cl_3\cdot 2H_2O(s)$ has been calculated to be $\Delta_f H_m^\theta$ [$Eu(Gly)_2(Ala)_3Cl_3\cdot 2H_2O(s)$, 298.15K] = - 4488.8 kJ/mol.

Introduction

Since the pioneering work of Anghileri[1], rare-earth coordination complexes have received a great deal of attention due to their potential use in the wool dyeing industry as dyeing accelerant and in agriculture as additive because of their physiological and biochemical effects[2]. For example, plenty of experimental results have shown that the rare earth complexes, compared with many other synthetic organic drugs and transition metal complexes, are of lower toxicity and lower accumulation in the body. So far, nearly Tens of millions of rare-earth compounds with L-amino acids have been reported, many research activities have focused on the syntheses of these coordination complexes and their relevant applications. It is necessary to obtain basic thermodynamic properties as the basis for theoretical research and industrial design when they are synthesized and developed industrially. However, until now, the basic thermodynamic properties of rare-earth coordination complexes were reported in literature rarely. Liu et al[3]. reported synthesis and characterization of the solid ternary complexes of rare earths with glycine and alanine, but the thermodynamic properties of $Eu(Gly)_2(Ala)_3Cl_3\cdot 2H_2O(s)$ have not been reported. To further research the complex, There needs to determine its basic thermochemical parameters. Therefore, with solution-reaction isoperibol calorimeter which is a broad and versatile technique that has the advantages of being rapid, accurate, economical, and convenient, the dissolution enthalpies of $EuCl_3\cdot 6H_2O(s)$, 2Gly(s) + 3Ala(s) and $Eu(Gly)_2(Ala)_3Cl_3\cdot 2H_2O(s)$ in 2mol/L HCl, were determined. By designing a thermochemical cycle according to Hess' law, the molar enthalpy of the following reaction was calculated: $EuCl_3\cdot 6H_2O(s)$ + 2Gly(s) + 3Ala(s) = $Eu(Gly)_2(Ala)_3Cl_3\cdot 2H_2O(s) + 4H_2O(l)$ and the standard molar enthalpy of formation of $Eu(Gly)_2(Ala)_3Cl_3\cdot 2H_2O(s)$ was estimated.

Experimental Section

Preparation. All regents were analytical grade and used without any further purification. The synthesis and purification of $Eu(Gly)_2(Ala)_3Cl_3\cdot 2H_2O$ was carried out as described in the literature[3]. In a typical synthesis of $Eu(Gly)_2(Ala)_3Cl_3\cdot 2H_2O(s)$, 16.1 mmol of $EuCl_3\cdot 6H_2O(s)$ was dissolved in 65 mL water, which was then added dropwise into 45 mL water solution (the pH was adjusted to 5.0 by adding a suitable amount of NaOH) possessing 30 mmol Glycine and 45 mmol

Alanine. The reaction mixture was refluxed for 2 h under vigorous magnetic stirring, and then cooled to room temperature. After overnight deposition and air pump filtration, a solid complex was obtained. The product was washed alternately with ethanol, acetone and water until no Cl^- was detected in the filtrate. After that, the product was dried in a vacuum desiccator at 60 ℃ until its mass remained constant.

Characterization. Elemental analyzer (Perkin-Elmer 2400 CHN, USA), thermogravimetrie analyzer (Perkin-Elmer TG6, at a heating rate of 10 ℃/min in flowing N_2, USA), Abbe refractometer (WAY, Shanghai, China), ultraviolet–visible spectrotometer (U-3010, HITACHI, Japan), solution-reaction isoperibol calorimeter (SRC 100, constructed by the thermochemical laboratory of Wuhan University, China), conductance (DDS-12A, Shanghai,China).

Results and discussion

The chemical composition of the synthetic sample was determined by elemental analysis for C, H, and N, by EDTA titration for Eu^{+}[4], by mercury salt titration for Cl^-, and by difference and TG-DTG curve for H_2O. The analysis results proved that the composition of the complex was $Eu(Gly)_2(Ala)_3Cl_3 \cdot 2H_2O$.

The results of solution-reaction isoperibol calorimeter and calibration were as follows. The principle and structure of the solution-reaction isoperibol calorimeter (SRC 100) were described in detail in reference[5].The calibration of the calorimeter was tested by measuring the dissolution enthalpies of THAM (NBS 742a, U.S.A.) in 0.1000mol/L HCl and KCl (calorimetric primary standard) in water, at 298.15 K. The mean dissolution enthalpies were – 29776 ± 16 J/mol for THAM and 17597 ± 17 J/mol for KCl, the results were in conformity with the published data (-29766 ± 31.5 J/mol for THAM[6] and 17536 ± 9 J/mol for KCl[7]), respectively. The uncertainties of both values were less than 0.5%. This showed that the device used in this experiment for measuring the enthalpy of solution was reliable.

The results of dissolution enthalpies were as follows. The method of dissolution enthalpies determination for the samples was the same as that for the calibration of the calorimeter with THAM and KCl. The temperature of the calorimetric experiment was set at 298.15K. During each electrical energy calibration, the electrical current (I) was set at 10.0016mA, and the resistance of the electrical heater was 1003.6 Ω.

$Eu(Gly)_2(Ala)_3Cl_3 \cdot 2H_2O$ could be regarded as the product of the following reaction(1), and the thermochemical cycle was designed as Fig. 1. The calorimetric results of reactions (2), (3) and (4) were listed in Table 1. The inevitable heat transfer and the generation of heat by friction were compensated and the corrected temperature ΔT^* change could be obtained according to Dickinson's method (the equal area method) [8].

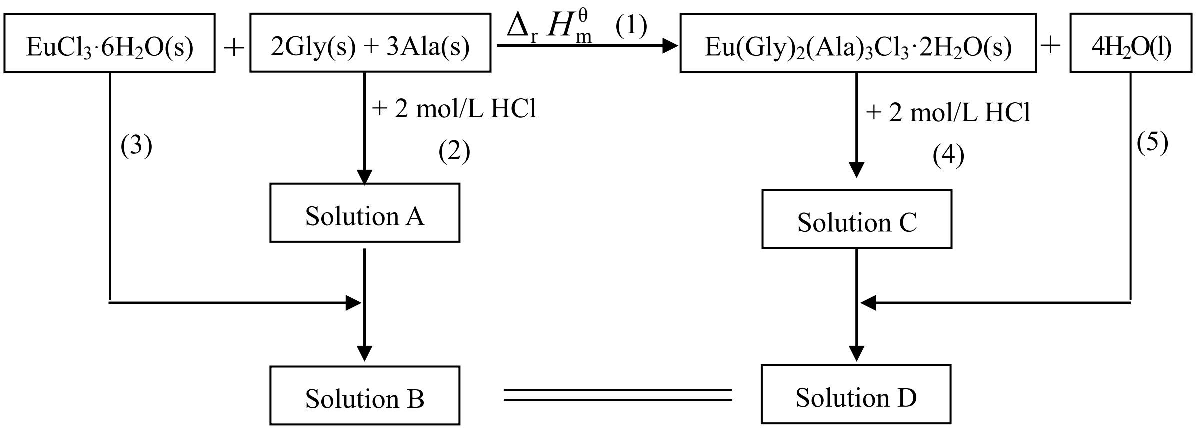

Fig. 1 Thermochemical cycle of the coordination reaction

Table 1 Dissolution enthalpies of [2Gly(s)+3Ala(s), [$EuCl_3 \cdot 6H_2O$(s)] and [$Eu(Gly)_2(Ala)_3Cl_3 \cdot 2H_2O$(s)] in 2 mol/L HCl at 298.15K. (R = 1003.6Ω, I = 10.0016 mA)

System	No.	m/g	ΔE_s/mV	ΔE_e/mV	t/s	Q_s/J	$\Delta_s H_m^\theta$ /(kJ/mol)
2Gly(s)+3Ala(s) in 2mol/L HCl	1	0.4186	5.650	6.560	366.8	33.2449	33.142
	2	0.4181	5.820	6.000	342.0	33.3040	33.249
	3	0.4188	5.610	6.120	355.0	33.2423	33.132
	4	0.4183	5.640	6.010	346.8	33.2490	33.168
	5	0.4118	5.690	6.140	356.6	33.2691	33.198
	$\Delta_s H_m^\theta(2) = \Delta_s H_m^\theta$ [2Gly(s) + 3Ala(s),298.15K] = 33.178 kJ/mol						
$EuCl_3 \cdot 6H_2O$(s) in 2Gly·3Ala·2 mol/L HCl	1	0.3633	7.355	7.426	690.6	-68.6680	-69.256
	2	0.3615	7.370	7.574	700.8	-68.4601	-69.390
	3	0.3642	7.312	7.595	711.2	-68.7386	-69.156
	4	0.3609	7.394	7.401	681.5	-68.3522	-69.396
	5	0.3651	7.301	7.637	718.4	-68.9483	-69.196
	$\Delta_s H_m^\theta(3) = \Delta_s H_m^\theta$ [$EuCl_3 \cdot 6H_2O$(s), 298.15K] = - 69.279 kJ/mol						
$Eu(Gly)_2(Ala)_3Cl_3 \cdot 2H_2O$ in 2mol/L HCl	1	0.6984	4.469	4.152	139.9	15.1172	15.406
	2	0.7047	4.472.	4.203	146.3	15.6274	15.783
	3	0.7035	4.493	4.358	152.5	15.7841	15.968
	4	0.7002	4.485	4.181	140.8	15.1630	15.413
	5	0.7103	4.458	4.176	147.4	15.7971	15.829
	$\Delta_s H_m^\theta(4) = \Delta_s H_m^\theta$ [$Eu(Gly)_2(Ala)_3Cl_3 \cdot 2H_2O$(s),298.15K] = 15.680 kJ/mol						

ΔE_s: the voltage change during the sample dissolution; ΔE_e: the voltage change during electrical calibration; t: heating period of electrical calibration; Q_s: heat effect; $\Delta_s H_m^\theta$: dissolution enthalpy. where $Q_s=(\Delta E_s/\Delta E_e)\cdot I^2Rt$, $\Delta_s H_m^\theta = Q_s(M/m)$, m is sample mass, M isapparent molecular mass.

According to Hess' Law, the standard molar reaction enthalpy of the reaction (1) could be obtained:

$$\Delta_r H_m^\theta(1) = \Delta_s H_m^\theta(2) + \Delta_s H_m^\theta(3) - \Delta_s H_m^\theta(4) - \Delta_d H_m^\theta(5)$$

in which $\Delta_d H_m^\theta$ (5) is the dissolution enthalpy of water as one of the products of products of the reaction in the solvent within the experimental error and may be omitted bacause the amount of H_2O is very low according to the stoichiomitric number of water.

So that $\Delta_r H_m^\theta(1) = -51.780$ kJ/mol.

The evaluation *of* $\Delta_f H_m^\theta$[$Eu(Gly)_2(Ala)_3Cl_3 \cdot 2H_2O$(s)]: According to thermodynamics principle, it was known that:

$$\Delta_r H_m^\theta = \Delta_f H_m^\theta[Eu(Gly)_2(Ala)_3Cl_3 \cdot 2H_2O, s, 298.15K] + 4\Delta_f H_m^\theta[H_2O, l, 298.15K]$$
$$- \Delta_f H_m^\theta[EuCl_3 \cdot 6H_2O, s, 298.15K] - 2\Delta_f H_m^\theta[Gly, s, 298.15K]$$
$$- 3\Delta_f H_m^\theta[Ala, s, 298.15K]$$

From the literature[9], the following data can be obtained:

$\Delta_f H_m^\theta$[H_2O, l, 298.15K] = -285.830 kJ/mol

$\Delta_f H_m^\theta$[$EuCl_3 \cdot 6H_2O$, s, 298.15K] = -2788.217 kJ/mol

$\Delta_f H_m^\theta$[Gly, s, 298.15K] = -537.23 kJ/mol

$\Delta_f H_m^\theta$[Ala, s, 298.15K] = -572.57 kJ/mol

and the value worked out previously was: $\Delta_r H_m^\theta = -51.780$ kJ/mol

So that $\Delta_f H_m^\theta$[$Eu(Gly)_2(Ala)_3Cl_3 \cdot 2H_2O$, s, 298.15K] = - 4488.8 kJ/mol

Validation of the themochemical cycle of reaction (1) was tested by releasing the sample cell containing the final solution from the products in the calorimeter, with no enthalpy change being detected. The UV spectrum and refractive indices of the final solution of the reactants and the final solution of the products can beused to determine if they have the same thermodynamicstate[10-12].

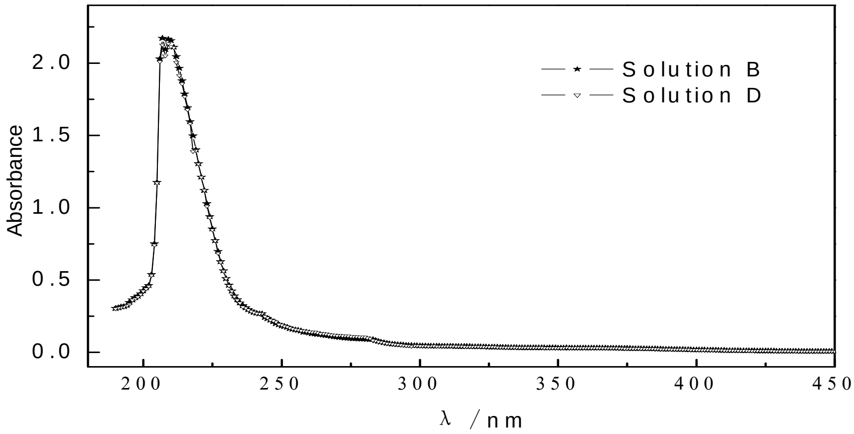

Fig. 2 UV spectrum of final dissolution state of reactants and products in 2 mol/L HCl

In the present experiments, we determined the spectrum and refractive indices of solution B and solution D in Fig. 1. The UV-visspectrum (Fig.2) and refractive indexes ($\eta_{25℃}$ = 1.3508) of solution B and solution D were identical. It proves that both have the same thermodynamic state and that the designed thermochemical cycle is reasonable and reliable. Therefore, the standard molar reaction enthalpy of the reaction (1) obtained according to Hess' Law and the standard molar enthalpy of formation of $Eu(Gly)_2(Ala)_3Cl_3{\cdot}2H_2O(s)$ through calculation were reliable as well.

Conclusion

On the basis of the experimental results and thermodynamic principles, the standard molar reaction enthalpy of the reaction $EuCl_3{\cdot}6H_2O(s)+2Gly(s)+3Ala(s) = Eu(Gly)_2(Ala)_3Cl_3{\cdot}2H_2O(s) + 4H_2O(l)$ and the standard molar enthalpy of formation of $Eu(Gly)_2(Ala)_3Cl_3{\cdot}2H_2O(s)$ were evaluated to be - 51.780 kJ/mol and - 4488.8 kJ/mol respectively.

Acknowledgments

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References

[1] L.J. Anghileri.: Arzneim Forsch.Vol.25(1975), p.793.

[2] J. Zhou; L. F. Wang; J. Y. Wang; et al.: J. Inorg. Biochem. Vol.83(2001), p.41.

[3] Y. P. Liu; J. X. Liu; Y. H. Sun; et al.: Acta Scientiarum Naturalium Universitatis Neimongol. Vol.27(1996), p.66.

[4] Z. Q. Xie.: Journal of Wuhan University(Natural Science Edition). Vol.2(1985), p.117.

[5] H. G. Yu; Y. Liu; Z. C. Tan; et al.:Thermochim. Acta.Vol.401(2003), p.217.

[6] P. Rychly; V. J. Pekarek.: J. Chem. Thermodyn. Vol.9(1977) , p.39.

[7] R. L. Montgomery; R. A. Melaugh; C. C. Lan.: J.Chem. Thermodyn. Vol.9(1977), p.915.

[8] Y. X. Kong; Y. B. Li; W. W. Yang.; et al.: Acta Chimica Sinica. Vol.66(2008), p609.

[9] B.P. Liu; Z. C. Tan.: Acta Phys.-Chim Sin. Vol.29(2013), p.17.

[10] J. L. Lu; B. P. Liu; Z. C.Tan; et al.: Acta Chim. Sin. Vol.65(2007), p.2349.

[11] Y. Y. Di; Z. C. Tan; Y. S. Li.: Acta Chim. Sin. Vol.64(2006), p.1393.

[12] Y. Y. Di; Z. C. Tan; G. Q. Zhang; et al.: Thermochim. Acta. Vol.400(2003), p.43.