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

Bin Deng\textsuperscript{a}, Haiying Huang\textsuperscript{b} and Qiangguo Li\textsuperscript{c}

Department of Chemistry and Life Sciences, Xiangnan University, Chenzhou 423000, China
\textsuperscript{a}dbhy88@sina.com, \textsuperscript{b}xnxyhy@126.com, \textsuperscript{c}pchem6@126.com

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Abstract: The ternary complex of Eu(Gly)\textsubscript{2}(Ala)\textsubscript{3}Cl\textsubscript{3}·2H\textsubscript{2}O (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\textsubscript{3}·6H\textsubscript{2}O(s), 2Gly(s) + 3Ala(s) and Eu(Gly)\textsubscript{2}(Ala)\textsubscript{3}Cl\textsubscript{3}·2H\textsubscript{2}O(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: \(\Delta_r H_m^\circ (298.15K) = -51.780 \text{ kJ/mol}\), and the standard enthalpy of formation of Eu(Gly)\textsubscript{2}(Ala)\textsubscript{3}Cl\textsubscript{3}·2H\textsubscript{2}O(s) has been calculated to be \(\Delta_f H_m^\circ [\text{Eu(Gly)}\textsubscript{2}(\text{Ala})\textsubscript{3}\text{Cl}\textsubscript{3}·2\text{H}\textsubscript{2}\text{O(s), 298.15K}] = -4488.8 \text{ kJ/mol}\).

Introduction

Since the pioneering work of Anghileri\textsuperscript{[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\textsuperscript{[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\textsuperscript{[3]}, reported synthesis and characterization of the solid ternary complexes of rare earths with glycine and alanine, but the thermodynamic properties of Eu(Gly)\textsubscript{2}(Ala)\textsubscript{3}Cl\textsubscript{3}·2H\textsubscript{2}O(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\textsubscript{3}·6H\textsubscript{2}O(s), 2Gly(s) + 3Ala(s) and Eu(Gly)\textsubscript{2}(Ala)\textsubscript{3}Cl\textsubscript{3}·2H\textsubscript{2}O(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\textsubscript{3}·6H\textsubscript{2}O(s) + 2Gly(s) + 3Ala(s) = Eu(Gly)\textsubscript{2}(Ala)\textsubscript{3}Cl\textsubscript{3}·2H\textsubscript{2}O(s) + 4H\textsubscript{2}O(l) and the standard molar enthalpy of formation of Eu(Gly)\textsubscript{2}(Ala)\textsubscript{3}Cl\textsubscript{3}·2H\textsubscript{2}O(s) was estimated.

Experimental Section

Preparation. All regents were analytical grade and used without any further purification. The synthesis and purification of Eu(Gly)\textsubscript{2}(Ala)\textsubscript{3}Cl\textsubscript{3}·2H\textsubscript{2}O was carried out as described in the literature\textsuperscript{[3]}. In a typical synthesis of Eu(Gly)\textsubscript{2}(Ala)\textsubscript{3}Cl\textsubscript{3}·2H\textsubscript{2}O(s), 16.1 mmol of EuCl\textsubscript{3}·6H\textsubscript{2}O(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 °C until its mass remained constant.

Characterization. Elemental analyzer (Perkin-Elmer 2400 CHN, USA), thermogravimetric analyzer (Perkin-Elmer TG6, at a heating rate of 10 °C/min in flowing N₂, USA), Abbe refractometer (WAY, Shanghai, China), ultraviolet–visible spectrometer (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 Eu⁴⁺, by mercury salt titration for Cl⁻, and by difference and TG-DTG curve for H₂O. The analysis results proved that the composition of the complex was Eu(Gly)₂(Ala)₃Cl₃·2H₂O.

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 1003.6Ω.

Eu(Gly)₂(Ala)₃Cl₃·2H₂O 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].

![Thermochemical cycle of the coordination reaction](image)

Fig. 1 Thermochemical cycle of the coordination reaction
Table 1 Dissolution enthalpies of [2Gly(s) +3Ala(s), [EuCl₃·6H₂O(s)] and [Eu(Gly)₂(Ala)₃Cl₃·2H₂O(s)] in 2 mol/L HCl at 298.15K. (R = 1003.6 Ω, I = 10.0016 mA)

<table>
<thead>
<tr>
<th>System</th>
<th>No.</th>
<th>m/g</th>
<th>ΔEₘV</th>
<th>ΔEₑₘV</th>
<th>t/s</th>
<th>Qₛ/J</th>
<th>Δₘ, Hₘ°/(kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2Gly(s)+3Ala(s) in 2mol/L HCl</td>
<td>1</td>
<td>0.4186</td>
<td>5.650</td>
<td>6.560</td>
<td>366.8</td>
<td>33.2449</td>
<td>33.142</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.4181</td>
<td>5.820</td>
<td>6.000</td>
<td>342.0</td>
<td>33.3040</td>
<td>33.249</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.4188</td>
<td>5.610</td>
<td>6.120</td>
<td>355.0</td>
<td>33.2423</td>
<td>33.132</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.4183</td>
<td>5.640</td>
<td>6.010</td>
<td>346.8</td>
<td>33.2490</td>
<td>33.168</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.4118</td>
<td>5.690</td>
<td>6.140</td>
<td>356.6</td>
<td>33.2691</td>
<td>33.198</td>
</tr>
<tr>
<td>EuCl₃·6H₂O(s) in 2Gly·3Ala·2 mol/L HCl</td>
<td>1</td>
<td>0.3633</td>
<td>7.355</td>
<td>7.426</td>
<td>690.6</td>
<td>-68.6680</td>
<td>-69.256</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.3615</td>
<td>7.370</td>
<td>7.574</td>
<td>700.8</td>
<td>-68.4601</td>
<td>-69.390</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.3642</td>
<td>7.312</td>
<td>7.595</td>
<td>711.2</td>
<td>-68.7386</td>
<td>-69.156</td>
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<tr>
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<td>4</td>
<td>0.3609</td>
<td>7.394</td>
<td>7.401</td>
<td>681.5</td>
<td>-68.3522</td>
<td>-69.396</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.3651</td>
<td>7.301</td>
<td>7.637</td>
<td>718.4</td>
<td>-68.9483</td>
<td>-69.196</td>
</tr>
<tr>
<td>Eu(Gly)₂(Ala)₃Cl₃·2H₂O in 2mol/L HCl</td>
<td>1</td>
<td>0.6984</td>
<td>4.469</td>
<td>4.152</td>
<td>139.9</td>
<td>15.1172</td>
<td>15.406</td>
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<tr>
<td></td>
<td>2</td>
<td>0.7047</td>
<td>4.472</td>
<td>4.203</td>
<td>146.3</td>
<td>15.6274</td>
<td>15.783</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.7035</td>
<td>4.493</td>
<td>4.358</td>
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<td>15.7841</td>
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<tr>
<td></td>
<td>4</td>
<td>0.7002</td>
<td>4.485</td>
<td>4.181</td>
<td>140.8</td>
<td>15.1630</td>
<td>15.413</td>
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<tr>
<td></td>
<td>5</td>
<td>0.7103</td>
<td>4.458</td>
<td>4.176</td>
<td>147.4</td>
<td>15.7971</td>
<td>15.829</td>
</tr>
</tbody>
</table>

ΔEs: the voltage change during the sample dissolution; ΔEₑ: the voltage change during electrical calibration; t: heating period of electrical calibration; Qₛ: heat effect; ΔsHₘ: dissolution enthalpy. Where Qₛ = (ΔEₛ/ΔEₑ)·I²Rt, ΔsHₘ = Qₛ((M/m), m is sample mass, M is apparent molecular mass.

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

\[ \Delta_r H_m^0(1) = \Delta_s H_m^0(2) + \Delta_s H_m^0(3) - \Delta_s H_m^0(4) - \Delta_s H_m^0(5) \]

in which \( \Delta_s H_m^0(5) \) is the dissolution enthalpy of water as one of the products of the products of the reaction in the solvent within the experimental error and may be omitted because the amount of H₂O is very low according to the stoichiometric number of water.

So that \( \Delta_r H_m^0(1) = -51.780 \text{ kJ/mol} \).

The evaluation of \( \Delta_r H_m^0[\text{Eu(Gly)₂(Ala)₃Cl₃·2H₂O(s)}] \): According to thermodynamics principle, it was known that:

\[ \Delta_r H_m^0[\text{Eu(Gly)₂(Ala)₃Cl₃·2H₂O(s)}] = 4 \Delta_r H_m^0[\text{H₂O, l, 298.15K}] - 2 \Delta_r H_m^0[\text{Gly, s, 298.15K}] - 3 \Delta_r H_m^0[\text{Ala, s, 298.15K}] \]

From the literature\(^{[9]}\), the following data can be obtained:

\[ \Delta_r H_m^0[\text{H₂O, l, 298.15K}] = -285.830 \text{ kJ/mol} \]
\[ \Delta_r H_m^0[\text{EuCl₃·6H₂O, s, 298.15K}] = -2788.217 \text{ kJ/mol} \]
\[ \Delta_r H_m^0[\text{Gly, s, 298.15K}] = -537.23 \text{ kJ/mol} \]
\[ \Delta_r H_m^0[\text{Ala, s, 298.15K}] = -572.57 \text{ kJ/mol} \]

So that \( \Delta_r H_m^0[\text{Eu(Gly)₂(Ala)₃Cl₃·2H₂O(s)}] = -4488.8 \text{ kJ/mol} \)

Validation of the thermochemical 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 be used to determine if they have the same thermodynamic state\(^{[10-12]}\).
In the present experiments, we determined the spectrum and refractive indices of solution B and solution D in Fig. 1. The UV-vis spectrum (Fig. 2) and refractive indexes (\( \eta_{25\degree C} = 1.3508 \)) 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 \( \text{EuCl}_3\cdot 6\text{H}_2\text{O}(s)+2\text{Gly}(s)+3\text{Ala}(s) = \text{Eu}(\text{Gly})_2(\text{Ala})_3\text{Cl}_3\cdot 2\text{H}_2\text{O}(s) + 4\text{H}_2\text{O}(l) \) 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.

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**References**