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Thermochemical properties of $Ln(Gly)_4Im(ClO_4)_3 \cdot nH_2O$ (Ln = Gd, Tb, Dy, Y)

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Abstract

The enthalpies of dissolution in water of new ternary complexes of four late trivalent lanthanide ions $Ln(Gly)_4Im(ClO_4)_3 \cdot nH_2O$ (Ln = Gd, Tb, Dy, Y; Gly: glycine; Im: imidazole and $n = 1$ or 2) were measured by means of a Calvet microcalorimeter. Empirical formulae for the calculation of the enthalpies of dissolution ($\Delta_{diss}H$), relative apparent molar enthalpies ($\Delta_{diss}H$ (app)), relative partial molar enthalpies ($\Delta_{diss}H$ (partial)) and enthalpies of dilution ($\Delta_{dil}H_{1,2}$) were obtained from the experimental data of the enthalpies of dissolution of these complexes. The plot of $\Delta_{diss}H_m^\Theta$, $\Delta_{diss}H$ (app) and $\Delta_{diss}H$ (partial) versus the values of the ionic radius of the lanthanide element (r) showed a grouping effect of the lanthanide elements, indicating that the coordinated bond between the lanthanide ions and the ligands has some covalent character. The unknown value of the standard enthalpy of dissolution for the similar complex: $Ho(Gly)_4Im(ClO_4)_3 \cdot H_2O$ was estimated according to the plot of $\Delta_{diss}H_m^\Theta$ versus r.

Keywords: Complex; Dissolution; Enthalpy; Lanthanide; Thermochemistry

1. Introduction

Trivalent lanthanide ions possess obvious foster effect on the growing of crop [1]. Amino acids are the structural units of proteins, and there are some reports [2,3] about the study on binary complexes of lanthanide ions with amino acids. Imidazole is a class of heterocyclic compound possessing bactericide and anti-infectional function. Therefore, it is predicted that the ternary complexes of the trivalent lanthanide perchlorates with glycine and imidazole would have a widely prospect of applications. The syntheses of ternary complexes of transition and lanthanide metallic ions with imidazole and amino acids have been reported [4–7], but study on thermochemical properties of this kind of complexes is not available.

In this study, the enthalpies of dissolution in water for four complexes $Ln(Gly)_4Im(ClO_4)_3 \cdot nH_2O$ (Ln = Gd, Tb, Dy, Y) were measured and four kinds of empirical formulae were obtained. It provides more information not only for the thermochemical database of lanthanide complexes as well as the grouping and separating of lanthanide elements.

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Table 1
Analytical results of the complexes

Complex	Rare earth (%)		C (%)		H (%)		N (%)	
	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found
$Gd(Gly)_4Im(ClO_4)_3{\cdot}H_2O$	18.59	18.68	15.69	15.43	3.11	2.70	9.98	10.19
$Tb(Gly)_4Im(ClO_4)_3{\cdot}H_2O$	18.79	18.84	15.66	15.89	3.11	2.82	9.96	10.20
$Dy(Gly)_4Im(ClO_4)_3{\cdot}H_2O$	19.23	19.18	15.59	15.98	3.09	2.79	9.92	10.44
$Y(Gly)_4Im(ClO_4)_3{\cdot}2H_2O$	11.30	11.23	16.69	16.53	3.57	3.87	10.62	10.84

2. Experimental

2.1. Complexes preparation

Four complexes were prepared as described in the literature [7]. The general formula of these complexes is $Ln(Gly)_4Im(ClO_4)_3{\cdot}nH_2O$. They were characterized by elemental analysis, IR spectra, UV spectra, and X-ray powder diffraction. The results of elemental analysis are listed in Table 1. The purities of the complex were more than 99.5%. Before experiments, all complexes were sifted through a 160 mesh sifter. The solvent used was deionized water, whose electrical conductivity was 5.48×10^{-8} s m^{-1}.

2.2. Measurement of enthalpies of dissolution of the complexes in water

All measurements of the dissolution in deionized water were made by using a Calvet microcalorimeter, type BT 215 from Setaram, France and operated at 298.15 ± 0.01 K. The experimental times of each complex are no less than six.

The experimental precision and accuracy of the calorimeter was frequently checked by measurement of the enthalpies of dissolution of crystalline KCl in deionized water at 298.15 K. The experimental value (17.22 ± 0.05 kJ mol^{-1}) is in excellent agreement with the value (17.23 ± 0.05 kJ mol^{-1}) reported [8].

3. Results and discussion

3.1. The enthalpies of dissolution for the complexes at different concentrations

The experimental and calculated values of enthalpy of dissolution in water for four complexes are given in Table 2. The relative apparent molar enthalpies (calculated) and relative partial molar enthalpies (calculated) of complexes are also given in Table 2. By substituting the values of b in Table 2 into Eq. (1) [9].

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

the empirical formulae of enthalpy $\Delta_{diss}H$ ($b = b$) of dissolution in water and the values of the standard enthalpies of dissolution $\Delta_{diss}H_m^{\Theta}$ ($b = 0$) for complexes are obtained:

for $Gd(Gly)_4Im(ClO_4)_3{\cdot}H_2O$,

$$\Delta_{diss}H = 69.5974 + 1.3576 \times 10^{-4}b - 2.7012 \times 10^{-2}b^{1/2}, \qquad \Delta_{diss}H_m^{\Theta} = 69.60\,\mathrm{kJ\,mol^{-1}}$$

for $Tb(Gly)_4Im(ClO_4)_3{\cdot}H_2O$,

$$\Delta_{diss}H = 25.4226 - 1.8448 \times 10^{-4}b + 21.3519 \times 10^{-2}b^{1/2}, \qquad \Delta_{diss}H_m^{\Theta} = 25.42\,\mathrm{kJ\,mol^{-1}}$$

for $Dy(Gly)_4Im(ClO_4)_3{\cdot}H_2O$,

$$\Delta_{diss}H = 37.4517 - 1.4648 \times 10^{-4}b + 16.7082 \times 10^{-2}b^{1/2}, \qquad \Delta_{diss}H_m^{\Theta} = 37.45\,\mathrm{kJ\,mol^{-1}}$$

for $Y(Gly)_4Im(ClO_4)_3{\cdot}2H_2O$,

$$\Delta_{diss}H = 59.3486 + 0.0326 \times 10^{-4}b + 5.0160 \times 10^{-2}b^{1/2}, \qquad \Delta_{diss}H_m^{\Theta} = 59.35\,\mathrm{kJ\,mol^{-1}}$$

3.2. The empirical formulae of the relative apparent molar enthalpy for complexes

According to the relationship as shown in Eq. (2) [9]

$$\Delta_{diss}H(\mathrm{app}) = \Delta_{diss}H(b = b) - \Delta_{diss}H(b = 0) \quad (2)$$

Table 2
The enthalpies of dissolution of the complexes in water

Complexes	b[a] ($\times 10^4$ mol kg^{-1})	$\Delta_{diss}H$ (kJ mol^{-1})		$\Delta_{diss}H$ (app) (kJ mol^{-1})	$\Delta_{diss}H$(partial) (kJ mol^{-1})
		Found	Calculated		
Gd	0.0000		69.60	0.00	0.00
	7.5491	72.44	72.42	2.85	9.41
	9.9247	74.53	74.56	4.99	14.24
	12.6566	77.16	77.17	7.61	20.02
	14.5307	79.07	79.03	9.47	24.09
	18.1073	82.67	82.69	13.14	32.02
	20.4829	85.20	85.18	15.64	37.38
Tb	0.0000		25.42	0.00	0.00
	8.9566	72.69	72.69	47.33	62.57
	10.3791	74.96	74.95	49.58	64.63
	12.4207	77.60	77.63	52.27	66.75
	14.1198	79.50	79.47	54.10	67.93
	16.3721	81.46	81.47	56.10	68.82
	17.2282	82.15	82.12	56.75	68.99
Dy	0.0000		37.45	0.00	0.00
	7.4236	72.09	72.10	34.69	46.63
	9.1812	74.65	74.63	37.23	49.15
	12.1060	77.85	77.85	40.47	51.88
	14.8341	80.06	80.07	42.70	53.24
	17.7459	81.85	81.84	44.48	53.79
	18.8067	82.31	82.29	45.01	53.81
Y	0.0000		59.35	0.00	0.00
	6.0920	71.92	71.93	12.57	18.95
	8.4361	74.21	74.19	14.83	22.38
	13.7981	78.62	78.60	19.06	28.80
	15.7352	79.76	79.76	20.39	30.81
	19.3988	82.08	82.08	22.69	34.33
	21.4903	83.33	83.30	23.92	36.20

[a] b: concentration.

from Eq. (1), the empirical formulae of relative apparent molar enthalpy $\Delta_{diss}H$ (app) for complexes are obtained:

for $Gd(Gly)_4Im(ClO_4)_3{\cdot}H_2O$,

$$\Delta_{diss}H(\text{app}) = 1.3576 \times 10^{-4}b - 2.7012 \times 10^{-2}b^{1/2}$$

for $Tb(Gly)_4Im(ClO_4)_3{\cdot}H_2O$,

$$\Delta_{diss}H(\text{app}) = -1.8448 \times 10^{-4}b + 21.3519 \times 10^{-2}b^{1/2}$$

for $Y(Gly)_4Im(ClO_4)_3{\cdot}2H_2O$,

$$\Delta_{diss}H(\text{app}) = -1.4648 \times 10^{-4}b + 16.7082 \times 10^{-2}b^{1/2}$$

for $Y(Gly)_4Im(ClO_4)_3{\cdot}2H_2O$,

$$\Delta_{diss}H(\text{app}) = 0.0326 \times 10^{-4}b + 5.0160 \times 10^{-2}b^{1/2}$$

3.3. The empirical formulae of relative partial molar enthalpies for complexes

According to the empirical formula as presented in Eq. (3) [9]

$$\Delta_{diss}H(\text{partial}) = b\left(\frac{\partial \Delta_{diss}H}{\partial b}\right) + \Delta_{diss}H(\text{app}) \quad (3)$$

from Eqs. (1) and (2), the following empirical formulae of the relative partial molar enthalpies $\Delta_{diss}H$ (partial) for the complexes are obtained:

for $Gd(Gly)_4Im(ClO_4)_3 \cdot H_2O$,

$$\Delta_{diss}H(\text{partial}) = 2.7152 \times 10^{-4}b - 4.0518 \times 10^{-2}b^{1/2}$$

for $Tb(Gly)_4Im(ClO_4)_3 \cdot H_2O$,

$$\Delta_{diss}H(\text{partial}) = -3.6896 \times 10^{-4}b + 32.0279 \times 10^{-2}b^{1/2}$$

for $Dy(Gly)_4Im(ClO_4)_3 \cdot H_2O$,

$$\Delta_{diss}H(\text{partial}) = -2.9291 \times 10^{-4}b + 25.0623 \times 10^{-2}b^{1/2}$$

for $Y(Gly)_4Im(ClO_4)_3 \cdot 2H_2O$,

$$\Delta_{diss}H(\text{partial}) = 0.0652 \times 10^{-4}b + 7.5240 \times 10^{-2}b^{1/2}$$

3.4. The empirical formulae of enthalpies of dilution for the complexes

According to the empirical formula described in Eq. (4) [9],

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

the following empirical formulae of dilution enthalpies $\Delta_{dil}H_{1,2}$ for the complexes are obtained:

for $Gd(Gly)_4Im(ClO_4)_3 \cdot H_2O$,

$$\Delta_{dil}H_{1,2} = 1.3576 \times 10^{-4}(b_2 - b_1) - 2.7012 \times 10^{-2}(b_2^{1/2} - b_1^{1/2})$$

for $Tb(Gly)_4Im(ClO_4)_3 \cdot H_2O$,

$$\Delta_{dil}H_{1,2} = -1.8448 \times 10^{-4}(b_2 - b_1) + 21.3519 \times 10^{-2}(b_2^{1/2} - b_1^{1/2})$$

for $Dy(Gly)_4Im(ClO_4)_3 \cdot H_2O$,

$$\Delta_{dil}H_{1,2} = -1.4648 \times 10^{-4}(b_2 - b_1) + 16.7082 \times 10^{-2}(b_2^{1/2} - b_1^{1/2})$$

for $Y(Gly)_4Im(ClO_4)_3 \cdot 2H_2O$,

$$\Delta_{dil}H_{1,2} = 0.0326 \times 10^{-4}(b_2 - b_1) + 5.0106 \times 10^{-2}(b_2^{1/2} - b_1^{1/2})$$

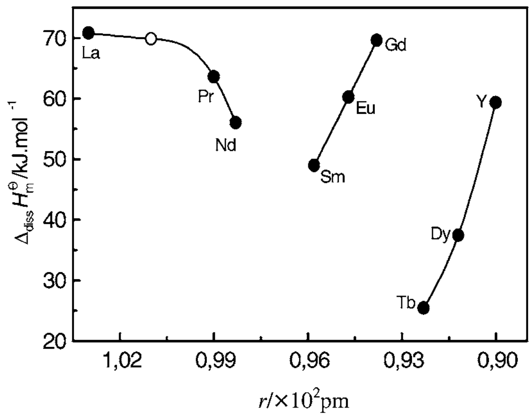

Fig. 1. Correlation of $\Delta_{diss}H_m^{\Theta}$ with r.

3.5. Correlation between the standard molar enthalpies of dissolution of the complexes and the ionic radius of the lanthanide elements

The plot of the enthalpies of dissolution for infinite dilution ($\Delta_{diss}H_m^{\Theta}$) of the four late lanthanide complexes against the ionic radius (r) of the late lanthanide element is shown in Fig. 1. For comparison, the values of $\Delta_{diss}H_m^{\Theta}$ for the five early lanthanide complexes [10] are also presented in Fig. 1.

From Fig. 1, it can be easily deduced that the correlation between $\Delta_{diss}H_m^{\Theta}$ and r is not monotonic and divided into three curves, as if the front three groups of "quadripartite effect". This phenomenon provides thermodynamic base for the grouping and separation of the lanthanide elements, showing that the coordinate

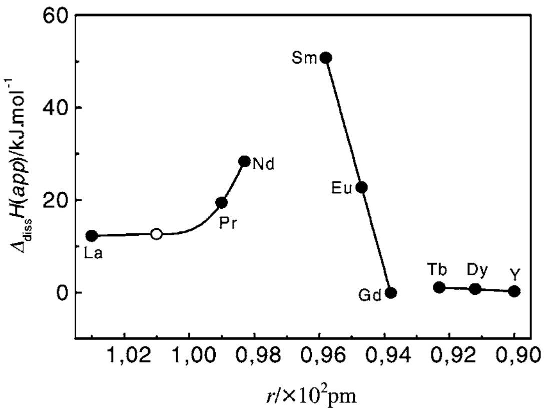

Fig. 2. Correlation of $\Delta_{diss}H$ (app) with r.

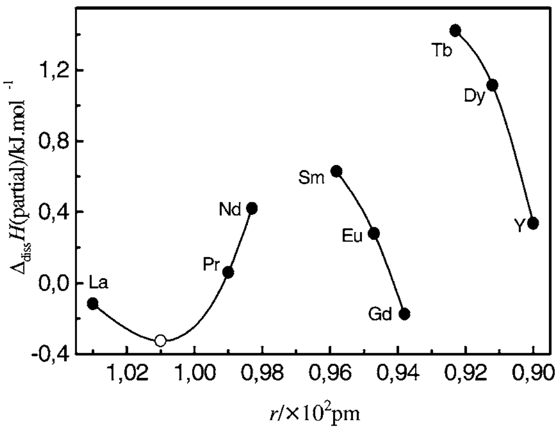

Fig. 3. Correlation of $\Delta_{diss}H$ (partial) with r.

bond formed between the lanthanide ions and ligands possesses a certain extent property of covalent bond that is differentiated through the lanthanide series [11]. From Fig. 1, the unknown standard enthalpy of dissolution for the similar complex $Ho(Gly)_4Im(ClO_4)_3 \cdot H_2O$ is estimated as 57.89 kJ mol^{-1}.

Two plots of the values of $\Delta_{diss}H$ (app) and $\Delta_{diss}H$ (partial) for four complexes corresponding to $b = 0.002$ mol kg^{-1} against the values of r, are shown in Figs. 2 and 3. At the same time, the values of $\Delta_{diss}H$ (app) and $\Delta_{diss}H$ (partial) [10] for five early lanthanide complexes at the same concentration are also shown in Figs. 2 and 3, respectively.

In these figures, it is also possible to observe the separation in three groups as it was observed in the Fig. 1. It can be deduced that the values of dilution enthalpy for the complexes would show this effect.

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