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The integral heats of solution of rare earth isothiocyanate hydrates in aqueous amino acid solutions

Jian-Hua Zhang, Hai-Feng Chen, Zhi-He Wang, Lei Li, Hong-Guo Liu and Ben-Gao Jiang *

Department of Chemistry, Shandong University, Jinan (People's Republic of China)

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Abstract

The integral heats of solution of nine kinds of $RE(NCS)_3 \cdot nH_2O$ ($n = 6$ for RE = Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Y) in aqueous glycine solution, of nine kinds of $RE(NCS)_3 \cdot nH_2O$ ($n = 7$ for RE = La, Pr, Nd; $n = 6$ for RE = Gd, Dy, Ho, Tm, Yb, Y) in aqueous alanine solution and of ten kinds of $RE(NCS)_3 \cdot nH_2O$ ($n = 7$ for RE = La, Pr, Nd; $n = 6$ for RE = Sm, Eu, Gd, Dy, Ho, Yb, Y) in aqueous serine solution have been measured calorimetrically at 298.15 ± 0.1 K. In the above measurements, the molar ratio of $RE(NCS)_3 \cdot nH_2O(c)$:amino acid(c):$H_2O(l)$ is 1:3:600. The integral heats of $Dy(NCS)_3 \cdot 6H_2O$ in more dilute aqueous solutions of glycine, alanine and serine were also measured separately. At this time, the molar ratio of $Dy(NCS)_3 \cdot 6H_2O(c)$:amino acid (c):$H_2O(l)$ was changed to 1:3:1200 and 1:3:2400. Some valuable results have been obtained and are analysed with discussion.

INTRODUCTION

Great interest has been aroused in the study of rare earths (REs) because of their special applications in physiology, biology and pharmacology [1]. The trivalent rare earth RE^{3+} ions can substitute Ca^{2+} in biological systems and have been used as Ca^{2+} probes [2]. It has been reported that lanthanum–glycine has better antineoplastic effects and less toxicity than lanthanum chloride [3]. In order to understand the effects of RE^{3+} ions in biological systems, it is very important to study the interaction between rare earth and amino acid.

The NCS^- ion can easily coordinate with an RE^{3+} ion. The rare earth isothiocyanates are important compounds. As the essential constituents of proteins, amino acids have many significant physiological effects. Glycine (Gly), alanine (Ala) and serine (Ser) are three typical α-amino acids. They are very important ligands of the metal elements in biological systems.

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* Corresponding author.

amino acid solution can supply some information about the interaction between rare earth and amino acid. In this paper, the integral heats of solution of a series of rare earth isothiocyante hydrates in aqueous solutions of the three amino acids mentioned above have been measured.

EXPERIMENTAL

Purification of amino acids and preparation of $RE(NCS)_3 \cdot nH_2O$

Glycine, alanine and serine (BR) were purified by means of recrystallization using twice-distilled water. The purified amino acids were then kept in desiccators containing $CaCl_2$ until their weights became constant.

TABLE 1

Results of component analysis of $RE(NCS)_3 \cdot nH_2O$

$RE(NCS)_3 \cdot nH_2O$	RE (%)	NCS (%)	H_2O (%)	Molar ratio (found) RE:NCS:H_2O
$La(NCS)_3 \cdot 7H_2O$	31.69	39.54	28.77	1:2.99:7.01
	(31.62)	(39.67)	(28.71)	
$Ce(NCS)_3 \cdot 7H_2O$	31.90	39.48	28.62	1:2.99:7.00
	(31.81)	(39.56)	(28.63)	
$Pr(NCS)_3 \cdot 7H_2O$	31.99	39.34	28.67	1:2.99:7.02
	(31.93)	(39.49)	(28.58)	
$Nd(NCS)_3 \cdot 7H_2O$	32.50	39.01	28.49	1:2.98:7.01
	(32.44)	(39.19)	(28.36)	
$Sm(NCS)_3 \cdot 6H_2O$	34.80	40.24	24.96	1:2.99:5.99
	(34.76)	(40.26)	(24.98)	
$Eu(NCS)_3 \cdot 6H_2O$	34.98	40.05	24.97	1:2.99:6.02
	(34.99)	(40.12)	(24.89)	
$Gd(NCS)_3 \cdot 6H_2O$	35.76	39.58	24.66	1:3.00:6.01
	(35.77)	(39.64)	(24.59)	
$Tb(NCS)_3 \cdot 6H_2O$	35.95	39.70	24.35	1:3.02:5.98
	(36.02)	(39.49)	(24.49)	
$Dy(NCS)_3 \cdot 6H_2O$	36.47	39.24	24.29	1:3.01:6.01
	(36.53)	(39.17)	(24.30)	
$Ho(NCS)_3 \cdot 6H_2O$	36.74	38.84	24.52	1:2.99:6.04
	(36.88)	(38.96)	(24.17)	
$Er(NCS)_3 \cdot 6H_2O$	37.35	38.64	24.01	1:2.98:5.97
	(37.20)	(38.76)	(24.04)	
$Tm(NCS)_3 \cdot 6H_2O$	37.52	38.57	23.91	1:2.99:5.98
	(37.44)	(38.61)	(23.95)	
$Yb(NCS)_3 \cdot 6H_2O$	37.90	38.45	23.65	1:3.02:6.00
	(38.00)	(38.26)	(23.74)	
$Y(NCS)_3 \cdot 6H_2O$	24.08	46.68	29.24	1:2.97:5.98
	(23.95)	(46.93)	(29.12)	

Note: calculated values in parentheses.

The aqueous amino acid solutions were prepared by weights.

RE_2O_3 (99.9–99.99%), sulphuric acid (reagent grade), $Ba(OH)_2 \cdot 8H_2O$ (analytical grade) and NH_4SCN (reagent grade) were used to prepare $RE(NCS)_3 \cdot nH_2O$ by the following double decomposition reaction.

$$3Ba(NCS)_2 + RE_2(SO_4)_3 = 3BaSO_4\downarrow + 2RE(NCS)_3$$

After recrystallization, the $RE(NCS)_3 \cdot nH_2O$ crystals were kept in desiccators containing 50–55% H_2SO_4 until their weight became constant.

Both chemical analyses and molecular structure determinations (by means of a Nicolet P3/F four-circle single-crystal X-ray diffractometer) proved that the compositions of $RE(NCS)_3 \cdot nH_2O$ are as follows: $n = 7$ for RE = La, Ce, Pr, Nd; $n = 6$ for RE = Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Y [4]. In every complex, the RE^{3+} ion is coordinated with the nitrogen atoms of three NCS^- ions and the oxygen atoms of $n - 1$ H_2O molecules. One water molecule which is not coordinated with an RE^{3+} ion therefore exists as structural water.

The rare earth content in $RE(NCS)_3 \cdot nH_2O$ was determined by EDTA titration. The NCS^- content was determined by the method of Volhard. The water content was calculated after the determination of the rare earth and NCS^- conents.

The results of component analyses of $RE(NCS)_3 \cdot nH_2O$ are listed in Table 1.

Calorimeter and calorimetric experiments

A modified RD-I heat conducting automatic calorimeter (The Scientific Instruments Factory of Sichuan University) was used for the caloric measurements. It has 144 pairs of thermocouples. Heat changes up to 2 J can be measured exactly.

Two calorimetric components with the same structure are arranged symmetrically in an aluminium block kept at constant temperature and connected in opposition to form a twin system. Therefore, attention should be paid to the symmetry and equivalence of the "working element" and the "reference element" in all respects when carrying out the measurements.

The heat effects due to the breaking of the glass ampoules are negligible compared with the measured heat.

Details of the apparatus principles and measurement have been published elsewhere [5, 6].

The reliability of the calorimetric system was monitored in the present experiments by measuring the integral heat of solution of 1 mol KCl (Merck) in 200 mol H_2O at 298.15 ± 0.1 K. The measured value is 17.59 ± 0.08 kJ mol^{-1}, which is consistent with the literature value of 17.524 ± 0.028 kJ mol^{-1} [7].

We measured the integral heats of solution of nine kinds of

$RE(NCS)_3 \cdot nH_2O$ ($n = 6$ for RE = Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Y) in aqueous glycine solution, of nine kinds of $RE(NCS)_3 \cdot nH_2O$ ($n = 7$ for RE = La, Pr, Nd; $n = 6$ for RE = Gd, Dy, Ho, Tm, Yb, Y) in aqueous alanine solution, and of ten kinds of $RE(NCS)_3 \cdot nH_2O$ ($n = 7$ for RE = La, Pr, Nd; $n = 6$ for RE = Sm, Eu, Gd, Dy, Ho, Yb, Y) in aqueous serine solution. In the above measurements, the molar ratio of $RE(NCS)_3 \cdot nH_2O$(c):amino acid(c):H_2O(l) is 1:3:600. We also measured the integal heats of $Dy(NCS)_3 \cdot 6H_2O$ in more dilute aqueous solutions of glycine, alanine and serine separately. Meanwhile, we changed the molar ratio of $Dy(NCS)_3 \cdot 6H_2O$(c):amino acid(c):H_2O(l) to 1:3:1200 and 1:3:2400.

Most of the measurements were repeated nine times. The uncertainty of the experimental results is expressed as twice the standard deviation of the mean.

RESULTS AND DISCUSSIONS

Component analyses of $RE(NCS)_3 \cdot nH_2O$

The results of component analyses of $RE(NCS)_3 \cdot nH_2O$ are listed in Table 1. The formulae of $RE(NCS)_3 \cdot nH_2O$ are as follows: $n = 7$ for RE = La, Ce, Pr, Nd; $n = 6$ for RE = Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Y.

Results of calorimetric experiments

The results of the calorimetric experiments are listed in Tables 2 and 3. It is clear that the integral heats of solution of $RE(NCS)_3 \cdot nH_2O$ in the above aqueous amino acid solutions are endothermic.

From Table 2 it can be seen that when the molar ratio of $RE(NCS)_3 \cdot nH_2O$(c):amino acid(c):H_2O(l) is 1:3:600 the integral heats of solution of the same $RE(NCS)_3 \cdot nH_2O$ in water and in aqueous solutions of glycine, alanine and serine are

$$\Delta H_{Ala} > \Delta H_{Gly}, \qquad \Delta H_{Ser} > \Delta H_{H_2O}$$

Perhaps this order is due to the difference of molecular interaction between different amino acid and water and the difference of coordinating ability of amino acid with RE^{3+} ion in aqueous solution.

From Table 3 we can see that the integral heats of solution of $Dy(NCS)_3 \cdot 6H_2O$ become smaller in more dilute solution of the same amino acid. We can also see that when the concentrations of the aqueous solutions of three amino acids decrease by equal amounts, the integral heats of solution of $Dy(NCS)_3 \cdot 6H_2O$ decrease most in alanine solution

TABLE 2

The integral heats of solution of $RE(NCS)_3 \cdot nH_2O$ in water and in aqueous solutions of glycine, alanine and serine (298.15 ± 0.1 K); the molar ratio of $RE(NCS)_3 \cdot nH_2O$(c):amino acid(c):H_2O(l) = 1:3:600

$RE(NCS)_3 \cdot nH_2O$	ΔH (kJ mol^{-1})			
	Glycine	Alanine	Serine	H_2O [9]
$La(NCS)_3 \cdot 7H_2O$	15.24 ± 0.07 [8]	18.50 ± 0.10	16.02 ± 0.07	14.55 ± 0.09
$Ce(NCS)_3 \cdot 7H_2O$	16.10 ± 0.10 [8]			15.05 ± 0.08
$Pr(NCS)_3 \cdot 7H_2O$	15.70 ± 0.10 [8]	17.91 ± 0.08	16.01 ± 0.13	15.06 ± 0.03
$Nd(NCS)_3 \cdot 7H_2O$	16.27 ± 0.09 [8]	19.02 ± 0.10	17.37 ± 0.12	15.18 ± 0.08
$Sm(NCS)_3 \cdot 6H_2O$	15.23 ± 0.11		15.19 ± 0.07	13.14 ± 0.06
$Eu(NCS)_3 \cdot 6H_2O$	16.36 ± 0.11		16.79 ± 0.20	14.16 ± 0.10
$Gd(NCS)_3 \cdot 6H_2O$	16.74 ± 0.10	18.23 ± 0.11	16.71 ± 0.09	13.91 ± 0.10
$Tb(NCS)_3 \cdot 6H_2O$	17.78 ± 0.14			(13.87)
$Dy(NCS)_3 \cdot 6H_2O$	17.35 ± 0.12	18.86 ± 0.14	16.67 ± 0.16	13.83 ± 0.10
$Ho(NCS)_3 \cdot 6H_2O$	18.05 ± 0.14	19.88 ± 0.15	17.44 ± 0.12	15.12 ± 0.12
$Er(NCS)_3 \cdot 6H_2O$	15.33 ± 0.13			(14.19)
$Tm(NCS)_3 \cdot 6H_2O$	16.00 ± 0.10	17.87 ± 0.18		(13.26)
$Yb(NCS)_3 \cdot 6H_2O$	16.25 ± 0.12	17.83 ± 0.11	16.14 ± 0.10	12.34 ± 0.08
$Y(NCS)_3 \cdot 6H_2O$	14.97 ± 0.06	16.04 ± 0.10	13.85 ± 0.11	

TABLE 3

The integral heats of solution of $Dy(NCS)_3 \cdot 6H_2O$ in aqueous amino acid solutions of different concentrations (298.15 ± 0.1 K)

Molar ratio	ΔH (kJ mol^{-1})		
$RE(NCS)_3 \cdot nH_2O$(c):amino acid(c):H_2O(l)	Glycine	Alanine	Serine
1:3:600	17.35 ± 0.12	18.86 ± 0.14	16.67 ± 0.16
1:3:1200	16.68 ± 0.09	17.43 ± 0.08	16.48 ± 0.14
1:3:2400	16.09 ± 0.12	15.80 ± 0.14	16.33 ± 0.17

and least in serine solution. This is possibly due to the different structures of glycine, alanine and serine and due to their differing coordinating abilities with RE^{3+} ion in aqueous solution.

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