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THE ENTHALPY OF SOLUTION IN WATER OF HISTIDINE COMPLEXES OF RE NITRATES

M. Ji[1], J. Liu[1], S. Gao[1], B. Kang[2], R. Hu[2] and Q. Shi[1]*

[1]Department of Chemistry, Northwest University, Xian 710069, Shaanxi
[2]Xian Modern Chemistry Research Institute, Xian 710065, Shaanxi, P. R. China

Abstract

The enthalpies of solution in water of RE(His)$(NO_3)_3 \cdot H_2O$ (*RE*=La–Nd, Sm–Lu, Y) were measured calorimetrically at 298.15 K, and the standard enthalpies of formation of $RE(His)^{3+}_{aq}$ (*RE*=La–Nd, Sm–Lu, Y) were calculated. The plot of the enthalpies of solution *vs.* the atomic numbers of the elements in the lanthanide series exhibits the 'tetrad effect'.

Keywords: enthalpy of solution, histidine, rare earth nitrate, solid complexes

Introduction

Great interest has been aroused in the past twenty years in the study of complexes of rare earth (RE) salts with amino acids, because the rare earth ions possess special functions in biochemistry and can be used as probes to label the calcium ion; moreover, the amino acids are structural units of proteins.

The phase equilibria of the ternary systems $RE(NO_3)_3$–His–H_2O have been investigated by means of a semi-micro method and fifteen solid complexes, RE(His)$(NO_3)_3 \cdot H_2O$ (*RE*=La–Nd, Sm–Lu, Y) have been prepared [1]. The combustion energies of these complexes have also been determined by using a precision rotating-bomb calorimeter, and the standard enthalpies of formation have been calculated [2].

In the present paper, the enthalpies of solution in water of RE(His)$(NO_3)_3 \cdot H_2O$ (*RE*=La–Nd, Sm–Lu, Y) have been determined by using a Calvet microcalorimeter, and the standard enthalpies of formation of $RE(His)^{3+}$aq (*RE*=La–Nd, Sm–Lu, Y) have been calculated. The relationship between the enthalpies of solution and the atomic numbers of the elements in the lanthanide series has been examined.

Experimental

Materials

On the basis of phase equilibrium data, fifteen solid complexes with a mole ratio of 1:1 prepared and kept in a desiccator containing P_4O_{10} until the mass of the crys-

* Author to whom all correspondence should be addressed.

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tals became constant. The analytical results are summarized in Table 1 RE^{3+} was determined complexometrically with EDTA. His was analysed by the formalin method. Before it was titrated, the RE^{3+} was removed by precipitation with $K_2C_2O_4$. Carbon, hydrogen and nitrogen analyses were performed on a 1106 type elemental analyzer.

All complexes were sieved through a 160 mesh and kept in a vacuum desiccator before use.

The conductivity of the deionized water used in the experiments was $5.48 \cdot 10^{-8}$ S cm^{-1}.

Experimental equipment and conditions

All measurements were made with a Calvet microcalorimeter, type RD496-II, (Southwest Institute of Electron Engineering, China) operated at 298.15±0.005 K.

The experimental precision and accuracy of enthalpies of solution were frequently checked by measurement of the enthalpies of solution ($\Delta_{sol}H^{\theta}_{\infty}$) of crystalline KCl in deionized water at 298.15 K. The experimental value of ($\Delta_{sol}H^{\theta}_{\infty}$)= 17.224±0.024 kJ mol^{-1} is in excellent accord with that of ($\Delta_{sol}H^{\theta}_{\infty}$)=17.234 kJ mol^{-1} reported in the literature [3]. This shows that the device for measurement of the enthalpy of solution used in this work is reliable.

Results and discussion

Enthalpies of solution of RE(His)$(NO_3)_3 \cdot H_2O$ in water

Results on the enthalpies of solution of RE(His)$(NO_3)_3 \cdot H_2O$ (*RE*=La–Nd, Sm–Lu, Y) in deionized water at 298.15 K are given in Table 2, where $\Delta_{sol}H^{\theta}_{m}$ denotes the enthalpy of solution in water of the complex, *m* is the mass of the complex, and *r* is the molar ratio $n(H_2O)/n(RE(His)(NO_3)_3 \cdot H_2O)$.

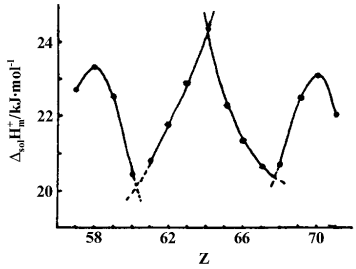

Fig. 1 Plot of $\Delta_{sol}H^{\theta}_{\infty}$ *vs.* the atomic numbers of the lanthanides

As the coordination of RE^{3+} with histidine occurs in water [4], and no solid residue was observed in the solution after calorimetry, the processes of dissolution of the complexes can be represented as

Table 1 Analytical results on compositions of the complexes (%)

Complex	RE		His		C		H		N	
	found	calcd.	found	calcd.	found	calcd.	found	calcd.	found	calcd.
$La(His)(NO_3)_3 \cdot H_2O$	27.57	27.89	31.17	31.15	14.21	14.47	2.14	2.23	16.92	16.87
$Ce(His)(NO_3)_3 \cdot H_2O$	28.22	28.06	31.28	31.07	14.07	14.43	2.12	2.22	16.89	16.83
$Pr(His)(NO_3)_3 \cdot H_2O$	27.91	28.18	30.90	31.03	14.10	14.41	2.07	2.22	16.72	16.80
$Nd(His)(NO_3)_3 \cdot H_2O$	28.53	28.65	30.72	30.82	14.02	14.32	2.03	2.20	16.54	16.69
$Sm(His)(NO_3)_3 \cdot H_2O$	29.54	29.51	30.65	30.45	13.98	14.14	2.05	2.18	16.28	16.49
$Eu(His)(NO_3)_3 \cdot H_2O$	29.57	29.73	30.14	30.36	13.92	14.10	1.99	2.17	16.16	16.44
$Gd(His)(NO_3)_3 \cdot H_2O$	30.44	30.45	29.96	30.04	14.14	13.95	2.32	2.15	16.03	16.27
$Tb(His)(NO_3)_3 \cdot H_2O$	30.91	30.67	30.07	29.95	14.05	13.91	2.20	2.14	16.31	16.22
$Dy(His)(NO_3)_3 \cdot H_2O$	31.23	31.15	29.40	29.74	13.89	13.81	2.24	2.13	16.24	16.11
$Ho(His)(NO_3)_3 \cdot H_2O$	31.77	31.47	29.44	29.60	13.64	13.75	2.11	2.12	16.07	16.03
$Er(His)(NO_3)_3 \cdot H_2O$	31.42	31.77	29.43	29.47	13.78	13.69	1.96	2.11	15.82	15.96
$Tm(His)(NO_3)_3 \cdot H_2O$	31.54	31.99	29.31	29.38	13.50	13.65	1.99	2.10	16.02	15.91
$Yb(His)(NO_3)_3 \cdot H_2O$	32.43	32.51	28.83	29.15	13.38	13.54	1.89	2.08	15.63	15.79
$Lu(His)(NO_3)_3 \cdot H_2O$	32.51	32.76	29.01	29.05	13.29	13.49	1.94	2.08	15.80	15.73
$Y(His)(NO_3)_3 \cdot H_2O$	19.82	19.84	34.25	34.63	15.96	16.08	2.53	2.47	18.84	18.75

Table 2 Enthalpies of solution in water of RE(His)$(NO_3)_3 \cdot H_2O$ at 298.15 K

Complex	Mass/mg	r	$\Delta_{sol}H_m^\theta$/kJ mol^{-1}	Mean/kJ mol^{-1}
La(His)$(NO_3)_3 \cdot H_2O$	6.218	35572	22.88	22.71±0.18
	6.664	33192	22.47	
	6.816	32451	22.64	
	7.436	29746	22.96	
	7.764	28489	22.76	
	8.088	27348	22.53	
Ce(His)$(NO_3)_3 \cdot H_2O$	6.154	36053	23.06	23.29±0.19
	6.228	35602	23.45	
	6.920	32042	23.27	
	7.486	29619	23.33	
	8.562	25897	23.54	
	9.118	24318	23.28	
Pr(His)$(NO_3)_3 \cdot H_2O$	5.475	40562	22.48	22.46±0.16
	6.342	35017	22.59	
	6.738	32959	22.43	
	7.405	29990	22.24	
	8.004	27746	22.68	
	8.672	25609	22.36	
Nd(His)$(NO_3)_3 \cdot H_2O$	6.492	34436	20.32	20.35±0.18
	7.104	31469	20.47	
	7.695	29052	20.04	
	8.426	26532	20.45	
	8.688	25732	20.29	
	9.302	24033	20.18	
Sm(His)$(NO_3)_3 \cdot H_2O$	5.602	40392	21.67	21.73±0.15
	6.684	33853	21.95	
	7.286	31056	21.54	
	7.552	29962	21.63	
	8.810	25684	21.78	
	9.038	25036	21.82	

Table 2 Continued

Complex	Mass/mg	r	$\Delta_{sol}H^{\theta}_{m}$/kJ mol^{-1}	Mean/kJ mol^{-1}
$Eu(His)(NO_3)_3 \cdot H_2O$	6.184	36705	22.86	22.82±0.13
	6.762	33568	22.73	
	7.464	30411	22.97	
	8.671	26178	22.94	
	8.912	25470	22.62	
	9.236	24576	22.79	
$Gd(His)(NO_3)_3 \cdot H_2O$	6.010	38159	24.56	24.35±0.14
	7.102	32292	24.42	
	7.272	31537	24.23	
	8.184	28022	24.28	
	8.660	26482	24.37	
	9.544	24029	24.14	
$Tb(His)(NO_3)_3 \cdot H_2O$	6.662	34536	21.97	22.23±0.17
	6.936	33172	22.30	
	7.514	30620	22.07	
	8.002	28753	22.42	
	8.540	26941	22.23	
	9.108	25261	22.35	
$Dy(His)(NO_3)_3 \cdot H_2O$	5.840	39669	21.43	21.31±0.16
	6.428	36040	21.31	
	6.890	33624	21.37	
	7.500	30889	21.05	
	8.472	27345	21.48	
	8.925	25957	21.19	
$Ho(His)(NO_3)_3 \cdot H_2O$	6.298	36956	20.68	20.59±0.18
	6.538	35599	20.43	
	7.256	32076	20.37	
	7.944	29298	20.75	
	8.452	27537	20.53	
	9.035	25760	20.80	

Table 2 Continued

Complex	Mass/mg	r	$\Delta_{sol}H^{\theta}_{m}$/kJ mol^{-1}	Mean/kJ mol^{-1}
$Er(His)(NO_3)_3 \cdot H_2O$	6.252	37393	20.97	20.72±0.16
	7.435	31443	20.52	
	7.568	30891	20.80	
	8.847	26425	20.62	
	9.264	25235	20.68	
	9.826	23792	20.75	
$Tm(His)(NO_3)_3 \cdot H_2O$	5.648	40523	22.30	22.49±0.14
	6.332	37038	22.68	
	7.090	33078	22.53	
	8.470	27689	22.39	
	9.322	25158	22.47	
	12.938	18127	22.58	
$Yb(His)(NO_3)_3 \cdot H_2O$	5.858	40346	23.35	23.17±0.16
	6.525	36222	23.06	
	7.180	32917	23.18	
	7.348	32165	22.90	
	8.018	29477	23.20	
	9.146	25842	23.29	
$Lu(His)(NO_3)_3 \cdot H_2O$	6.280	37771	21.76	22.02±0.15
	7.735	30666	21.94	
	7.968	29769	22.18	
	8.350	28408	22.02	
	9.902	23955	21.97	
	10.588	22403	22.10	
$Y(His)(NO_3)_3 \cdot H_2O$	6.544	30407	19.44	19.44±0.12
	7.645	26028	19.60	
	7.990	24904	19.27	
	8.762	22710	19.49	
	9.180	21676	19.35	
	9.518	20906	19.51	

$$RE(His)(NO_3)_3{\cdot}H_2O(s) \xrightarrow{\Delta_{sol}H_m^{\theta}} RE(His)^{3+}(aq,\infty) + 3NO_3^-(aq,\infty) + H_2O(l) \quad (1)$$

In process (1), large values of r were used. The mean of $\Delta_{sol}H_m^{\theta}$ in Table 2 can therefore be considered to relate to infinite dilution.

In Fig. 1, the $\Delta_{sol}H_m^{\theta}$ values of the complexes are plotted *vs.* the atomic numbers of the elements in the lanthanide series. It is seen that the curve displays the 'tetrad effect'.

Standard enthalpies of formation of RE(His)$^{3+}$(aq,∞)

The standard enthalpies of formation of $RE(His)^{3+}$ (aq, ∞) (*RE*=La–Nd, Sm–Lu, Y) were calculated by Hess's law according to the thermochemical equation:

$$\Delta_{f,RE(His)^{3+}(aq)}H^{\theta} = \Delta_{sol,coor(s)}H_m^{\theta} - 3\Delta_{f,NO_3^-(aq)}H^{\theta} - \Delta_{f,H_2O(l)}H^{\theta} + \Delta_{f,coor(s)}H^{\theta} \quad (2)$$

where $\Delta_{sol,coor(s)}H_m^{\theta}$) are the results from Table 2, $\Delta_{f,NO_3^-(aq)}H^{\theta}$=–207.36 kJ mol^{-1} and $\Delta_{f,H_2O(l)}H^{\theta}$=–285.83±0.042 kJ mol^{-1} [5].

The following results are taken from Ref [2]: $\Delta_{f,coor(s)}H_m^{\theta}$= 2005.30±3.12 (La), –2461.83±2.39 (Ce), –2145.06±2.46 (Pr), –2227.81±2.61 (Nd), –1982.90±4.04 (Sm), –2125.84±2.83 (Eu), –2547.04±4.13 (Gd), –2210.12±3.23 (Tb), –2079.35±5.97 (Dy), –1939.63±6.3 (Ho), –2165.00±4.48 (Er), –2184.13±7.32 (Tm), –2121.84±4.66 (Yb), –1803.25±8.20 (Lu), –1942.24±3.13 (Y) kJ mol^{-1}.

The standard enthalpies of formation of $RE(His)^{3+}$(aq) are –1074.68±3.13 (La), –1530.63±2.40 (Ce), –1214.69±2.47 (Pr), –1299.55±2.62 (Nd), –1053.26±4.04 (Sm), –1195.11±2.83 (Eu), –1614.78±4.13 (Gd), –1279.98±3.23 (Tb), –1150.13±5.97 (Dy), –1011.13±6.31 (Ho), –1236.37±4.48 (Er), –1253.73±7.23 (Tm), –1190.76±4.66 (Yb), –873.32±8.20 (Lu), –1014.89±3.13 (Y) kJ mol^{-1}.

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