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CALORIMETRIC TITRATION OF COMPLEXATION OF LANTHANIDE α-HYDROXYCARBOXYLATES WITH 1,10-PHENANTHROLINE

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Abstract—Thermodynamic properties of the complexation of the lanthanide (La^{III}, Eu^{III}) α-hydroxycarboxylates with 1,10-phenanthroline (phen) in methanol–water (v/v, 3:2) were studied at 25°C by calorimetric titration. The stability constants of the ternary complexes and enthalpies of coordination were calculated directly. Furthermore, we have evaluated the entropies (ΔS) and free energies (ΔG). The thermodynamic parameters are discussed according to the change of substituent group of α-hydroxy-acid as primary ligand. It is found that the enthalpy–entropy compensation effect exists in the present case. It is also found that a linear free energy relationship exists between the stability of the La–α-hydroxycarboxylate–phen ternary complex and the acid strength of α-hydroxy-acid as primary ligand, but the linear free energy relationship does not exist in the Eu–α-hydroxycarboxylate–phen ternary complex.

α-Hydroxy-acids and their lanthanide complexes have been extensively investigated. For example, the stability constants of complexes of α-hydroxy-acid with lanthanide elements were determined by various methods.[1] The thermodynamic parameters (ΔH, ΔS, ΔG) were also calculated.

Studies on the stability constants and thermodynamic parameters (ΔH, ΔS, ΔG) of ternary complexes of α-hydroxy-acid, EDTA (or CDTA, NTA) with lanthanides have been reported.[2] However, no paper concerning the study of ternary complexes of lanthanide with α-hydroxy-acid and 1,10-phenanthroline (phen) has been seen. Also, in our previous work[3] we have reported the synthesis, structure and properties of lanthanide complexes with mandelic acid and phen and an Eu^{III} complex with glycolic acid and phen. We also reported the thermodynamic properties of the complexation of seven lanthanide mandelates with phen in methanol–water (v/v, 3:2) at 25°C determined by calorimetric titration.

In order to study the effect of substituent groups on the thermodynamic function of coordination of lanthanide α-hydroxycarboxylates with phen, we now report the thermodynamic properties of the complexation of La^{III}, Eu^{III} glycolate, La^{III}, Eu^{III} lactate and La^{III}, Eu^{III} atrolactate with phen in methanol–water (v/v, 3:2) at 25°C determined by calorimetric titration.

EXPERIMENTAL

Reagents

The chemicals used included phen·H_2O (AR grade), lactic acid (AR grade), atrolactic acid (AR

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grade, Serva Entwigklwgsla BOk, Heidelberg), glycolic acid (CP grade), lanthanide oxide (99.99% Yaolong Chemical Works, Shanghai, China), which were transformed into carbonates, and methanol (AR grade), which was purged by distillation. The conductance of doubly distilled water was $(1.0–1.2)\times 10^{-6}$ S cm^{-1}.

Preparation of solutions

A phen solution (0.1 mol dm^{-3}) was prepared in 70% volume percentage methanol–water medium by direct weighing. The lanthanide α-hydroxycarboxylate solutions were prepared using lanthanide carbonate and α-hydroxy-acid in doubly distilled water. The exact concentrations of lanthanide α-hydroxycarboxylates were determined by titration with standard EDTA solution, using xylenol orange as indicator and hexamethylenetetramine as buffer. Then a measured 40.00 cm^3 volume of the lanthanide α-hydroxycarboxylate solution was pipetted into a 100 cm^3 beaker and diluted to 100 cm^3 with methanol. La^{III}, Eu^{III} glycolate, La^{III}, Eu^{III} lactate and La^{III}, Eu^{III} atrolactate solutions were prepared as described above. The molar conductances of lanthanide α-hydroxycarboxylate solutions mentioned above were measured. As seen in Table 1, the molar conductance data show that they exist as non-electrolytes[4] in methanol–water (v/v, 3:2). In other words, the dissociation of lanthanide α-hydroxycarboxylates may be neglected in this experiment. Since the dissociation of primary complexes does not take place in the range of dissociation of secondary ligand, it can be considered that the secondary ligand combines with the primary complex, just as it does with $[M(aq)_n]^{3+}$ in a binary system, in this experiment.[5] It is therefore more convenient to deal with the experimental data.

Apparatus

The apparatus used for this study included a DDS-11A molar conductometer, an LKB-8721-2 titration calorimeter (Sweden). The details of the instruments used, the procedure employed, conditions maintained, definitions of symbols, the methods of calculations used and correction experiment are the same as before.[6] Throughout the titrations temperature was kept at 25°C. All the calculations were performed on a TP-801 computer.

Experimental procedure and calculation methods

The experimental procedure and the procedure used for calculating the heat data at each titration point during the complexation reaction were similar to those described previously.[6]

In continuous titration calorimetry, the net reaction heat of coordination for any data point p between point x and point y along the titration curve shown as in ref. 6 can be calculated by using eq. (1):

$$Q_{C,p} = Q_p - Q_{HL,p} - Q_{TC,p} - Q_{D,p}, \qquad (1)$$

where Q_p is the total apparent heat at point p and $Q_{HL,p}$ is the total contribution of non-chemical heat effects from the start of the titration (point x) to any time during the run (point p) (depending on the rate of heat loss); $Q_{TC,p}$ is the heat correction term arising from the temperature difference between the titrant and titrate at point p; $Q_{D,p}$ is the heat of dilution of the titrant (the magnitude of the dilution heat effects was determined by experimentation).[6] The equations used to calculate $Q_{HL,p}$ and $Q_{TC,p}$ are given in ref. 7. The complete array of values obtained is given in Table 2.

Assume the reactions in this experiment can be represented as

$$LnL_3 + phen \rightleftharpoons LnL_3phen.$$

Table 1. The concentrations and molar conductances for solutions of lanthanide α-hydroxycarboxylates

Complex	Concentration (mol dm^{-3})	Molar conductance (S cm^2 mol^{-1})
$La(CH_2OHCOO)_3$	2.1837×10^{-3}	33.0
$Eu(CH_2OHCOO)_3$	3.0256×10^{-3}	13.9
$La(CH_3CHOHCOO)_3$	2.7798×10^{-3}	30.0
$Eu(CH_3CHOHCOO)_3$	2.5383×10^{-3}	12.6
$La(C_6H_5CH_3COHCOO)_3$	1.4916×10^{-3}	28.0
$Eu(C_6H_5CH_3COHCOO)_3$	0.4821×10^{-3}	24.9

Table 2. Titration calorimetric data and heat corrections for the titration of a 2.7798 mol dm^{-3} La(CH$_3$CHOHCOO)$_3$ solution with a 0.1000 mol dm^{-3} phen solution at 25°C in methanol–water (v/v, 3 : 2)

Time (min)	$-Q_p$ (J)	$-Q_{HL,p}$ (J)	$Q_{TC,p}$ (J)	$-Q_{D,p}$ (J)	$-Q_{C,p}$ (J)
1.00	0.25483	0.201305	6.4326×10^{-4}	0.028186	0.082354
2.00	0.59661	0.407048	1.2865×10^{-3}	0.059105	0.131754
3.00	0.96207	0.618385	1.9297×10^{-3}	0.075365	0.270237
4.00	1.30847	0.834947	2.5730×10^{-3}	0.098397	0.377705
5.00	1.65720	1.056328	3.2162×10^{-3}	0.137438	0.466655
6.00	1.94341	1.281337	3.8595×10^{-3}	0.204653	0.461263
7.00	2.33980	1.512073	4.5027×10^{-3}	0.256694	0.575544
8.00	2.67357	1.748954	5.1460×10^{-3}	0.294983	0.634817
9.00	3.00947	1.988886	5.7893×10^{-3}	0.370724	0.655633
10.00	3.36941	2.234377	6.4326×10^{-3}	0.401991	0.739484
11.00	3.70967	2.484801	7.0759×10^{-3}	0.483626	0.748345

The equilibrium constants of the reactions can be expressed as

$$K = \frac{[\mathrm{LnL_3phen}]}{[\mathrm{LnL_3}][\mathrm{phen}]}, \qquad (2)$$

where L represents CH$_2$OHCOO$^-$, CH$_3$CHOHCOO$^-$ and C$_6$H$_5$CH$_3$COHCOO$^-$, respectively; Ln represents La^{III} or Eu^{III}.

The net heat due to the complexation reaction from the start of the titration to any point p on the thermogram is

$$Q_{C,p} = \Delta H \times \Delta n_p, \qquad (3)$$

where ΔH is the change in enthalpy for the reaction and Δn_p is the number of moles of LnL$_3$phen formed from the start of the titration to point p and is a function of the equilibrium constants of the reactions mentioned above. The best values of K and ΔH are calculated by a least-squares analysis:

$$\Delta H = \sum_{p=1}^{m} Q_{C,p}\Delta n_p \Big/ \sum_{p=1}^{m} (\Delta n_p)^2; \qquad (4)$$

the error square sum over the m data points is given by

$$U(K, \Delta H) = \sum_{p=1}^{m} (Q_{C,p} - \Delta H \times \Delta n_p)^2, \qquad (5)$$

where the subscript p is over all the data points. The best log K and ΔH values are found by varying the log K value until the minimum in the error square sum is found. The recalculation results of six complexes are all $u < 10^{-4}$ (omitting data). The best K and ΔH value are obtained by iterative convergence and favour the formation of the 1 : 1 complex in solution. In other words, it is proved that the correct reactions (LnL$_3$+phen $\rightleftharpoons$ LnL$_3$phen) have been used. The change in free energy (ΔG) is then determined by the relationship $\Delta G = -RT \ln K$ and the change in entropy (ΔS) by the relationship $\Delta S = (\Delta H - \Delta G)/T$.

The values of thermodynamic stability constants and other parameters obtained are summarized in Table 3. For comparison, the thermodynamic stability constants and other parameters of the ternary complexes of La^{III}, Eu^{III} mandelate with phen are also given in Table 3.

RESULTS AND DISCUSSION

As seen from Table 3, the ΔG values of all the coordination reactions are negative, which indicates that the given reactions occur spontaneously. It is further observed that ΔH is also negative in all cases, which suggests that the reactions are exothermic. Therefore, lower temperature will favour the formation of the ternary complexes. The positive values of ΔS for all the reactions indicate that the entropy term is also favourable for their formation. Formally, the reaction system is a process in which the number of molecules is reduced, but for the coordination of phen as secondary ligand, the whole system adds a five-membered ring again so that it obtains a bigger chelate entropy. Besides, the decrease in positive electron density of Ln^{III} after complexation with ligands results in the loss of attraction of solvent molecules and an increment in the entropy of the reaction system.

As seen from Table 3, the order of the stability constants of ternary complexes with change in primary ligands is atrolactate > mandelate > lactate > glycolate for Eu^{III} or atrolactate > mandelate > lactate ≈ glycolate for La^{III}. It is

Table 3. Thermodynamic parameters for complexation of several lanthanide α-hydroxycarboxylates with phen in methanol–water (v/v, 3:2) at 25°C[a]

	Thermodynamic parameters				
Complex	Log K	$-\Delta H$ (kJ mol^{-1})	$-\Delta G$ (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	$T\Delta S$ (kJ mol^{-1})
$La(CH_2OHCOO)_3$ phen	2.18±0.01	8.11±0.01	12.431	14.50	4.322
$La(CH_3CHOHCOO)_3$ phen	2.17±0.02	8.03±0.04	12.377	14.59	4.351
$La(C_6H_5CHOHCOO)_3$ phen	2.44±0.01	3.97±0.03	13.965	33.36	9.944
$La(C_6H_5CH_3COHCOO)_3$ phen	2.78±0.03	5.18±0.12	15.855	35.78	10.672
$Eu(CH_2OHCOO)_3$ phen	2.04±0.01	11.37±0.03	11.633	0.882	0.263
$Eu(CH_3CHOHCOO)_3$ phen	2.41±0.03	10.70±0.01	13.744	1.020	3.043
$Eu(C_6H_5CHOHCOO)_3$ phen	2.51±0.09	10.58±0.17	14.317	12.54	3.741
$Eu(C_6H_5CH_3COHCOO)_3$ phen	2.99±0.04	11.16±0.14	17.050	19.77	5.890

[a] Data are average values of three runs. The uncertainties are expressed as the standard deviation from the mean

clear that atrolactate and mandelate lanthanide complexes are more stable than the corresponding lactates and glycolates. This definitely proves that the substituent effect does not play a predominant role amongst the factors that govern the complexing behaviour of the phen ligand. Log K values of ternary complexes appear to increase as the substituent groups of the α-hydroxy-acid increase and become large, but the range of increase is very small. This is because the intermolecular hydrogen bonding of lanthanide α-hydroxycarboxylates, $Ln(CH_2OHCOO)_3$, $Ln(CH_3CHOHCOO)_3$, $Ln(C_6H_5CHOHCOO)_3$ and $Ln(C_6H_5CH_3COHCOO)_3$ with the H_2O molecule appears to decrease as the substituent groups of α-hydroxy-acid increase and become large, and is favourable for the coordination of phen. The enhancement of stability of ternary complexes in the order mentioned above was also explained by possible aromatic ring stacking (benzene ring of α-hydroxy-acid and phen ring). For a given α-hydroxycarboxylate and phen ligands the order of ternary complex stability is $La^{III} < Eu^{III}$ (except glycolate complexes), which confirms our previous result.[7]

For a given lanthanide, in all these systems, both the enthalpy ($\Delta H < 0$) and entropy ($\Delta S > 0$) of formation contribute to the stability of the complexes. It is found that an enthalpy–entropy compensation effect exists in the ternary coordination system.[8] Plots of $T\Delta S$ against ΔH for ternary complexes of lanthanide α-hydroxycarboxylate with phen are given in Figs 1 and 2.

The linear relationship between ΔH and $T\Delta S$ indicates that the change in $T\Delta S$ is proportional to the change in ΔH, which is due to the nature of bonding of ligands with lanthanides, and the structures of the ternary complexes are similar. In other words, these complexes have similar thermodynamic states. The change in primary ligand

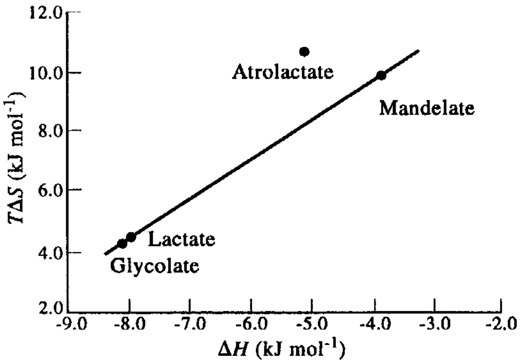

Fig. 1. Plot of $T\Delta S$ against ΔH for ternary complexes of La(III) α-hydroxycarboxylate with phen.

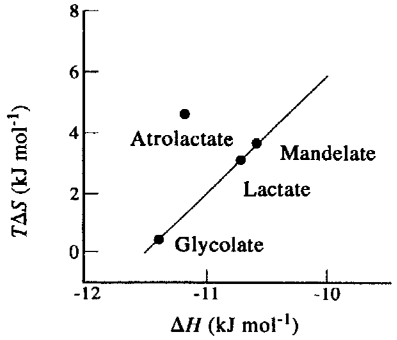

Fig. 2. Plot of $T\Delta S$ against ΔH for ternary complexes of Eu(III) α-hydroxycarboxylate with phen.

does not exert a sharp enthalpy and entropy effect and is in agreement with the linear relationship of the enthalpy–entropy compensation effect. Comparing Fig. 1 with Fig. 2, it is clear that the slope of Fig. 1 is larger than that of Fig. 2. The larger slope causes a correspondingly larger tendency of the enthalpy–entropy compensation effect. The intercept ($T\Delta S$) of Fig. 2 is bigger than that of Fig. 1, which is due to the difference between the La^{III} and Eu^{III} character, which results from the solvation between EuL_3 and solvents being greater than that of LaL_3 and solvents. The force of desolvation is greater for EuL_3 than for LaL_3 when coordinated with phen.

As seen from Table 3 and Figs 1 and 2, it was found that the negative value of ΔH for the reaction of $Ln(C_6H_5CH_3COHCOO)_3$ with phen is higher than that of the same lanthanide complexes of other α-hydroxy-acids, and does not agree with the relationship of the enthalpy–entropy compensation effect. This is due to $C_6H_5CH_3COHCOO^-$ of the binary complexes having the most volumetrical effect that could shield lanthanide ions from combining with solvent molecules. Thus, the degree of solvation of $Ln(C_6H_5CH_3COHCOO)_3$ is lower than that of $Ln(CH_2OHCOO)_3$, $Ln(CH_3CHOHCOO)_3$ and $Ln(C_6H_5CHOHCOO)_3$ ($Ln = La^{III}$, Eu^{III}), the number of molecules of solvation is small in the reaction system and the energy required to destroy solvation is also small when it bonds with phen. This gives rise to the negative value of ΔH of the reaction of $Ln(C_6H_5CH_3COHCOO)_3$ with phen increasing. In the meantime, the increment in entropy is also small. In other words, the configuration of solvation of $Ln(C_6H_5CH_3COHCOO)_3$ differs from the other lanthanide α-hydroxycarboxylates and the enthalpy–entropy compensation effect that we have discussed above does not exist in the ternary coordination system of $Ln(C_6H_5CH_3COHCOO)_3$ with phen.

The order of acid dissociation constants was reported as mandelic acid (pK_a 3.41) > atrolactic acid > glycollic acid (pK_a 3.83) > lactic acid (pK_a 3.86). It is further observed that a linear free energy relationship exists between the stability of the La–α-hydroxycarboxylate–phen ternary complex and the acid strengths of α-hydroxy-acid as primary ligand[9] (see Figs 3 and 4). However, the linear free energy relationship does not exist in the Eu–α-hydroxycarboxylate–phen ternary complex. The cause of this is not entirely clear, since the thermodynamic parameters are governed by several factors. In addition, as seen from Figs 3 and 4, the ternary complex of $La(C_6H_5CH_3COHCOO)_3$ with phen is not in agreement with the linear free energy relationship; this is also because of the volumetrical effect of $C_6H_5CH_3COHCOO^-$ of the binary complexes mentioned above.

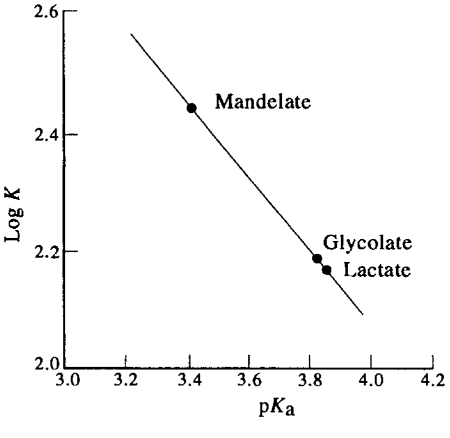

Fig. 3. Log K values of the La(III) ternary complex plotted against the pK_a values of α-hydroxy-acid as primary ligand.

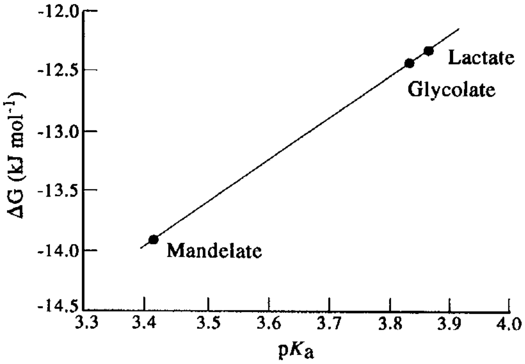

Fig. 4. ΔG values of the La(III) ternary system plotted against the pK_a values of α-hydroxy-acid as primary ligand.

REFERENCES

1. H. Thun and F. Ferbeek, *J. Inorg. Nucl. Chem.* 1966, **28**, 1949.
2. *Gmelin Handbook RE Main*, Vol. D5, p. 222 (1984).
3. W. Liufang, R. Yanping, L. Yizhi, P. Zhouren and W. Jigui, *J. Inorg. Chem.* (*China*) 1993, **9**, 124.
4. W. Geary, *J. Coord. Chem. Rev.* 1971, **7**, 81.
5. T. H. Mhaskb and K. N. Munshi, *J. Indian Chem. Soc.* 1976, **LIII**, 11.
6. L. Yu and H. Jing, *Acta Physico-chim. Sinica* 1987, **3**, 11.
7. L. Ginhui and S. Mengchang, *Acta Chim. Sinica* 1984, **42**, 861.
8. Y. Inoue and T. Hakushi, *J. Chem. Soc., Perkin Trans. II* 1985, 935.
9. C. Rongdi and X. Y. Yujing, *Acta Chim. Sinica* 1979, **37**, 167.