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A STUDY OF THE THERMODYNAMICS OF LANTHANOID-CROWN COORDINATION COMPOUNDS. CALORIMETRIC TITRATION FOR COORDINATION REACTION OF LANTHANUM PERCHLORATE WITH DIBENZO-30-CROWN-10 IN WATER–ACETONITRILE *

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ABSTRACT

The water content in H_2O–CH_3CN solvents has a strong effect on the coordination reaction of lanthanum perchlorate with dibenzo-30-crown-10 (DB30C10) in such solvents. A set of experiments in solvents with different volume percentages of water was made at 298.15 K using calorimetric titration, and the corresponding values of $\log K$ and ΔH for the coordination reaction are calculated by using a self-developed program on an APPLE-II computer. Some valuable results have been obtained and analysed with a discussion.

INTRODUCTION

Recently, studies of the coordination reaction of lanthanoid(III)-crown in solution have attracted more and more researchers. Numerous papers have been published by different authors [1–5]. Massaux et al. [3] hold the opinion that the water content of the solution has a strong effect on the stability constants of the lanthanoid adducts with crown due to the solvent effect.

Investigating the influence of the water content on the stability constant of the coordination compound $Nd(NO_3)_3$-18-crown-6 by ^{1}H-NMR at room temperature, Bünzli and Wessner [4] found that the stability constant remains almost unchanged when the water content of the solution is not too high.

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Using calorimetric titration, Luo et al. [5] investigated the effects of heat and stability constants of coordination reactions of La(NO_3)$_3$ with some 18-membered cyclic polyethers and pointed out that, qualitatively, the heat effects and stability constants of such reactions are strongly affected by the water content.

Based on the previous investigations, this paper studies the coordination reaction of La(ClO_4)$_3$ with DB30C10 in H_2O–CH_3CN solvents with different water contents by calorimetric titration and obtains some useful results from data treatment using a self-developed program on an APPLE-II computer.

A discussion on the effect of the water content on this type of coordination reaction has been pursued quantitatively.

EXPERIMENTAL

Materials and their purification

The materials used were La_2O_3 (99.99%), $HClO_4$ (G.R.), HCl (G.R.), Tris (B.D.H.), and KCl (Merck), boiled doubly-distilled water (electrical conductivity less than 1×10^{-6} Ω^{-1} cm^{-1}), CH_3CN (A.R.) was purified by distillation after drying with CaH_2 (electrical conductivity less than 5×10^{-7} Ω^{-1} cm^{-1}). Dibenzo-30-crown-10 and -18-crown-6 (Tuojiang Chemical Plant, Sichuan, P.R. China) were dried by placing them under vacuum for 24 h.

Solution preparation and titration procedure

The anhydrous acetonitrile solution of La(ClO_4)$_3$ was prepared by dissolving lanthanum perchlorate (from treating La_2O_3 with perchloric acid) in the appropriate anhydrous acetonitrile followed by evaporation and repeating this treatment before storing it under vacuum over P_2O_5 for several days and finally dissolving it with anhydrous acetonitrile to give a concentration of 0.10 M. The infrared spectrum showed no indication of hydroxyl bands due to water. The content of La^{3+} in the solution was standardized volumetrically with EDTA. The H_2O–CH_3CN solutions of DB30C10 (about 0.006 M) were prepared by dissolving known weights of DB30C10 in H_2O–CH_3CN solvents (by volume of H_2O and CH_3CN). The anhydrous acetonitrile solution of La(ClO_4)$_3$ was used as titrant and the H_2O–CH_3CN solutions of DB30C10 as titrate. When thermal equilibrium was reached, the incremental titration began with the quantities of titrant added each time being equal. Heat of dilution corrections were made by titrating anhydrous acetonitrile solution of La(ClO_4)$_3$ into the corresponding H_2O–CH_3CN solvents. All calorimetric determinations were made at 298.15 K.

The calorimeter and its calibration

The calorimeter used in our research was the LKB 8721-2 Precision Titration Calorimeter made in Sweden. The basic principle and general experimental procedure of the calorimeter were given by Wadsö [6] and in the instrument specifications. The temperature-sensing element of the calorimeter was a thermistor which was monitored by a precision Wheatstone bridge. Within the scope of the measurements, the relationship between resistance and temperature was given by

$$\ln R = -3.7018 + \frac{3369.14}{T} \tag{1}$$

where R (Ω) is the measured resistance and T (K) is the temperature corresponding to R. For a given point P during the titration, the total heat capacity of the measured system, $C_{\mathrm{p,p}}$(J K^{-1}) was given by

$$C_{\mathrm{p,p}} = 142.60 + 2.4027 V_{\mathrm{s,w}} + 1.7591 V_{\mathrm{t,p}} \tag{2}$$

where $V_{\mathrm{s,w}}$ (ml) is the water content of the measured system and $V_{\mathrm{t,p}}$ (ml) is the volume of titrant added from the start of the titration to point P.

The reliability of the calorimetric system was checked by measuring the heat of reaction of Tris with HCl in aqueous solution at 298.15 K. The measured value in our laboratory is -47.47 kJ mol^{-1}, which is in good agreement with the literature value (-47.49 kJ mol^{-1}) [7]. The value of $\log K$ of the coordination reaction of KCl with 18-crown-6 in aqueous solution was also measured at 298.15 K, and resulted in a value of 2.01, which is consistent with the value of 2.03 reported by Izatt et al. [8].

CALCULATION

For a given point P during the titration, the total apparent heat Q_{p} appearing in the reaction vessel from point X (the starting point of the titration, see Fig. 1) to point P is given by

$$Q_{\mathrm{p}} = -C_{\mathrm{p,p}}(T_{\mathrm{p}} - T_{\mathrm{X}}) \tag{3}$$

where T_{p} and T_{X} are the temperatures at P and X, respectively. Q_{p} must be corrected for all heat effects other than that due to the coordination reaction before they can be used to calculate the stability constant. Those corrections are described briefly below.

Correction for non-chemical energy

According to the literature [6,9], provided that the energy due to stirring and resistance heating of the thermistor remains constant during the titra-

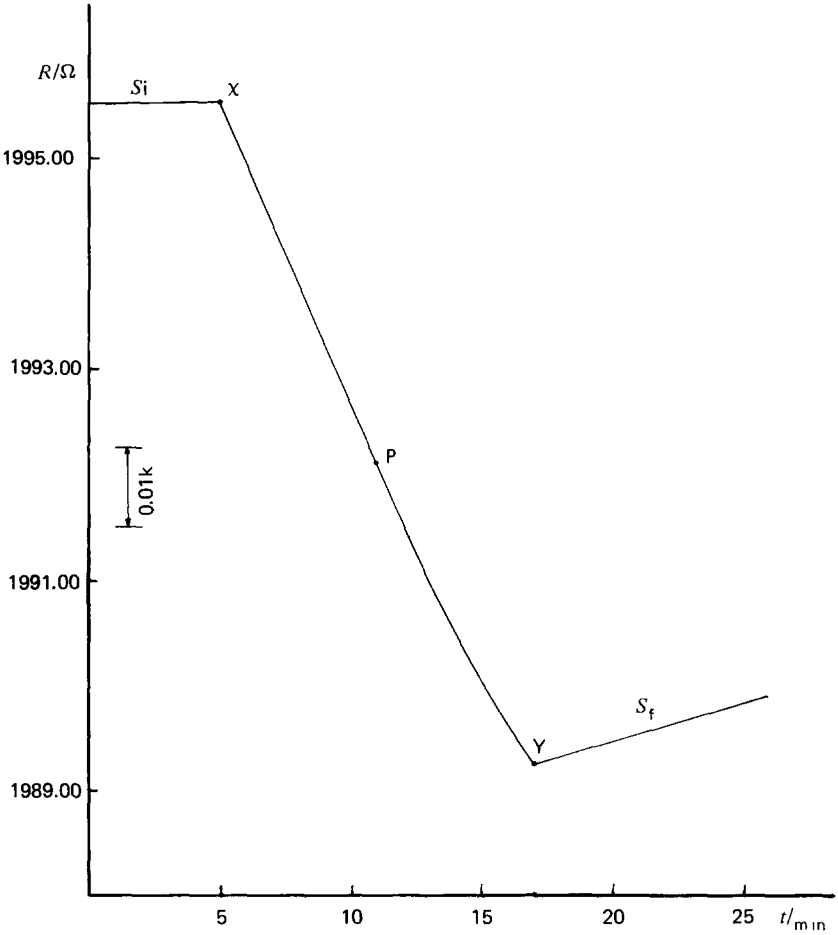

Fig. 1. Calorimetric curve for the titration of 0.005734 M DB30C10 (in 0.2 vol.% H_2O) with 0.09332 M $La(ClO_4)_3$.

tion and that of the heat exchange between the reaction vessel and its surroundings obeys Newton's law of cooling the correction value for non-chemical energy, $Q_{HL,p}$, can be evaluated by

$$Q_{HL,p} = -C_{p,p}\left[S_{f,p} - k\left(T_{m,p} - T_p\right)\Delta t\right] \qquad (4)$$

where

$$k = \frac{(S_f - S_i)}{(T_i - T_f)} \qquad (5)$$

$$S_{f,p} = S_i + (S_f - S_i)\frac{(T_p - T_i)}{(T_f - T_i)} \qquad (6)$$

$$T_{m,p} = \frac{(T_p + T_i)}{2} \qquad (7)$$

where k is the heat leakage constant, $S_{f,p}$ and T_p are the rate of increase of temperature (due to the non-chemical energy) and the temperature at point P, $T_{m,p}$ and Δt are the mean temperature and time interval from point X to point P, and T_i, S_i and T_f, S_f are the mean temperature and rate of increase of temperature before and after titration, respectively.

Correction for the temperature difference between the titrant and titrate

The heat effect, $Q_{TC,p}$, due to the temperature difference between the titrant and titrate may be neglected because both of them were kept in the thermostatic bath for more than 5 h before titration.

Correction for the heat of dilution

The heat of dilution of the titrate may be neglected because of the large volume and low concentration of the DB30C10 solution. The only correction to be taken into consideration is that for the heat of dilution of the titrant, $Q_{D,p}$, which is measured separately.

Assuming the stoichiometry of the coordination reaction is 1 : 1, i.e.

$M + L \rightleftharpoons ML$

then

$$K = \frac{[ML]}{[M][L]} \tag{8}$$

where K is the stability constant.

The net heat, $Q_{C,p}$, gained due to the coordination reaction under consideration is given by

$$Q_{C,p} = Q_p - Q_{HL,p} - Q_{TC,p} - Q_{D,p} \tag{9}$$

There is a relationship between $Q_{C,p}$ and ΔH, i.e.

$$Q_{C,p} = \Delta H \, \Delta n_p \tag{10}$$

where ΔH is the enthalpy change of the cordination reaction of interest and Δn_p is the number of moles of coordination compound formed in the vessel from point X to point P. It can be calculated by eqn. (8) based on the assumed K and the known total concentrations of the metal ion and ligand.

The sum of the square of the errors from 1 through m is given by

$$U(K,\Delta H) = \sum_{p=1}^{m} (Q_{C,p} - \Delta H \, \Delta n_p)^2 \tag{11}$$

The optimum value of ΔH corresponding to the assumed K is given by

$$\Delta H = \frac{\sum_{p=1}^{m} Q_{C,p} \, \Delta n_p}{\sum_{p=1}^{m} (\Delta n_p)^2} \tag{12}$$

By repeatedly varying the value of K, we can find the minimum sum of the square of the errors.

RESULTS AND DISCUSSION

All the results obtained from experiments and calculations, such as $\log K$, ΔH, ΔG, and ΔS, are summarized in Table 1.

It can be seen from Table 1 that, when the water content of the solvents increases to 5 vol.%, the value of $\log K$ cannot remain accurate because of the lower heat of reaction and higher heat of dilution than in the cases with lower water contents.

When the coordination reaction of interest proceeds in anhydrous CH_3CN, the value of $\log K$ will be far beyond the accuracy of measurement in calorimetric titration, but we can obtain the value of ΔH with sufficient accuracy because, in this case, ΔH is independent of $\log K$ (see Table 2).

The value of ΔH in Table 2, obtained under experimental conditions, is 18.48 kJ mol^{-1}, and if the reaction goes completely in 1 : 1 proportion, we have $\Delta H = 19.03$ kJ mol^{-1}; both values are in the same range of error. That certifies that the assumption is correct.

Massaux's value of log K [10], obtained from the same reaction proceeding in a solution of anhydrous propylene carbonate at 25 °C, is much smaller than ours obtained from the reaction in anhydrous acetonitrile, but it is very close to that obtained in the solvent with 0.4 vol.% of water content. The reason might be that the solvation ability of propylene carbonate is stronger than that of acetonitrile.

The values of log K and $-\Delta H$ are reduced significantly by adding small amounts of water(see Table 1). This result certifies that the effect of the

TABLE 1

Thermodynamic data for the coordination reaction of La $(ClO_4)_3$ with DB30C10 in H_2O–CH_3CN solvents of varying compositions at 298.15 K

Vol.% H_2O [a]	$\log K$			$-\Delta H$ (kJ mol^{-1})			$-\Delta G$ (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
	No. 1	No. 2	Ave.	No. 1	No. 2	Ave.		
0				18.48	18.28	18.38		
0.2	4.77	4.90	4.84	13.13	12.71	12.92	27.63	49.34
0.4	4.62	4.35	4.48	7.64	7.92	7.78	25.58	59.70
1	2.83	2.74	2.78	4.69	4.43	4.56	15.87	37.93
2	2.80	2.68	2.74	3.28	4.15	3.72	15.64	39.98
5	2.92	2.47	2.70	−2.88	−1.81	−2.34	15.41	59.53
10 [b]			2.92			−4.52	16.67	71.07

[a] Water content in the initial titrate expressed as volume percentage.

[b] Only one measurement was made.

TABLE 2

Calculation of log$K$ and ΔH values for the coordination reaction of $La(ClO_4)_3$ with DB30C10 in anhydrous CH_3CN

log$K$	$-\Delta H$ (kJ mol^{-1})	$U \times 10^4$	$-\log U$
6.00	18.50909	2.62453642	3.58094740
6.50	18.48732	2.54188644	3.59484386
7.00	18.48020	2.51486297	3.59948568
7.50	18.47792	2.50622063	3.60098070
8.00	18.47720	2.50347806	3.60145621
8.50	18.47697	2.50260895	3.60160701
9.00	18.47690	2.50233456	3.60165463
9.50	18.47687	2.50224771	3.60166970
10.00	18.47687	2.50222038	3.60167444
10.50	18.47686	2.50221155	3.60167598
11.00	18.47686	2.50220930	3.60167637
11.50	18.47686	2.50220783	3.60167662
12.00	18.47686	2.50220781	3.60167663

water content of the solvent on the coordination reaction of such reactants is significant.

For lanthanoid(III) cations, water is a rather strong ligand and therefore, the crown, as a ligand usually cannot compete with it successfully. As a matter of fact, most of the lanthanoid(III)-crown coordination compounds are easily dissociated, but difficult to form in water because of the latter's strong polarity.

DB30C10, however, has a certain affinity for La^{3+}, even if the water content reaches 10 vol.%. This might be explained because DB30C10, as a ligand, is more flexible and has more oxygen atoms in which to wrap La^{3+}.

Once there is water in the solvent, DB30C10 would immediately attack and finally break the H_2O–La^{3+} bond. (It is possible to maintain one or two coordinated molecules of water to meet the need of La^{3+} for its coordination number). Such a process requires more energy, and for different systems, the demand for the energy used to break the H_2O–La^{3+} bond is also different. That is why the coordination enthalpy changes from exothermic to endothermic with the increase of the water content of the system.

It is difficult to explain clearly the DB30C10–La^{3+} interaction by using a model which describes how the central ion occupies the centre of the cavity of the crown because the cavity diameter of DB30C10 (> 4 Å) is too large to fit the La^{3+} ion. At present, most people think that the DB30C10 coordinates with the metal ion in the form of a "wrap around" structure [10] because a large cavity diameter with sufficient flexibility makes the coordination of DB30C10 with the metal ion in a self-fold manner more effective.

This hypothesis has been verified by the measurement of the single-crystal structure of coordination compounds of DB30C10 which is formed with alkali and alkaline earth metal ions. The results obtained in our experiments also support this point of view. It can be seen from Table 1 that the entropy changes remain positive in any case, and therefore the entropy effect is a factor which favours the formation of the coordination compound.

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