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Calorimetric titration for coordination reactions of dibenzo-30-crown-10 with rare earth perchlorates in titrate of acetonitrile containing 0.5 vol.% water

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Abstract

The coordination reactions of RE$(ClO_4)_3$ (RE = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Tm, Yb or Lu) with dibenzo-30-crown-10 (DB30C10) acetonitrile containing 0.5 vol.% water were investigated at 298.15 K by titration calorimetry. The formation constants and enthalpies of coordination adducts were calculated by using a program developed for use on an IBM computer. Furthermore, the formation free energies and entropies of the coordination adducts were obtained. The results show that adducts of 1:1 stoichiometry between each of the above 12 rare earth cations and DB30C10 are formed under the experimental conditions used, and all the formation enthalpies are negative.

INTRODUCTION

Great interest has been aroused in the study of the coordination chemistry of rare earth (RE) cations with crown ethers in solution [1]. Because water has a strong coordinating effect on the rare earth cations, it is usual to use non-aqueous systems to study the solution coordination chemistry of rare earth cations with crown ethers. Although some work has been concerned with the influence of water on this kind of coordination reaction [2–5], systematic and quantitative researches are lacking. Huang et al. [6] studied the coordination reaction of La$(ClO_4)_3$ with dibenzo-30-crown-10 (DB30C10) in H_2O–CH_3N solvents with different volume percentages of water by titration calorimetry. In order to investigate the effect of water on this type of coordination reaction both systematically and quantitatively, we studied the coordination reactions of a series of RE$(ClO_4)_3$ with DB30C10

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in acetonitrile containing 0.5 vol.% water by titration calorimetry and have obtained some useful results from data treatment using a program developed by us on an IBM computer. The results of the analysis are discussed.

EXPERIMENTAL

Purification of materials and preparation of solutions

Acetonitrile (A.R.) was purified by distillation after drying with CaH_2 (electrical conductivity less than 5×10^{-7} Ω^{-1} cm^{-1}). DB30C10 from Tuojiang Chemical Plant, Sichuan, People's Rep. of China, was dried by placing it in vacuum for 24 h.

An anhydrous acetonitrile solution of DB30C10 was prepared by dissolving a known weight of DB30C10 in sufficient anhydrous acetonitrile to give a concentration of 0.035 06 M.

The method used to prepare the H_2O–CH_3CN solutions of $RE(ClO_4)_3$ is as follows. The oxide RE_2O_3 (99.99%) or Pr_6O_{11} and Tb_4O_7 for Pr and Tb respectively, was treated with perchloric acid (G.R.); for Pr_6O_{11} and Tb_4O_7, sufficient H_2O_2 was added to reduce Pr(IV) and Tb(IV) to the trivalent form. Acetonitrile solutions of $RE(ClO_4)_3$ were prepared by dissolving the rare earth perchlorates so obtained in anhydrous acetonitrile, and evaporating. This treatment was repeated before storing the salts under vacuum over P_2O_5 for several days and finally dissolving them in anhydrous acetonitrile. The IR spectra showed no indication of hydroxyl bands due to water. The contents of RE^{3+} in the solutions were determined by ethylenediaminetetraacetic acid (EDTA) titration. The H_2O–CH_3CN solutions of $RE(ClO_4)_3$ were prepared by transferring an accurately measured volume of the anhydrous acetonitrile solution of $RE(ClO_4)_3$ into a 250 ml volumetric flask, adding exactly 1.25 ml of water and making up to the mark with anhydrous acetonitrile. In this way, acetonitrile solutions of RE^{3+} containing 0.5 vol.% of water were prepared and the concentration of RE^{3+} (0.005 M) was accurately calculated.

The calorimeter and the calorimetric experiments

The calorimeter used in our research was an LKB 8721-2 precision titration calorimeter made in Sweden. The temperature-sensing element of the calorimeter was a thermistor, the output from which was monitored by a precision Wheatstone bridge. The 100 ml reaction vessel was made of stainless steel. The basic principles and the general experimental procedure for the use of the calorimeter are given by Wadsö [7] and in the instrument specification.

The reliability of the calorimetric system was checked by measuring the heat of reaction of Tris (BDH) with HCl (G.R.) in aqueous solution at

298.15 K. The measured value was -47.48 kJ mol^{-1}, which is in good agreement with the literature value of -47.49 kJ mol^{-1} [8].

The anhydrous acetonitrile solution of DB30C10 was used as the titrant and the acetonitrile–0.5% water solutions of RE$(ClO_4)_3$ as the titrate. When thermal equilibrium was reached, incremental titration was started, with the quantity of titrant added each time being the same. All calorimetric determinations were made at 298.15 ± 0.001 K.

Acetonitrile containing 0.5% of water was used for the titrate and anhydrous acetonitrile for the titrant. At a given point P during the titration, the total heat capacity of the measured system was obtained by electrical calibration. The influence of the rare earth perchlorates and DB30C10 on the heat capacity was ignored because of their low concentrations. According to ref. 7, the term T_m^2 in $\Delta R T_m^2/R_m$ may be taken as a constant, and the temperature change is thus a function of $\Delta R/R_m$. Here R_m is the mean resistance of the thermistor at the point P, $\Delta R = R - R_1$, where R is the value of thermistor resistance at point P, and R_1 is the mean resistance before titration.

CALCULATION

The heat capacities of the experimental system at different volumes, as determined by electrical calibration, are listed in Table 1.

The use of an anhydrous acetonitrile solution of DB30C10 to titrate an acetonitrile–0.5% water solution of $Dy(ClO_4)_3$ is described to exemplify the calculation procedure.

The calorimetric curve of the titration of 0.005 113 M $Dy(ClO_4)_3$ with 0.035 06 M DB30C10 is shown in Fig. 1. Here S_i and S_f are the rates of

TABLE 1

Heat capacity data C_p (J) for the reaction systems of DB30C10 with RE$(ClO_4)_3$ measured electrically at 298.15 K [a]

No.	$V_{t,p}$ [b] (ml)					
	50.768	51.567	52.367	53.164	53.966	54.768
1	4238.5	4260.8	4359.8	4392.2	4461.7	4472.2
2	4216.6	4264.0	4358.6	4380.0	4451.8	4468.2
3	4228.5	4282.1	4351.9	4361.2	4430.4	4476.5
4	4260.6	4278.1	4340.6	4360.3	4443.1	4471.2
5	4263.8	4290.1	4369.9	4378.6	4387.7	4471.0
Ave.	4241.6	4275.0	4356.2	4374.5	4434.9	4471.8
Relative accuracy (‰)	2.1	1.3	1.1	1.4	3.5	0.3

[a] According to ref. 7, the temperature change may be expressed in terms of $\Delta R/R_m$, and therefore the unit of heat capacity (C_p) is the joule.

[b] $V_{t,p}$ is the total volume of the reaction system at data point P.

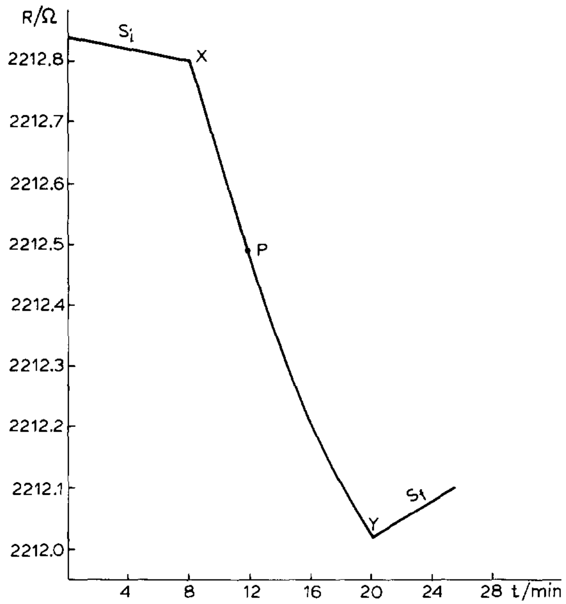

Fig. 1. Calorimetric curve for the titration of acetonitrile solutions (containing 0.5 vol.% of water) of 0.005113 M Dy(ClO_4)$_3$ with anhydrous acetonitrile solution of 0.03506 M DB30C10.

change of resistance before and after titration, respectively. As described in ref. 7, the values of the resistance change at every data point were corrected, and the values of heat Q_p for every data point were calculated using the corresponding heat capacity. The net heat $Q_{C,p}$ gained by virtue of the coordination reaction under consideration is given by

$$Q_{C,p} = Q_p - Q_{D,p} - Q_{TC,p}$$

where $Q_{D,p}$ is the heat of dilution at data point P and $Q_{TC,p}$ is the heat caused by the temperature difference between the titrate and the titrant.

Calculation of Q_p

According to the literature [7], provided that the energy due to stirring and to resistance heating of the thermistor remains constant during the titration 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 can be calculated from

$$\Delta R_{corr,p} = \left[\frac{R_{m,p}}{R_f} S_f + K(R_f - R_{m,p}) \right] \Delta t$$

where $\Delta R_{corr,p}$ is the resistance correction term due to the non-chemical energy, K is the heat leakage constant, R_f is the mean resistance after titration (after point Y, see Fig. 1) and $R_{m,p}$ and Δt are the mean resistance and the time interval from point X to point P respectively. The value of resistance change, excluding the resistance correction term $\Delta R_{corr,p}$ is given by

$$\Delta R_p = \Delta R_{exp,p} - \Delta R_{corr,p}$$

where $\Delta R_{exp,p}$ is the value of the thermistor resistance change at data point P obtained from the experiment and $\Delta R_{exp,p} = R_p - R_X$. Using ΔR_p, $R_{m,p}$ and the corresponding heat capacity C_p, Q_p can be calculated.

Correction for the heat of dilution

It was proved experimentally that the heat of dilution of the titrate may be neglected because of the large volume and the low concentration of the $RE(ClO_4)_3$ solution. The heat of dilution of the titrant $Q_{D,p}$ is measured separately.

Correction for the heat caused by the temperature difference between the titrate and titrant

In this paper the point X is taken as the initial state and the point P as the final state. The volumes of titrant added at point X and at point P are 0 ml and V_p ml respectively. The heat $Q_{TC,p}$ is given by

$$Q_{TC,p} = C_B(T_0 - T_B)V_p\rho$$

where C_B is the heat capacity of the titrant, T_0 is the initial temperature of the titrate, T_B is the temperature of the titrant and ρ is the density of the titrant. In our experiment, the titrate and the titrant were kept in a thermostatted water bath for more than 5 h before the titration; thus T_0

TABLE 2

Values of resistance change and heat data for the coordination reaction of DB30C10 with $Dy(ClO_4)_3$ in a titrate of acetonitrile containing 0.5% of water at 298.15 K ($S_i = -0.005$ Ω min^{-1}, $S_f = 0.0125$ Ω min^{-1}, $V_0 = 49.968$ ml)

P	V_p [a] (ml)	$\Delta R_{exp,p}$ (Ω)	$\Delta R_{corr,p}$ (Ω)	ΔR_p (Ω)	Q_p (J)	$Q_{D,p}$ (J)	$Q_{C,p}$ (J)
1	0.800	−0.182	−0.005	−0.177	−0.3393	−0.0115	−0.3278
2	1.599	−0.346	−0.003	−0.343	−0.6627	−0.0357	−0.6270
3	2.399	−0.480	0.005	−0.485	−0.9549	−0.0679	−0.8870
4	3.196	−0.598	0.018	−0.616	−1.2179	−0.1077	−1.1102
5	3.998	−0.690	0.034	−0.724	−1.4526	−0.1494	−1.3032
6	4.800	−0.780	0.053	−0.833	−1.6837	−0.1818	−1.5019

[a] V_0 is the volume of titrate and V_p is the total volume of titrant added at data point P.

approaches T_B. It is proved experimentally that the term $Q_{TC,p}$ is too small to measure, and $Q_{TC,p}$ is therefore ignored in this paper.

The values of the resistance change and heat data are listed in Table 2.

Formation enthalpy and formation constant

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

$$M + L = ML$$

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

where K is the formation constant. The coefficients of activity are taken as approximating to unity for the low concentrations of $RE(ClO_4)_3$ and DB30C10.

The relationship that exists between $Q_{C,p}$ and ΔH [9] is

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

where ΔH is the formation enthalpy of the coordination adduct and Δn_p is the number of moles of the coordination adduct formed in the vessel from point X to point P. This number can be calculated on the basis of the assumed K value and the known total concentrations of the metal ion and ligand.

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

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

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

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

By repeatedly varying the value of K, we can find the minimum sum of the square of the errors and the log K and ΔH values of the coordination adduct are obtained.

The results of the calculation of log K and ΔH values for the coordination adduct of $Dy(ClO_4)_3$ with DB30C10 are summarized in Table 3.

RESULTS AND DISCUSSION

The thermodynamic data for the adducts of 12 species of $RE(ClO_4)_3$ with DB30C10 in a titrate of acetonitrile containing 0.5% of water are summarized in Table 4.

TABLE 3

Calculation of log K and ΔH values for the coordination reaction of $Dy(ClO_4)_3$ with DB30C10 in a titrate of acetonitrile containing 0.5% of water

log K	$-\Delta H$ (kJ mol^{-1})	$U \times 1000$	$-\log U$
2.39	20.33452	4.015554	2.396255
2.40	20.12493	4.006540	2.397231
2.41	19.91957	3.999443	2.398001
2.42	19.71833	3.994272	2.398563
2.43	19.52113	3.990993	2.398919
2.44	19.32789	3.989705	2.399059
2.45	19.13851	3.990278	2.398997
2.46	18.95291	3.992801	2.398723
2.47	18.77101	3.997300	2.398233
2.48	18.59274	4.003740	2.397534
2.49	18.41800	4.012175	2.396620

It can be seen from Table 4 that each of the 12 RE^{3+} species can coordinate with DB30C10 to form an adduct of 1:1 stoichiometry, and the formation enthalpies and formation constants of the adducts are calculated accurately.

The formation constants of the adducts of RE^{3+} with DB30C10 are higher than $10^{2.3}$ under the experimental conditions. This shows that although there is a certain amount of water in the systems, which has a stronger coordination effect on the rare earth cations, DB30C10 can coordinate sufficiently with RE^{3+}. The literature [10] includes a study of the coordination reactions of La^{3+} and Yb^{3+} with DB30C10 in anhydrous acetonitrile. The results show that the formation constants exceed 10^{12}. The formation constant values obtained from our experiments are lower than those reported in the literature [10]. This shows that water has a great influence on the formation constants of adducts of RE^{3+} with DB30C10.

The ligand DB30C10 is a very large macrocycle. Its cavity diameter is more than 4 Å [6]. The radii of the RE^{3+} ions are much smaller than this. For La^{3+} the largest among the RE^{3+} ions, the radius is 1.06 Å [11]. From the point of view of the central ion occupying the centre of the cavity of the crown, it seems obvious that DB30C10 cannot adequately coordinate with RE^{3+}. In addition, water is a rather strong ligand for RE^{3+} and therefore the crown, as a ligand, usually cannot compete with it successfully [2,5]. However, the formation constants of adducts of RE^{3+} with DB30C10 in this experiment are higher than $10^{2.3}$. This might be explained by considering that DB30C10, as a ligand, is flexible and has several oxygen atoms available to coordinate with RE^{3+}. The DB30C10 coordinates with the metal ion in the form of a "wrap around" structure because a large cavity diameter with sufficient flexibility makes the coordination of DB30C10 with the metal ion in a self-folding manner more effective. This hypothesis

TABLE 4

Thermodynamic data for the coordination reactions of DB30C10 with RE(ClO_4)$_3$ in a titrate of acetonitrile containing 0.5% of water at 298.15 K

RE	No.	log K	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J^{-1} K^{-1} mol^{-1})
La	1	2.47	−14.098	−17.610	−11.779
	2	2.44	−13.927	−16.970	−10.206
	ave.	2.46	−14.013	−17.290	−10.993
Pr	1	2.44	−13.927	−14.760	−4.135
	2	2.37	−13.527	−15.883	−7.902
	Ave.	2.41	−13.727	−15.322	−6.019
Nd	1	2.33	−13.299	−12.226	3.599
Sm	1	2.41	−13.765	−15.398	−5.507
	2	2.46	−14.041	−15.119	−3.616
	Ave.	2.44	−13.899	−15.259	−4.562
Eu	1	2.51	−14.326	−16.242	−6.426
	2	2.48	−14.155	−16.274	−7.107
	Ave.	2.50	−14.241	−16.258	−6.767
Gd	1	2.49	−14.212	−16.212	−6.708
	2	2.51	−14.326	−16.055	−5.799
	Ave.	2.50	−14.269	−16.134	−6.254
Tb	1	2.37	−13.527	−21.031	−25.169
	2	2.45	−13.984	−20.190	−20.815
	Ave.	2.41	−13.756	−20.611	−22.992
Dy	1	2.44	−13.927	−19.302	−18.028
	2	2.44	−13.927	−19.328	−18.115
	Ave.	2.44	−13.927	−19.315	−18.072
Ho	1	2.49	−14.212	−23.570	−31.387
	2	2.48	−14.155	−24.087	−33.312
	Ave.	2.49	−14.184	−23.829	−32.350
Tm	1	2.47	−14.098	−27.180	−43.877
	2	2.50	−14.269	−25.704	−38.360
	Ave.	2.49	−14.184	−26.442	−41.118
Yb	1	2.44	−13.927	−26.771	−43.079
	2	2.46	−14.041	−27.255	−44.320
	Ave.	2.45	−13.984	−27.013	−43.699
Lu	1	2.57	−14.669	−21.989	−24.551
	2	2.58	−14.726	−23.834	−30.548
	Ave.	2.58	−14.698	−22.912	−27.550

has been verified by the measurement of the single-crystal structure of coordination compounds of DB30C10 with K^+, Ba^{2+} and Tl^+ ions [12–14]. References 15, and 16 include discussions of the coordination reaction of DB30C10 with RE^{3+} ions and alkaline earth metal ions respectively, in propylene carbonate. Metal cations coordinate with DB30C10 with 1:1 stoichiometry, and DB30C10 adopts a "wrap around" type of coordination. The results obtained in our experiments also support this point of view.

All the formation enthalpies are negative; thus the coordination reactions are exothermic. The formation enthalpies of adducts of DB30C10 with heavy rare earth cations are greater than those of DB30C10 with light rare earth cations.

Water is a rather strong ligand for the rare earth cations. The complex ions formed in the titrate are shown to be $RE(H_2O)_n(CH_3CN)_m^{3+}$. From ref. 17, ClO_4^- ions do not coordinate with RE^{3+} ions even in anhydrous acetonitrile. When the titrant is added, DB30C10 reacts with the complex ions. This process includes the formation of new bonds, breaking of old bonds and flexing of DB30C10, etc. The solid complexes of 1 : 1 stoichiometry between rare earth perchlorates and DB30C10 have been isolated by Ciampolini and Nardi [17]. The compositions of the heavy rare earth complexes differ from those of the light rare earth complexes. From La to Eu, the chemical formula is $RE(ClO_4)_3(DB30C10)$, whereas from Gd to Yb it is $RE(ClO_4)_3(DB30C10)(H_2O)_n(CH_3CN)_m$ ($n = 1$ or 2, $m = 1.5$ or 2). It is possible that the number of H_2O–RE and CH_3CN–RE bonds broken when DB30C10 reacts with the complex ions is different for the light and the heavy rare earth complexes, and that the energy required in this process is also different. This may be the reason that the values of $-\Delta H$ for the heavy rare earth adducts are greater than those for the light rare earth adducts.

It can be seen from Table 4 that the coordination entropies are negative except for the Nd^{3+} adduct, and the values of $-\Delta S$ of the heavy rare earth adducts are greater than those of the light rare earth adducts. The formation of these adducts is characterized by a large negative entropy [15,16]. Our work supports this point of view.

The results show that the adducts of rare earth perchlorates with DB30C10 are enthalpy stabilized under the experimental conditions used.

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