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[CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

A Calorimetric Study of the Reaction of Rare-earth Ions with EDTA in Aqueous Solution[1]

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The heats of reaction for the rare earths with EDTA in solution at 25° and $\mu = 0.1\ M$ (KNO_3) have been measured using a calorimetric method. The method was based on the replacement of one chelated metal ion by another and offers several advantages for studies of EDTA-like ligands. The thermodynamic quantities ΔF^0, ΔH^0 and ΔS^0 for the reaction of rare-earth ions with EDTA in 0.1 M KNO_3 are reported. These quantities indicate that the rare-earth chelates of EDTA fall into two series. Reasons for the existence of the two series were discussed, and it was suggested that a basic trend in ΔH^0 occurs in the rare-earth series, which is independent of the complexing or chelating ligand.

Introduction

Studies of metal complexes and chelates in solution have been confined primarily to the determination of the stability constants of species formed from metal ions and various ligands and correlation of these constants with ionic properties such as radius, charge, electronegativity and electronic structure. Recently, however, experimental studies have been concerned with a more complete thermodynamic description of complex and chelate formation. In addition to the free energies of formation of the complex species, which are derived from formation constants, measurements of the heats of reaction have been made. Knowing these quantities, entropy changes can be calculated from the equation

$$\Delta F = \Delta H - T\Delta S$$

ΔH's are generally determined either from the temperature dependence of the equilibrium constant or by direct calorimetric measurements.

In view of many recent studies of the stability constants of complexes and chelates of the rare-earth elements and the current interest in correlating and explaining the orders of stability observed, it seemed appropriate to measure the thermodynamic quantities of chelate formation for a complete rare-earth series. In this paper we report data for ethylenediamine-N,N,N′,N′-tetraacetic acid (EDTA), which was the first chelating agent for which all the rare-earth–chelate stability constants were obtained.[2]

Studies of the heats and entropies of reaction of a number of bivalent metal ions with EDTA have appeared,[3] and Staveley and Randall[4] have reported values for six trivalent metals including cerium, neodymium, gadolinium and yttrium. Betts and Dahlinger[5] have reported the heats and entropies of association of the rare earths with EDTA using a method based on the temperature dependence of the equilibrium constants for exchange reactions of the type

$$ACh^- + B^{3+} \rightleftarrows BCh^- + A^{3+}$$

The exchange constants at various temperatures were determined by radiochemical techniques. The accuracy of the data is subject to the usual limitations of the temperature-dependence method, such as the limited temperature range available and the small variation in log K with temperature. The method used also introduced a cumulative uncertainty into the values of ΔH since the exchange reactions had to be measured progressively. The value for lutetium, for example, was obtained from the Lu–Yb exchange and the value for ytterbium was obtained from the Yb–Er exchange, etc. This led to a possible error in the case of lutetium nearly as large as ΔH itself. A considerable difference was observed between the temperature-dependence values and those determined calorimetrically by Staveley and Randall. Consequently, it was desirable to redetermine the heats for the formation of the rare-earth chelates in solution using a calorimetric method.

Experimental

The calorimetric method used in this work differed somewhat from the method used by Staveley, *et al.*[3b,4] Their procedure required first the measurement of the enthalpy change for the addition of a slight excess of EDTA (primarily the tetrapotassium salt) to a solution of the metallic nitrate in 0.1 M KNO_3. Enough dilute nitric acid was added to give a final pH of 4.5. Next, the same amount of EDTA was added to a solution without the metallic nitrate, but otherwise the same. In order to calculate the heat of chelation of the metal ion with EDTA in solution, it was necessary to determine the pH's of the initial and final solutions accurately, because it was necessary to consider the third and fourth ionization constants of EDTA and the enthalpy changes associated with these ionizations. Due to the uncertainties related to pH dependence, it seemed advantageous to employ a calorimetric method which allows a more direct comparison of the heats of reaction of the rare earths with EDTA.

The method used in the present work was based on the replacement of one chelated metal ion by another. The procedure consisted of three steps. First, the change in heat content was measured when a relatively concentrated solution of magnesium chelate at its neutral equivalence

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[1] Contribution No. 1065. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] E. J. Wheelwright, F. H. Spedding and G. Schwarzenbach, *J. Am. Chem. Soc.*, **75**, 4196 (1953).

[3] (a) R. C. Charles, *ibid.*, **76**, 5854 (1954); (b) L. A. K. Staveley and R. A. Care, *J. Chem. Soc.*, 4571 (1956).

[4] L. A. K. Staveley and T. Randall, *Discussions Faraday Soc.*, No. 26, 157 (1958).

[5] R. H. Betts and O. F. Dahlinger, *Can. J. Chem.*, **37**, 91 (1959).

point was added to a dilute solution of rare-earth nitrate at its neutral point. Both solutions were 0.1 *M* in KNO_3.

$$MgY^{2-}(\sim 0.5\ M) + R^{3+}(\sim 0.01\ M) \longrightarrow RY^{-}(\sim 0.01\ M) + Mg^{2+}(\sim 0.01\ M) + q_1 \quad (1)$$

Next, the change in heat content was measured when an equivalent amount of magnesium chelate was added to a solution 0.1 *M* in KNO_3 but without rare-earth nitrate.

$$MgY^{2-}(\sim 0.5\ M) \longrightarrow MgY^{2-}(\sim 0.01\ M) + q_2 \quad (2)$$

Finally, in order to calculate the absolute values for the heat of formation of the rare-earth chelate in solution, it was necessary to know the enthalpy change for the reaction

$$Mg^{2+}(\sim 0.01\ M) + Y^{4-}(\sim 0.01\ M) \longrightarrow MgY^{2-}(\sim 0.01\ M) + q_3 \quad (3)$$

The value of ΔH_3 for this reaction has been reported by Staveley and Care[5b] as 3,140 cal./mole. The enthalpy change for the reaction

$$R^{3+} + Y^{4-} \longrightarrow RY^{-} + q_4 \quad (4)$$

was obtained using the law of Hess so that eq. 4 = eq. 1 − eq. 2 + eq. 3 and $\Delta H_4 - \Delta H_1 - \Delta H_2 + \Delta H_3$.

The use of magnesium chelate has several advantages. First, reaction 1 goes to completion, so that all the magnesium is replaced by rare earth, since

$$K_1 = \frac{[RY^-][Mg^{2+}]}{[MgY^=][R^{3+}]} = \frac{K_{RY}}{K_{MgY}} > 10^{6.50}$$

Furthermore, the use of magnesium chelate eliminates the need to consider the presence of any protonated species of EDTA, so that experimental *p*H's do not enter into a comparison of the heats of formation of the individual rare-earth chelates.

Materials and Equipment.—The isothermally jacketed calorimeter used in this work has been previously described.[6,7] Consequently, no description of the apparatus is necessary.

A solution of $K_2H_2(EDTA)$ was prepared from the acid by adding an appropriate amount of KOH. The dipotassium salt was then precipitated from solution by addition of alcohol. Solutions of the $K_2H_2(EDTA)$ were finally standardized volumetrically against weighed amounts of pure metallic magnesium dissolved in acid, using Eriochrome black T indicator.

The pure MgO was prepared by igniting reagent grade $Mg(NO_3)_2$. A standard solution of 0.5 *M* $K_2Mg(EDTA)$ was then prepared by reacting equivalent amounts of magnesium oxide and the dipotassium salt of EDTA. Reagent grade potassium nitrate was added to make this solution 0.1 *M* in KNO_3.

The rare earths were supplied in the form of oxides by the rare earth separation group at the Ames Laboratory of the Atomic Energy Commission and were greater than 99.9% pure. Stock solutions of the nitrates were prepared by dissolving the respective oxides in a slight excess of nitric acid. The solutions were then brought to the basic side of the neutral equivalence point by several evaporations to incipient dryness. Aliquots of each solution were titrated potentiometrically to determine the pH of the respective neutral equivalence point, and the stock solutions were adjusted to this pH with nitric acid. The rare-earth solutions were finally standardized against the dipotassium salt of EDTA using a mercury indicator electrode.[8,9] All solutions were prepared from conductance water.

Experimental Procedure.—Solutions for the actual calorimetric determinations were prepared by weight, making the necessary correction to weights in vacuum. In each experiment approximately 30 ml. of the 0.5 *M* $K_2Mg(EDTA)$ solution was weighed into the container jacket of the calorimeter and potassium nitrate was added to make the solution 0.1 *M* in KNO_3. The resulting solution was about 1500 ml. in total volume. The calorimeter was assembled and placed in the constant temperature bath kept at 25°. Each run consisted of an electrical calibration, an interval in which the 0.5 *M* $K_2Mg(EDTA)$ solution was allowed to react with the rare-earth solution and a second electrical calibration. The reaction between $K_2Mg(EDTA)$ and rare-earth solution was very rapid and all the heat was evolved in about two minutes. For the dilution experiment the same procedure was followed, except that no rare earth was present. The temperature changes were in the range 0.03 to 0.06° for reaction 1, and the heat capacity of the system was obtained from the electrical calibrations. The final ionic strength for these experiments was approximately 0.15.

Results

The results for the experiments to determine ΔH_1 and ΔH_2 are recorded in Table I. The heats are expressed in thermochemical calories (=4.1840 absolute joules). Table II shows the results for the heats of reaction for the rare-earth ions with EDTA in solution (reaction 4). Other values reported in the literature are shown for comparison.

TABLE I

EXPERIMENTAL RESULTS FOR THE HEATS OF REACTION

Reaction 1

Experiment	Mmoles $K_2Mg(EDTa)$ = mmoles $R(NO_3)_3$	*Q* (cal.)	ΔH_1 (cal./mole)
LaI	15.0002	87.927	−5862
II	14.7689	85.964	−5821
Ce I	15.0061	87.472	−5829
II	14.9992	88.100	−5876
Pr I	14.3647	88.220	−6141
II	14.7233	89.606	−6086
Nd I	14.9971	98.117	−6517
II	14.9958	97.972	−6533
III	14.9994	98.100	−6540
Sm I	14.6348	91.768	−6271
II	14.9923	93.648	−6246
III	14.9994	94.133	−6276
Eu I	14.9815	81.399	−5433
II	14.2122	78.358	−5513
Gd I	14.9998	69.590	−4639
II	15.0002	69.763	−4651
Tb I	14.9995	60.255	−4017
II	15.0009	60.610	−4040
Dy I	13.9745	57.257	−4097
II	14.5506	60.453	−4155
Ho I	14.9910	63.733	−4251
II	14.9938	64.338	−4291
Er I	15.0008	69.382	−4625
II	14.9988	69.326	−4797
Tm I	14.9958	71.932	−4797
II	14.9952	71.561	−4772
Yb I	14.9995	78.572	−5238
II	13.9650	72.766	−5211
Lu I	14.9961	81.199	−5415
II	15.0050	81.607	−5439
Y I	15.0000	52.600	−3507
II	14.9988	52.608	−3508
III	15.0013	52.433	−3495

Reaction 2

	Mmoles $K_2Mg(EDTA)$	*Q* (cal.)	ΔH_2 (cal./mole)
I	14.9988	−3.204	214
II	14.5572	−3.459	238
III	14.9491	−3.518	235
IV	13.8112	−2.954	214
			Av. 225

Discussion

It is the opinion of the authors that the method used in this work yields relative values for ΔH_4

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(6) F. H. Spedding and C. F. Miller, *J. Am. Chem. Soc.*, **74**, 3158 (1952).

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TABLE II

HEATS OF REACTION FOR THE RARE EARTHS WITH EDTA IN SOLUTION AT 25° AND $\mu = 0.1\ M$ (KNO_3)

Rare earth	ΔH_4,[a] this work	ΔH, Betts and Dahlinger[4]	ΔH, Staveley and Randall[5]
La	−2926 ± 21	−800	
Ce	−2938 ± 24	−470	−2430
Pr	−3198 ± 28	−800	
Nd	−3623 ± 5	−800	−2980
Sm	−3349 ± 18	−800	
Eu	−2558 ± 40	−160	
Gd	−1730 ± 6	+430	−1110
Tb	−1114 ± 12	+1500	
Dy	−1211 ± 29	+1500	
Ho	−1356 ± 20	+1250	
Er	−1708 ± 2	+1500	
Tm	−1870 ± 13	+1580	
Yb	−2310 ± 14	+1320	
Lu	−2512 ± 12	+640	
Y	− 588 ± 8		+320

[a] These values were computed from the average values of ΔH_1 and ΔH_2 from Table I and the value of 3, 140 ± 150 cal./mole for ΔH_3 reported by Staveley and Care.[3b] The error shown here is in each case the deviation of the individual experimental values from their mean and does not include the inherent error due to uncertainties in ΔH_2 and ΔH_3. Since the same values of ΔH_2 and ΔH_3 were used to obtain all these values, the additional errors introduced need not be considered in making individual comparisons. The deviations in absolute magnitude probably do not exceed ± 190 cal. in any case. The data are reported in sufficient detail in Table I to permit recalculation of ΔH_4 if a more accurate value of ΔH_3 becomes available.

that are accurate within 2%. It is interesting to note that, in spite of a relatively large difference in magnitude between our values and those of Betts and Dahlinger,[4] the same trends are apparent. The few calorimetric data reported by Staveley and Randall[5] agree reasonably well, although not perfectly, with our results.

It is possible to derive the thermodynamic quantities, ΔF^0, ΔH^0 and ΔS^0, within the accuracy of the data for the reaction of rare-earth ions with the EDTA anion to form 1:1 chelates in 0.1 M KNO_3 solution and to see if the results lead to an understanding of factors which are important in complex and chelate formation in this series. Table III gives the thermodynamic quantities. For ΔF^0 the stability constants of Betts and Dahlinger[5] were used. These are concentration constants measured at 0.1 M ionic strength and 25°.

The ΔH's listed in Table II were also measured in a KNO_3 solution of constant ionic strength at 25°, although μ was 0.15 instead of 0.10. The equations, $\Delta F^0 = RT \ln K$ and $\Delta F^0 = \Delta H^0 - T\Delta S^0$, were applied to a reaction measured in a constant salt medium. Consequently, the thermodynamic quantities will differ somewhat from the values determined at extreme dilution. ΔH^0 for the reaction in $\mu = 0.15$ KNO_3 differs from that in $\mu = 0.1$ KNO_3 only by the difference in heats of dilution of the products and reactants; a quantity which should be small and nearly the same in the case of each rare earth.

The reported uncertainty in the relative values for ΔF^0 vary from ± 10 cal./mole for the lanthanum chelate to ± 35 cal./mole for the lutetium chelate. The corresponding uncertainties in the relative values of ΔH^0 are less than 50 cal./mole. so that the values for ΔS^0 in Table III should have a relative uncertainty less than ± 1. e.u.

TABLE III

THERMODYNAMIC QUANTITIES FOR THE FORMATION OF RARE-EARTH–EDTA CHELATES IN SOLUTION AT 25° AND $\mu = 0.1$

Rare earth	ΔF^0, cal./mole	ΔH^0, cal./mole	ΔS^0, cal./mole/°C.
La	−20,720	−2926	59.7
Ce	−21,070	−2938	60.8
Pr	−21,490	−3198	61.4
Nd	−21,890	−3623	61.3
Sm	−22,540	−3349	64.4
Eu	−22,720	−2558	67.6
Gd	−22,940	−1730	71.2
Tb	−23,620	−1114	75.5
Dy	−24,250	−1211	77.3
Ho	−24,610	−1356	78.0
Er	−25,060	−1708	78.3
Tm	−25,440	−1870	79.1
Yb	−25,910	−2310	79.2
Lu	−26,110	−2512	79.1
Y	−23,701[a]	− 588	77.5

[a] Calculated from log $K_{Y(EDTA)}$ value from Wheelwright, Spedding and Schwarzenbach[2] corrected to 25°.

The values in Table III indicate the significance of the entropy term in formation of rare-earth–EDTA chelates. The only regularity apparent in Table III is the increase of ΔS^0 with decreasing radius. Such a trend in ΔS^0 was also noted by Staveley and Randall[4] for some divalent and trivalent ions. Although yttrium is not a true lanthanide, its ΔS^0 value falls in the position expected from a consideration of its radius.

The data for ΔH^0 are particularly interesting. The values appear to fall into two series, one for the light and one for the heavy rare earths, with a gradual transition between the two series around europium. The ΔH^0 values for the heavy-rare-earth series are actually lower than those for the light-rare-earth series, a phenomenon which is masked in the stability constant series by the large values for ΔS^0. Duncan[10] has shown by using a simple electrostatic model that ΔH^0 for complex formation should be a linear function of the reciprocal radius of the metal ion for a given ligand, provided the members of the series have a similar structure. The values for ΔH^0 given in Table III indicate that other factors are indeed involved in the association of EDTA with the rare earths.

Two additional contributing factors have been suggested from a consideration of stability constant data for the rare-earth series. It has been suggested that the simple electrostatic model should be modified by possible ligand-field stabilization of the 4f electrons.[4,11] The lack of stabilization was thought to explain the "gadolinium break" observed for all aminopolycarboxylic acid chelates as well as the depressed values for yttrium stability constants. If such stabilization is really important, it should be evident in the values of ΔH^0. The data in Table II show, however, that ΔH^0 for gadolinium EDTA is greater than

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(10) J. F. Duncan, *Australian J. Chem.*, **12**, 346 (1959).

(11) P. George, D. S. McClure, J. S. Griffith and L. E. Orgel, *J. Chem. Phys.*, **24**, 1269 (1956).

most of the ΔH^0 values for the heavy rare earths. The inference is that the "gadolinium break" is not primarily due to ligand-field stabilization.

It has also been suggested that the stability of the rare-earth–EDTA chelates can be explained by a change in the number of coördination positions occupied by the EDTA due to increased steric hindrance as the radii of the rare-earth ions decrease across the series.[1,5] Betts and Dahlinger[5] have interpreted their values for the entropy of chelation with EDTA as showing a change from penta-coördination to tetra-coördination. They expressed ΔS^0 in terms of the relative partial molal entropies of the ions involved. The quantity

$$\Delta S^0 = \bar{S}^0{}_{\mathrm{RY}^-} - \bar{S}^0{}_{\mathrm{R}^{3+}} - \bar{S}^0{}_{\mathrm{Y}^{4-}} \qquad (6)$$

($\Delta S^0 + \bar{S}^0{}_{\mathrm{R}3+}$) then provides a measure of $\bar{S}^0{}_{\mathrm{RY}-}$, since $\bar{S}^0{}_{\mathrm{Y}4-}$ is a common factor. On this basis the rare-earth chelates divided into two subgroups (La to Gd and Tb to Lu) which differed from each other by more than 6 e.u. Our results show approximately the same thing. Rather than interpret this phenomenon in terms of a change from penta-coördination to tetra-coördination, we would only suggest that ΔS^0, like ΔH^0, indicates that the rare-earth chelates of EDTA fall into two series. There is, in fact, substantial evidence opposed to any abrupt change in the number of points of attachment of the chelate. Schwarzenbach and Gut[12] have pointed out that both the EDTA and the nitrilotriacetate (NTA) stability constants of the rare earths divide into two series around gadolinium. Since NTA has only four coördinating groups, it seems unlikely that the discontinuity at gadolinium is due to a change in the number of points of attachment of the chelate. Kolat and Powell's data for the acid dissociation constants of rare-earth–EDTA chelates indicate no change in the number of coördinated positions occupied by the ligand.[13]

Staveley and Randall[4] have pointed out from a study of molecular models that it is possible to arrange all six coördinating groups of EDTA around a relatively large central metal ion and still have room for the close approach of at least one water molecule. Finally, we would like to cite that recent determinations of the formation constants of simple rare-earth complexes with ligands such as acetate[14,15] and thioglycolate[15] show the same trends that are apparent in our ΔH^0 values. The constants fall into two groups with the heavy-rare-earth constants actually smaller than those for the light-rare-earths. Since the entropy terms are usually small for the formation of simple complexes, this suggests a basic trend in ΔH^0 for the rare-earth series, independent of the complexing or chelating ligand. This basic trend would be obscured in the stability constants of extremely stable chelates due to the large entropy terms involved. Such a basic trend or "natural order" has been found for the bivalent transition-metal complexes.[16]

In summary, ΔH^0 and ΔS^0 data for the formation of rare-earth-EDTA species show two series within the rare-earth series. The exact reasons for the existence of two series are not clear, but evidence indicates that the phenomenon is general for rare-earth complexes rather than being a unique occurrence in the case of EDTA-like ligands and explainable by an abrupt change in the number of points of attachment of the ligand to the central metal ions. Accurate calorimetric data are needed for other complexes and chelates of the rare earths in order to either substantiate or refute our present theories.

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[12] G. Schwarzenbach and R. Gut, *Helv. Chim. Acta*, **39**, 1589 (1956).

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[Contribution No. 2237 from the Kodak Research Laboratories, Eastman Kodak Company, Rochester, New York]

Kinetics of Reaction of Nucleophilic Reagents with Naphthoquinone Imine Dyes in Alkaline Solution

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The kinetics of the reaction of two indoaniline dyes with OH^-, $SO_3^=$, and CN^- are in agreement with the general scheme

$$X + B^- \underset{k_2}{\overset{k_1}{\rightleftarrows}} Z \xrightarrow{k_3} P_1 \qquad X + B^- \xrightarrow{k_4} P_2$$

where X = dye, B^- = a nucleophile, Z = a complex and the P's represent the products of irreversible reactions. The reaction with OH^- shows all the features of this general scheme, the reaction with $SO_3^=$ does not proceed beyond complex formation, *i.e.*, $k_3 = k_4 = 0$, and the reaction with CN^- leads to products without measurable presence of the complex at any stage of the reaction. Equilibrium constants and rate constants have been evaluated.

Introduction

The instability of indoaniline dyes has led us to investigate some of the reactions leading to their decomposition. Little has been reported on the chemistry of these reactions. In the following we call dye "bleaching" the decolorization arising from dark reactions and reserve the term "fading" for photochemical reactions. The present study