[CONTRIBUTION NO. 243 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE. PART OF THE WORK WAS PERFORMED IN THE AMES LABORATORY OF THE ATOMIC ENERGY COMMISSION]

The Stability of the Rare Earth Complexes with Ethylenediaminetetraacetic Acid

BY E. J. WHEELWRIGHT, F. H. SPEDDING AND G. SCHWARZENBACH[1]

RECEIVED OCTOBER 30, 1952

The stability constants of the complexes formed between the rare earth metal ions and the anion of ethylenediaminetetraacetic acid have been measured at a temperature of 20° and an ionic strength of $\mu = 0.1$ by two independent methods. The two methods are shown to supplement each other, one being more accurate for the lighter rare earths and the second method more accurate for the heavy rare earths. The first, a potentiometric method, involves the formation constants of copper with the anion of ethylenediaminetetraacetic acid and of copper with the trihydrochloride of β,β',β''-triaminotriethylamine. The second method involves the polarographic determination of the amount of free copper in the presence of both the copper and rare earth tetraacetate complexes.

Introduction

The tervalent rare earth cations, all having the same charge and apparently the same electronic configuration of the outer orbitals, form a unique series for the study of the influence of the size of a cation upon its physical and chemical properties. Complex formation of these cations in homogeneous solution is of special interest in this connection, because of its independence of crystal structure and lattice requirements of a solid phase. Very few quantitative data of this nature have been obtained because of the small tendency of the rare earth cations to form complexes. It is known, however, that the rare earths form stable complexes with the anion of ethylenediaminetetraacetic acid. The symbol H_4Y is used in this paper to designate the acid. This substance has been used for an improved fractional separation of the rare earths one from another.[2] Stability constants of the rare earth–ethylenediaminetetraacetate complexes have been reported by Vickery.[3a] However, we do not consider the method used by this author to be applicable.[3b]

The equilibrium between the copper complex CuY^{-2}, uncomplexed cupric ions Cu^{+2} and the rare earth complex MY^- in the presence of uncomplexed rare earth cation M^{+3} has been investigated in order to obtain the stability constants of these complexes. The rare earth complex is defined as

$$K_{MY} = \frac{[MY]}{[M][Y]}$$

The brackets denote concentrations and all data obtained are valid for an aqueous salt solution of ion strength $\mu = 0.1$ and a temperature of 20°.

The Potentiometric Method.—Because of the great difficulty of measuring the concentration [M] of the uncomplexed rare earth cation potentiometrically, a process was sought wherein the complex MY^- would be formed or decomposed simultaneously with the production or consumption of an equivalent amount of hydrogen ions. The concentration of the hydrogen ion, [H], would give information as to the extent to which this reaction had proceeded, and would allow the calculation of its equilibrium constant. A simple exchange of the protons by the metal cation in the reaction

$$M^{+3} + H_xY^{\,x-4} \rightleftarrows MY^- + xH^+ \qquad \text{(I)}$$

was used in order to obtain the stability constants of the calcium complex CaY^{-2} and the other alkaline earth complexes. This is not suitable for the purpose if M is a rare earth metal, since the equilibrium of (I) lies too far to the right hand side. A mixture equivalent in rare earth salt and the salt Na_2H_2Y behaves very much like a strong acid. The hydrogen ion concentration of such a mixture is only slightly less than twice the total concentration, $[M]_t$, of the metal or the complexing agent, $[Y]_t$. Only a very small amount of uncomplexed M^{+3} is left over; the concentration of this is obtained as difference between two nearly equal quantities: $[M]_t - 2[H]$. This example indicates that accurate measurements by means of pH determinations can best be made when the reaction in question exerts a buffer action in a suitable pH range, which has to be between pH 4 and pH 10.

It has been found that reaction (II) is suitable for the purpose[4]

$$CuY^{-2} + H_3\,tren^{+3} + M^{+3} \rightleftarrows MY^- + Cu\,tren^{+2} + 3H^+ \qquad \text{(II)}$$

If a mixture of the copper complex of ethylenediaminetetraacetic acid, Na_2CuY, the rare earth salt, MCl_3, and the trihydrochloride of β,β',β''-triaminotriethylamine, $N(CH_2–CH_2–NH_2)_3$, designated as "tren," is titrated with NaOH, three formula weights of the base are used in a buffer region between pH 4 and 5.5. During this process, reaction (II) is delivering the protons.

The tri-(β-aminoethyl)-amine, "tren," is a strong triprotonic base with the pK values of 10.29 (= log K_{Htren}), 9.59 (= log K_{H_2tren}) and 8.56 (= log K_{H_3tren}) and therefore we have

$$\frac{[H_3tren]}{[H]^3 \times [tren]} = \bar{K}_{H_3tren} = K_{Htren} \times K_{H_2tren} \times K_{H_3tren} = 10^{28.44} \qquad (1)$$

The tri-(β-aminoethyl)-amine, "tren," also forms a very stable complex with bivalent copper[5]

$$K_{Cutren} = \frac{[Cu\,tren]}{[Cu][tren]} = 10^{19.1} \qquad (2)$$

---

[1] Dr. Schwarzenbach held the position of "Distinguished Visiting Professor" in the Institute during 1951 while on leave from the University of Zurich, Switzerland.

[2] G. Beck, *Mikrochemie*, **33**, 344 (1948); *Anal. Chim. Acta*, **3**, 41 (1949); J. K. Marsh, *J. Chem. Soc.*, 1819 (1950); 3057 (1951).

[3] (a) R. C. Vickery, *ibid.*, 1817 (1951); 421 (1952); 1895 (1952). (b) Vickery defined the constants by the equation $K \equiv [MHY]/[M]\cdot[HY]$, and reported values which are approximately the same as those reported in this paper. Complexes of the composition MHY, containing a proton and the rare earth cation simultaneously, do not occur in the equilibrium mixtures.

[4] G. Schwarzenbach and E. Freitag, *Helv. Chim. Acta*, **34**, 1503 (1951).

[5] J. E. Prue and G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 963 (1950).

This value has been obtained from the equilibrium constant of reaction (III): $K_{\mathrm{III}} = 10^{-9.3}$

$$Cu^{+2} + H_3tren^{+3} \rightleftarrows Cutren^{+2} + 3H^{+} \qquad (III)$$

which exhibits a buffer action between *p*H 3.9 and 4.8.

The stability constant[6] of the complex CuY^{-2}, of copper and ethylenediaminetetraacetate, is somewhat smaller than K_{Cutren}

$$K_{\mathrm{CuY}} = \frac{[\mathrm{CuY}]}{[\mathrm{Cu}][\mathrm{Y}]} = 10^{18.38} \qquad (3)$$

Because of the greater proton affinity of the base "tren" in comparison to the anion "Y," the complex $Cutren^{+2}$ is less stable than the complex CuY^{-2} in a *p*H range below 8.5. If NaOH is added to an equivalent mixture of CuY^{-2} and H_3tren^{+3}, a buffer region between *p*H 8.5 and *p*H 9.5 is observed during which the copper changes over from the "Y" to the "tren"

$$CuY^{-2} + H_3tren^{+3} \rightleftarrows Cutren^{+2} + HY^{-3} + 2H^{+} \qquad (IV)$$

If a cation capable of binding the complexing agent "Y" is added during this neutralization, not only two, but three hydrogen ions can be neutralized in a buffer region which lies below the buffer region of (IV). In the presence of calcium ions the reaction takes place around *p*H 7, in the presence of manganous ions around *p*H 6 and in the presence of lead ions around *p*H 4. Reaction (II), with a rare earth metal as additional cation, has, as mentioned above, a buffer action between *p*H 4 and *p*H 5.5, the heavy rare earths being similar to lead and the first member of the series similar to zinc or manganous ion.

Solutions. A. 0.01 *M* Na_2CuY.—A solution of exactly 0.1 *M* $CuCl_2$ was prepared. Ten ml. was titrated with approximately 0.1 *M* Na_2H_2Y after the addition of 5 ml. of ammonia and diluting to 300 ml., using murexide as indicator. For this titration 10.20 ml. was needed. One hundred ml. of the original copper chloride solution was therefore mixed with 102.0 ml. of Na_2H_2Y. This mixture is strongly acid because of reaction (V).

$$Cu^{+2} + H_2Y^{-2} \longrightarrow CuY^{-2} + 2H^{+} \qquad (V)$$

Therefore, the solution was carefully adjusted to *p*H 6 with NaOH and diluted to 1000 ml. Solution A then contains

$$[\mathrm{Na}] = 0.04,\ [\mathrm{CuY}] = 0.01,\ [\mathrm{Cl}] = 0.02$$

B. 0.01 *M* "tren."—One-hundredth molecular weight of the pure hydrochloride of the tri-(β-aminoethyl)-amine base: tren·3HCl was dissolved in water and diluted to 1000 ml. Solution B contains

$$[\mathrm{H_3tren}] = 0.01,\ [\mathrm{Cl}] = 0.03$$

C. 0.01 *M* MCl_3.—Sufficient pure rare earth oxide[7] was dissolved in a slight excess of *N* HCl to give a solution of 0.001 molar weight in MCl_3. A sample of this solution was titrated with NaOH using a glass electrode as indicator, and from a graph Δ *p*H/Δ ml. against ml. of the base added, the *p*H of a neutral solution was obtained. These *p*H values ranged from 5.2 for lanthanum down to 4.70 for lutecium. Then the two solutions were recombined, adjusted to this *p*H value and diluted to 100 ml. Solution C contains

$$[\mathrm{M}] = 0.01,\ [\mathrm{Na}] \cong 0.01,\ [\mathrm{Cl}] \cong 0.04$$

Procedure.—Five solutions were made up in 100-ml. volumetric flasks, each containing 10 ml. of solution A, 10 ml. of solution B, 10 ml. of solution C and 9.00 ml. of 1.00 *M* KCl. Next, different amounts of 0.01 *M* NaOH were added, for instance 5 ml. to the first flask, 10 ml. to the second, 15 ml. to the third and so on. Each mixture was brought up to a volume of 100 ml., placed in a thermostat set at 20.00 ± 0.02° and allowed to equilibrate for 24 hours. At the end of this period the *p*H was determined using a glass electrode and a Beckman *p*H meter. Check determinations were made, allowing 48 hours equilibration, for praseodymium, neodymium, samarium and yttrium. Since the results were the same as those obtained with 24-hour equilibration, the practice was discontinued.[8] The *p*H meter was calibrated against a solution of 0.001 *M* HCl containing 0.10 *M* KCl which gave a *p*H of 3.00 at a constant ionic strength of $\mu = 0.10$. Note that the concentration and not the activity of the hydrogen ion was measured. Several check solutions were independently prepared and all checked at a *p*H of 3.00 ± 0.02 relative to each other.

The experimental results are given in Table I, "*a*" denoting the number of equivalents of NaOH added per equivalent of rare earth cation. K_{II} denotes the equilibrium constant of reaction (II)

$$K_{\mathrm{II}} = \frac{[\mathrm{MY}][\mathrm{Cutren}][\mathrm{H}]^3}{[\mathrm{CuY}][\mathrm{H_3tren}][\mathrm{M}]} = \frac{K_{\mathrm{Cutren}} \times K_{\mathrm{MY}}}{\bar{K}_{\mathrm{H_3tren}} \times K_{\mathrm{CuY}}} \qquad (4)$$

Calculation of K_{II}.—For the calculation of the equilibrium constant of reaction II from "*a*" and *p*H, the following equations have been used

$$\left.\begin{array}{lll} [\mathrm{Cu}]_t & = 10^{-3} = [\mathrm{CuY}] + \alpha[\mathrm{Cutren}] & \text{(a)} \\ [\mathrm{M}]_t & = 10^{-3} = [\mathrm{MY}] + [\mathrm{M}] & \text{(b)} \\ [\mathrm{Y}]_t & = 10^{-3} = [\mathrm{CuY}] + [\mathrm{MY}] & \text{(c)} \\ [\mathrm{tren}]_t & = 10^{-3} = [\mathrm{Cutren}] + [\mathrm{H_3tren}] & \text{(d)} \\ [\mathrm{H}]_t & = (3 - a) \times 10^{-3} = [\mathrm{H}] + 3[\mathrm{H_3tren}] & \text{(e)} \end{array}\right\} (5)$$

Equation (5a) is valid if no complexes of copper containing both "tren" and "Y" are present. Since "tren" is tetradentate and "Y" is hexadentate, each is capable of satisfying the coördination number of 4 which is typical for copper. Therefore, it seems unlikely that mixed complexes would form. The last term of (5a) takes account of the complex $Cutren^{+2}$ as well as of the uncomplexed copper

$$\alpha[\mathrm{Cutren}] = [\mathrm{Cutren}] + [\mathrm{Cu}]$$

The latter can be obtained from the concentration of H_3tren^{+3} and the *p*H value

$$[\mathrm{Cu}] = [\mathrm{Cutren}] \times \frac{[\mathrm{H}]^3 \times \bar{K}_{\mathrm{H_3tren}}}{[\mathrm{H_3tren}] \times K_{\mathrm{Cutren}}}$$

Therefore we obtain

$$\alpha = 1 + \frac{[\mathrm{H}]^3 \times \bar{K}_{\mathrm{H_3tren}}}{[\mathrm{H_3tren}] \times K_{\mathrm{Cutren}}} \qquad (6)$$

Equation (5b) is true only if M^{+3} does not form a complex with the base "tren." This assumption is justified because of the low *p*H ranges of the measurements. Denoting the stability constant of the complex as K_{Mtren}, we obtain for the acid decomposition

$$3H^{+} + Mtren^{+3} \rightleftarrows M^{+3} + H_3tren^{+3} \qquad (VI)$$

the equilibrium constant

$$K_{\mathrm{VI}} = K_{\mathrm{H_3tren}}/K_{\mathrm{Mtren}} \qquad (7)$$

This shows that, with a maximum concentration of M^{+3} and H_3tren^{+3} of 10^{-3}, K_{Mtren} would have to be larger than 10^{12} in order to make the concentration of $Mtren^{+3}$ exceed 10^{-5}, which is 1% of $[\mathrm{M}]_t$. Since very little is known about the ammonia complexes of the rare earth metals, it seems very improbable that the rare earth tren complexes should be more stable than $Mntren^{+2}$ or $Fetren^{+2}$ which have stability constants of $10^{5.8}$ and $10^{8.8}$ and certainly would not be nearly as stable as the cobalt(II) complex ($10^{12.8}$) and the zinc complex ($10^{14.6}$).[9]

---

[6] G. Schwarzenbach and E. Freitag, *Helv. Chim. Acta*, **34**, 1503 (1951).

[7] The rare earths used in this research were separated on ion-exchange columns according to the method of Spedding, *et al.* (THIS JOURNAL, **69**, 2786 (1947); **72**, 2354 (1950), *etc.*), and each rare earth was spectrographically pure.

[8] In preliminary runs on La and Y, equilibration rates of a few minutes to a few hours were tried. In the former it was evident that equilibrium while approached had not been reached and in the latter case the approach to equilibrium was so close that it seemed evident that in 24 hours equilibrium would be attained.

[9] J. E. Prue and G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 963 (1950).

TABLE I

pH VALUES OF SOLUTIONS CONTAINING Na_2CuY, $[H_3tren]Cl_3$, MCl_3, EACH IN A CONCENTRATION OF 0.001 M AND NaOH IN A CONCENTRATION OF "a" × 10^{-3} M. SUPPORTING ELECTROLYTE IS 0.09 M KCl

Metal M	"a"	pH	$-\log K_{II}$	Av. $-\log K_{II}$	$\log K_{MY}$	Metal M	"a"	pH	$-\log K_{II}$	Av. $-\log K_{II}$	$\log K_{MY}$
La^{+3}	0.50	4.92	13.05			Dy^{+3}	0.50	4.15	10.05		
	0.85	5.12	13.00				0.85	4.29	10.31		
	1.20	5.29	13.00	13.02 ± 0.06	14.72 ± 0.06		1.20	4.44	10.20	10.17 ± 0.13	17.57 ± 0.13
	1.50	5.44	13.02				1.50	4.55	10.17		
	1.75	5.56	13.01				1.75	4.65	10.13		
Ce^{+3}	0.50	4.71	12.29			Ho^{+3}	0.50	4.14	10.00		
	0.85	4.92	12.39				0.85	4.28	10.04		
	1.20	5.08	12.35	12.35 ± 0.06	15.39 ± 0.06		1.20	4.40	10.08	10.07 ± 0.15	17.67 ± 0.15
	1.50	5.21	12.33				1.55	4.55	10.08		
	1.75	5.36	12.40				1.75	4.65	10.13		
Pr^{+3}	0.50	4.60	12.04			Er^{+3}	0.50	4.09	9.61		
	0.85	4.80	12.02				0.85	4.22	9.67		
	1.20	4.92	11.87	11.99 ± 0.06	15.75 ± 0.06		1.20	4.37	9.86	9.76 ± 0.2	17.98 ± 0.2
	1.55	5.15	12.05				1.55	4.49	9.81		
	1.75	5.22	11.98				1.75	4.58	9.84		
Nd^{+3}	0.51	4.51	11.70			Tm^{+3}	0.50	4.03	8.95		
	0.84	4.70	11.72				0.85	4.15	9.02		
	1.20	4.86	11.68	11.68 ± 0.06	16.06 ± 0.06		1.20	4.26	9.06	9.15 ± 0.25	18.59 ± 0.25
	1.50	5.00	11.68				1.50	4.39	9.32		
	1.75	5.10	11.62				1.75	4.49	9.38		
Sm^{+3}	0.50	4.36	11.17			Yb^{+3}	0.50	4.03	8.95		
	0.85	4.54	11.18				0.85	4.13	8.76		
	1.20	4.72	11.23	11.19 ± 0.07	16.55 ± 0.07		1.20	4.26	9.06	9.06 ± 0.3	18.68 ± 0.3
	1.55	4.85	11.14				1.55	4.39	9.32		
	1.75	4.97	11.21				1.75	4.46	9.19		
Eu^{+3}	0.50	4.33	11.04			Lu^{+3}	0.50	4.00	8.42		
	0.85	4.50	11.03				0.85	4.12	8.60		
	1.20	4.65	11.01	11.05 ± 0.08	16.69 ± 0.08		1.20	4.23	8.71	8.68 ± 0.4	19.06 ± 0.4
	1.50	4.81	11.09				1.50	4.33	8.76		
	1.75	4.93	11.09				1.75	4.44	8.92		
Gd^{+3}	0.50	4.32	11.00			Y^{+3}	0.49	4.15	10.10		
	0.85	4.50	11.03				0.84	4.31	10.22		
	1.20	4.63	10.93	11.04 ± 0.08	16.70 ± 0.08		1.19	4.48	10.39	10.36 ± 0.15	17.38 ± 0.15
	1.55	4.83	11.07				1.59	4.67	10.48		
	1.75	4.94	11.12				1.79	4.80	10.59		
Tb^{+3}	0.50	4.21	10.46								
	0.85	4.36	10.46								
	1.20	4.52	10.53	10.49 ± 0.11	17.25 ± 0.11						
	1.50	4.64	10.51								
	1.75	4.74	10.47								

Equation (5c) is true if there is no uncomplexed "Y," which would have to be present mainly in the form of the ion H_2Y^{-2}. It can be shown that the concentration of this ion will be below 10^{-9} by equations (1), (2) and (3) if we introduce

$$[H_3tren] = [Cutren] = [CuY] = 5 \times 10^{-4}$$

Equation (5d) follows from the assumption that there will be no $Mtren^{+3}$. The complexing agent "tren" therefore can be present only in the form of the copper complex or uncomplexed

$$\text{total "tren"} = [Cutren] + [H_3tren] + [H_2tren] + [Htren] + [tren]$$

The last three terms of the equation are so small that they can be neglected in the pH ranges concerned.

The total amount of acid hydrogen available is summarized in equation (5e).

With the equation (5), the calculation proceeds as follows: (e) gives immediately $[H_3tren]$ from the experimental values of [H] and "a." "α" is calculated with (6) and introduced into (5a–d) from which the concentrations [CuY], [Cutren], [MY] and [M] are found. These quantities are introduced into equation (4) for the calculation of K_{II} and finally K_{MY}. The results are summarized in Table I.

The errors connected with K_{II} and K_{MY} result from the pH measurements, accurate only to ±0.02 unit. For the lighter rare earth cations up to samarium, this produces an error of ±0.06 unit in the logarithm of K_{II} and K_{MY} because [H] enters with the third power in equation (4). With increasing stability of the Y-complex, however, the coefficient "α" in equation (5a) deviates more and more from the value $\alpha = 1$. In equation (6), [H] enters again with the third power creating an inaccuracy in "α" and with it in the concentrations [CuY], [MY] and [M]. Consequently the errors of K_{II} and K_{MY} grow as we go up the series of rare earth metals.

A more qualitative consideration reveals the same thing. As soon as the stability of the rare earth complex MY^- is no longer smaller than the stability of the copper complex CuY^{-2}, reaction VII will take place to a considerable extent upon mixing solutions A and C

$$CuY^{-2} + M^{+3} \longrightarrow MY^- + Cu^{+2} \qquad \text{(VII)}$$

In the case of a complete displacement of equilibrium (VII) to the right hand side ($K_{MY} \gg K_{CuY}$), the complex MY^- would be formed to 100% during the mixing process, and the neutralization of the solution with NaOH would not be influenced by the formation of the rare earth complex.

This neutralization would simply be reaction (III) and it would be impossible to obtain any information as to the stability of the complex MY^- from the *p*H measurements of such a titration. Increased stability of MY^- will shift the equilibrium (VII) more and more to the right, increasing the uncertainty of the information obtained from the neutralization.

The figures in Table I show that the results, *i.e.*, the constants K_{MY}, are fairly accurate up to the element terbium. However, only very approximate values can be obtained for the last six elements. This was the reason a second method for the determination of the K_{MY} values was adopted.

The Polarographic Method.—This method is based on the fact that it is possible to measure the concentration of free uncomplexed copper ion Cu^{+2} polarographically in the presence of its complex CuY^{-2}. This determination can be carried out much more easily and more accurately in a solution which does not contain any chloride ion. The salt KNO_3 has therefore been used this time as supporting electrolyte. In such a solution a mixture of Cu^{+2} and CuY^{-2} produces two separated waves. The first of these has the shape of a two-electron wave with $E_{1/2} = -0.04$ v. *vs*. S.C.E. (*versus* saturated calomel electrode). It is due to the reduction of Cu^{+2} to the metal at the surface of the mercury drop. The second is about as steep as a one-electron wave and is due to the reduction of the complex CuY^{-2}, its $E_{1/2}$ being -0.32 v. Between the two waves the diffusion current i_d remains constant and is proportional to the concentration of free uncomplexed Cu^{+2} present.

Mixtures were prepared containing: copper complex Na_2CuY (0.001), rare earth nitrate $M(NO_3)_3$ (0.001), sodium acetate (0.01), acetic acid (0.01) and KNO_3 (0.091). In these solutions equilibrium VII is set up. The polarogram was taken after the addition of two drops of basic fuchsin (0.2%) to suppress the maxima. The i_d value for each rare earth nitrate solution was evaluated from these polarograms at $E = -0.17$ v. A reference i_d value for 100% uncomplexed copper was obtained from a polarogram of a solution containing $CuSO_4$ instead of Na_2CuY. The percentage of uncomplexed copper was calculated from the i_d value for each rare earth and the i_d value for 100% uncomplexed copper. The results are summarized in Table II.

TABLE II

POLAROGRAPHIC DETERMINATION OF UNCOMPLEXED COPPER IN AN EQUIVALENT MIXTURE OF Na_2CuY AND RARE EARTH NITRATE $M(NO_3)_3$, BOTH AT A CONCENTRATION OF 0.001 *M* IN KNO_3, $\mu = 0.1$

Rare earth	Uncomplexed Cu, %	log K_{VII}	log K_{MY}
La	Uncertain	....	....
Ce	4.1 ± 2	−2.75 ± 0.4	15.6 ± 0.4
Pr	4.6 ± 2	−2.63 ± .34	15.8 ± .34
Nd	5.9 ± 2	−2.4 ± .25	16.0 ± .25
Sm	8.7 ± 2	−2.1 ± .2	16.3 ± .2
Eu	10.4 ± 2	−1.91 ± .15	16.5 ± .15
Gd	11.9 ± 2	−1.74 ± .15	16.6 ± .15
Tb	24.1 ± 2	−1.00 ± .10	17.38 ± .10
Dy	32.5 ± 2	−0.63 ± .08	17.75 ± .08
Ho	48.1 ± 2	−0.07 ± .07	18.31 ± .07
Er	55.0 ± 2	+0.17 ± .07	18.55 ± .07
Tm	68.8 ± 2	+0.69 ± .08	19.07 ± .08
Yb	76.3 ± 2	+1.01 ± 1.10	19.39 ± .10
Lu	81.3 ± 2	+1.27 ± 1.12	19.65 ± .12
Y	28.1 ± 2	−0.82 ± .08	17.56 ± .08

The equilibrium constant of reaction VII is calculated from the percentage of uncomplexed copper in the mixtures. The equality of the total concentrations $[M]_t$, $[Cu]_t$, and $[Y]_t$ leads to the expression (8)

$$K_{VII} = (\%Cu)^2/(100 - \%Cu)^2 \qquad (8)$$

From the equilibrium constant of reaction VII, K_{MY}, the formation constant of the complex MY^- is

$$K_{VII} = K_{MY}/K_{CuY}$$

The error made in the estimation of the percentage of uncomplexed copper amounts to about ±2% and will be roughly the same for all the metals investigated. By introduction of these limits in equations (8) and (9), the uncertainty ranges for log K_{VII} and log K_{MY} given in Table II are obtained. It is seen that the polarographic method gives better values for the heavy rare earths and uncertain values for the light metals. The potentiometric procedure and the polarographic method supplement each other.

The uncertainty ranges of the values obtained by the two independent methods overlap up to the element dysprosium (see Fig. 1). The heavy rare earth polarographic values are definitely higher than the potentiometric values. It was felt that this difference was real, in spite of the fact that the potentiometric data for the heavy rare earths involve large errors. If this is so, the difference must be due to the change in the supporting electrolyte, *i.e.*, resulting from substitution of KNO_3 for KCl. These differences can be explained if we assume that the rare earth cations form chloro complexes to a slight extent in 0.1 *M* KCl, thus reducing the apparent formation constant of the complex MY^-. If only the most simple of such chloro complexes with the composition MCl^{+2} are considered the stability constant can be calculated from the difference of the two values found for K_{MY} in 0.1 *M* KCl and 0.1 *M* KNO_3. The value of 28 for the stability constant of $LuCl^{+2}$ explains quantitatively the difference found for K_{MY}, namely, $10^{19.07}$ from the potentiometric method and $10^{19.65}$ from the polarographic method. The chloro complexes would be less stable for the other metals. It seems that the formation of chloro complexes to such a slight extent is not unlikely for the triple-charged cations of the rare earths.

In order to prove this assumption, the polarographic method was applied to solutions containing chloride. The same equivalent mixtures of CuY^{-2} and M^{+3} were prepared with 0.1 *M* KCl instead of KNO_3. The polarograms of these chloride-containing solutions have a different appearance. Instead of the original two-electron wave with $E_{1/2} = -0.04$, we now have two one-electron waves due to the stepwise reduction of uncomplexed copper Cu(II)–Cu(I), and Cu(I)–Cu(O). The first step is situated to the left and the second to the right of the original two-electron wave observed in KNO_3. The first lies in the positive potential range (*vs*. S.C.E.) and overlaps with the anodic oxidation of mercury: Hg(O)–Hg(I), so that it is impossible to determine its height. The height of the second step is proportional to the concentration of uncomplexed Cu^{+2}; it is impossible to measure this height exactly because of partial overlapping of the first step and some interference from the wave representing the reduction of the complex CuY^{-2}. The error involved in the determination of the uncomplexed copper is therefore much larger in KCl solution than in KNO_3 solution. We estimate this error to be ±4%. This is so large that the method cannot be applied to the lighter members of the rare earth series. The results for the heavier mem-

TABLE III

POLAROGRAPHIC DETERMINATION OF UNCOMPLEXED COPPER IN AN EQUIVALENT MIXTURE OF Na_2CuY AND RARE EARTH CHLORIDE MCl_3, BOTH AT A CONCENTRATION OF 0.001 *M* IN KCl, $\mu = 0.1$

Rare earth	Uncomplexed Cu, %	log K_{VII}	log K_{MY}
Gd	16 ± 4	−1.4 ± 0.3	17.0 ± 0.3
Tb	24 ± 4	−0.98 ± .2	17.4 ± .2
Dy	33 ± 4	− .60 ± .16	17.78 ± .16
Ho	40 ± 4	− .33 ± .15	18.05 ± .15
Er	50 ± 4	.00 ± .14	18.38 ± .14
Tm	57 ± 4	+ .24 ± .14	18.62 ± .14
Yb	64 ± 4	+ .50 ± .16	18.88 ± .16
Lu	69 ± 4	+ .69 ± .17	19.07 ± .17

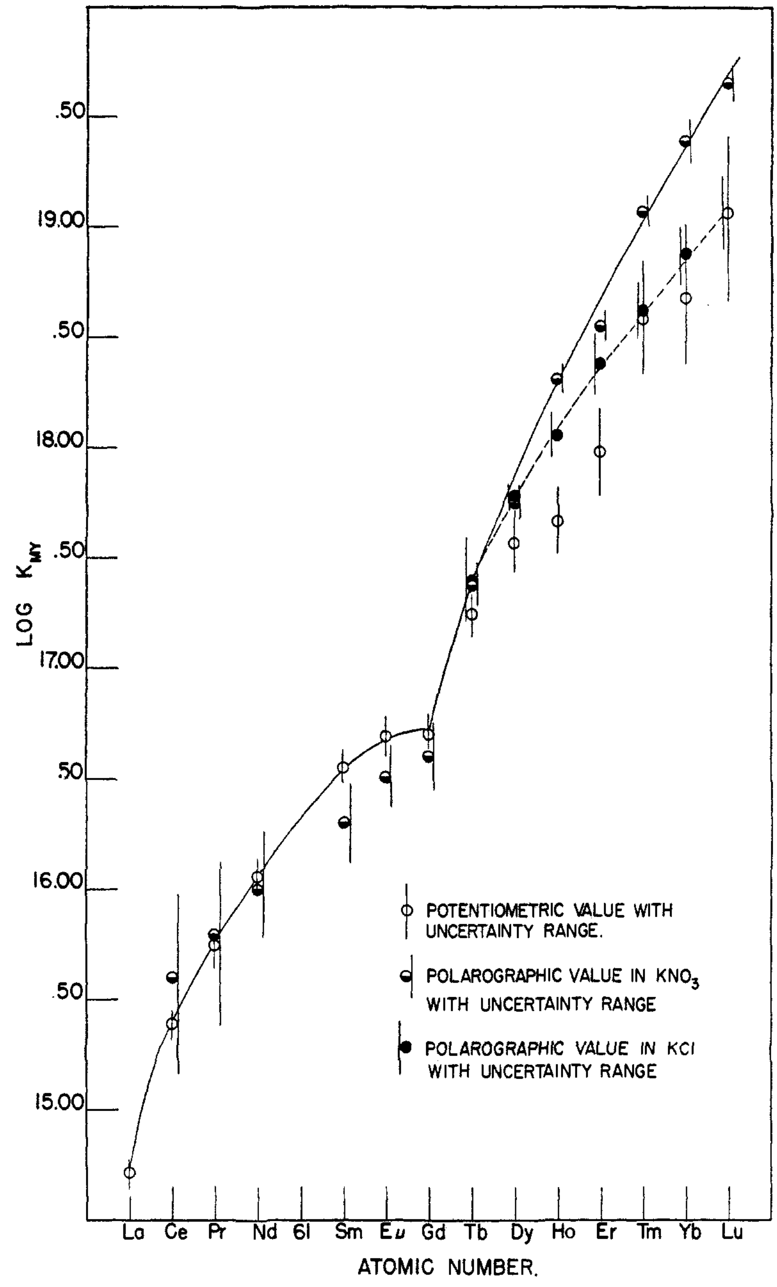

Fig. 1.—Logarithms of complex formation constants *versus* atomic number.

bers, giving rise to uncomplexed copper of more than 10% in the mixtures, are summarized in Table III. These results are now consistent with the potentiometric measurements except in two cases, Ho and Er, where the errors possibly have been underestimated.

In order to recheck the assumption of the formation of rare earth chloro complexes, the Yb value was redetermined with perchlorate as the supporting electrolyte. This value was identical with the value reported with the nitrate electrolyte.

Discussion of the Results

In Fig. 1, a smooth curve has been drawn through the points representing the better data, using the potentiometric values for the light and the polarographic values for the heavier rare earths. The following points are of interest.

1. The difference in K_{MY} between the individual metals is astonishingly large. This difference corresponds to a factor of $10^{4.9}$, or, as a mean from one metal to the next, of $10^{0.377}$. This difference is very large in comparison with the difference calculated from literature information. Crouthamel and Martin[10] give the following values for the stability of the mono-oxalate complexes $M(ox)^+$

$$\frac{[M(ox)]}{[M][ox]} = \text{in the case of Ce } 10^{6.6}\text{, Nd } 10^{7.2}\text{, Yb } 10^{7.3}$$

A rather large difference has been found between Ce and Nd and a very small difference exists between Nd and Yb, the ionic radii of which are considerably different from each other.

From the data in this paper, *i.e.*, from the *p*H values of the dilute (approximately 0.01 *M*) rare earth chloride solutions, approximate values of the stability constants of the hydroxy complexes MOH^{+2} can be calculated

$$K_{M(OH)} = \frac{[MOH]}{[M][OH]} = \frac{[H]^2}{cK_W} \quad (10)$$

c = concn. of rare earth salt
[H] = hydrogen ion concn. of this sol.
K_W = ion product of water

Equation (10) gives the stability constant of the hydroxy complex $La(OH)^{+2}$ as $10^{5.6}$ and for $Lu(OH)^{+2}$ as $10^{6.6}$, the difference being a factor of 10.

Larger differences between individual rare earths must be expected in cases of chelating agents in comparison to simple ligands such as OH^- groups. A polydentate complexing agent possesses a number of ligand atoms which are donated to the metal cation during complex formation. Each of these will be bound more firmly by the cation of a heavier member, in comparison to the cation of a lighter member. All of these differences are cumulative in arriving at the stability constants of the two chelate complexes, the logarithms of which are proportional to the free energies to be gained during the addition of the whole polydentate group to the two cations to be compared. In the case of a simple complex such as $M(OH)^{+2}$ one water molecule is replaced by OH^- during complex formation. In the case of MY^- probably all the water molecules of the hydrated cation are expelled and replaced by the atoms of the hexadentate agent Y^{-4}. This explains the comparatively large differences between the individual rare earth cations.

2. There is a large increase of K_{MY} from La^{+3} to Ce^{+3}. This large jump is paralleled by a similarly rapid decrease of the ionic radius from La to Ce.

3. The curve of log K_{MY} shows an irregularity

---

[10] C. E. Crouthamel and D. S. Martin, This Journal, **72**, 1382 (1950); **73**, 569 (1951).

around gadolinium which is not paralleled by the curve of the radii. It is true that there is an irregularity in the radii curve at erbium if the published radii are plotted against atomic number, but this may be accidental and due to errors connected with measuring the radii to ±0.01 Å. unit.

The break in the curve of the log K_{MY} observed at the point of gadolinium (substantiated by the change in slope when the "a" values as shown in Table I are plotted against *p*H for the individual rare earths) might be explained as follows: the carboxylate groups of the anion Y^{-4} are bulky groups and will have difficulty in finding enough room around the rare earth cation during coördination. This difficulty will increase as we go up the series because of the decrease in size of the cation. There should be a critical point after which no longer all four, but only three, of the $-COO^-$ groups can be coördinated. This must cause a break in the curve log K_{MY} *versus* atomic number. With gadolinium and the lighter members below it, the anion Y^{-4} will probably function as a hexadentate group. Going up the series from lanthanum to lutecium, the growing steric hindrance mentioned will prevent a large increase in stability, until at the point of gadolinium the complexing agent can no longer function as a hexadentate group, but only as a pentadentate group. From this point upward, the stability increases again steadily as the ionic radius becomes smaller. A new steric hindrance does not seem to take place in the range gadolinium to lutecium.

AMES, IOWA

[CONTRIBUTION FROM THE RICHARDSON CHEMISTRY LABORATORY OF TULANE UNIVERSITY]

Studies of Metallated Dye Complexes. II. Copper(II) Complexes with 2-Carboxyphenyl-azo-β-naphthol and 2-Carboxyphenyl-azo-β-naphthylamine

BY HANS B. JONASSEN AND JOHN S. WILSON

RECEIVED MARCH 2, 1953

The azo dyes, 2-carboxyphenyl-azo-β-naphthol and 2-carboxyphenylazo-β-naphthylamine were treated with copper(II) ion. A one to one reaction ratio was established in both cases by the method of continuous variation and by conductometric titrations. Evidence was advanced supporting the postulated structure involving the displacement of a hydrogen ion from each ortho substituted group of the dyes. On the basis of spectrophotometric measurements a monohydroxy addition complex was postulated for the copper(II)-2-carboxyphenyl-azo-β-naphthol compound and a dihydroxy complex for the copper(II)-2-carboxyphenyl-azo-β-naphthylamine.

Introduction

Many metal lakes of the azo dyes have been prepared but few studies of these lakes are reported in the literature. The lakes are formed between coördinating metal ions and azo dyes substituted in the ortho position by groups such as the carboxy, hydroxy, or amino. The metal ion is postulated to react with the dye by replacing hydrogen ions in the substituent groups and coördinating to the azo group.[1]

It is well known that the introduction of certain metal ions to an azo dye, used for dyeing cotton, produces better colors and greater resistance to fading. This increased stability may be explained on the basis of coördination. The dye may not occupy all the positions in the coördination sphere of the metal ion. These unoccupied positions may be occupied by hydroxy groups of the cellulose fiber thus creating a chemical bond between the fiber and the mordant dye.

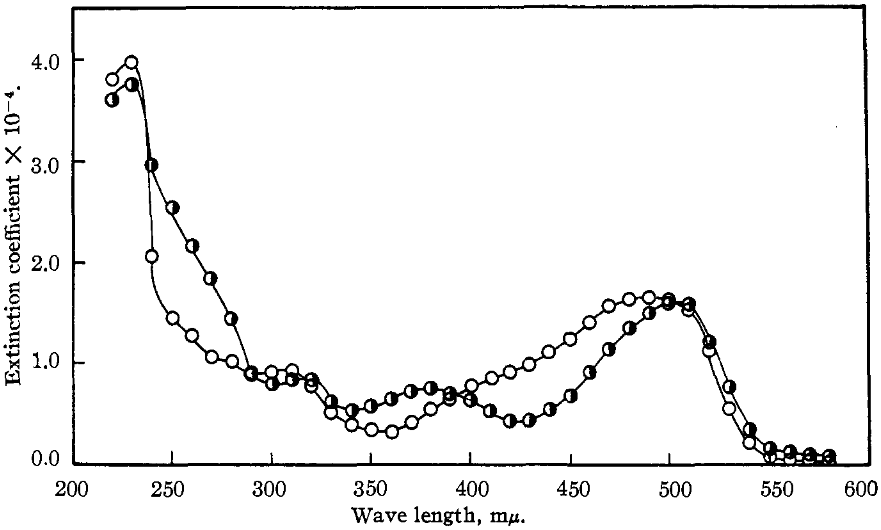

Fig. 1.—Absorption spectra of 2-carboxyphenyl-azo-β-naphthol, ○ and Cu(II)-2-carboxyphenyl-azo-β-naphthol, ◑. Temperature = 30°; 1-cm. matched corex cells; 95% ethanol solutions.

This study has attempted to show by spectrophotometric and conductometric methods that the unoccupied positions in the copper(II) coördination sphere of copper(II) azo dye complexes may be occupied by free hydroxy groups. A previous study[2] of the copper(II) complex of *o,o'*-dihydroxyazobenzene has been reported, verifying the postu-

---

[1] M. Elkins and L. Hunter, *J. Chem. Soc.*, 1598 (1935).

[2] H. B. Jonassen, Mae M. Cook and J. S. Wilson, THIS JOURNAL, **73**, 4683 (1951).