with the cerous concentration, being slightly higher at the higher concentration of supporting electrolyte, and it increases linearly with the volume of the solution. A similar, though smaller, increase of the diffusion current was also produced by the addition of small amounts of sodium hydroxide to a fresh solution. These phenomena may be related to the formation of a partially hydrolyzed cerium(III) species.

Typical polarograms of nitrate in 0.1 *M* cerous chloride in the presence of various concentrations of sodium sulfate are shown in Fig. 2. Even very low concentrations (*ca.* 1.5 m*M*) of sulfate radically alter the shape of the wave, transforming it into the form shown in curve b. With higher sulfate concentrations the sharp "break" at the foot of the wave disappears completely. With 0.5 *M* sulfate a large precipitate is formed, presumably of cerous sulfate, and the wave practically disappears.

These results are difficult to explain on the basis of the "ion pair" theory of Tokuoka and Ruzicka. It seems very improbable that 1.5 m*M* sulfate should be able to replace most of the nitrate from the cerous nitrate complex in the presence of a large excess of cerium(III).

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS, BROOKHAVEN NATIONAL LABORATORY AND CORNELL UNIVERSITY]

Determination of Dissociation Constants of Complex Ions by a Radioactive Indicator Method[1a]

BY C. M. COOK, JR.,[1b] AND F. A. LONG[1b]

A radioactive indicator method for determining the dissociation constants of highly stable complex ions can be used when the complex ion is formed from the conjugate base of a weak acid with known ionization constants and when the complex ion interchanges its central metal ion only slowly. The method involves a determination of the metal ion concentration in a complex solution of sufficient acidity so that partial dissociation has occurred. Application of the method to ferroin gives a K_d value of 8×10^{-22} which agrees fairly well with the value obtained by Kolthoff and co-workers. A similar investigation of NiEdt$^=$, the complex formed from nickel ion and ethylenediaminetetraacetic acid, gives $K_d = 1 \times 10^{-19}$.

The determination of dissociation constants of highly stable complex ions is frequently a matter of some difficulty, particularly if the complex ion is only weakly colored or if the metal ion does not form a reversible electrode with its metal. A procedure which involves the use of radioactive indicators and which should have utility for certain common types of complex ions is outlined below; also given are results of the application of this method to two complex ions, ferroin and ethylenediaminetetra-acetato nickelous ion.

Consider a complex ion, MeA_x, formed from a metal ion and the conjugate base of a weak acid. In acid solutions this complex will undergo partial dissociation caused by removal of A by hydrogen ions. If the ionization constants of the weak acids formed from A are known, the dissociation constant of the complex can be calculated from the concentration of Me ions present in an equilibrated MeA_x solution of known acidity; this Me ion concentration can be determined by use of a radioactive indicator.

Suppose the undissociated complex ion will undergo radioactive exchange with added Me ions only slowly. (This will commonly be true for complex ions of high stability.) If one adds Me ions to an acidified and equilibrated solution of MeA_x which has been made from isotopically labeled Me of known radioactivity, and subsequently removes from solution a portion of the Me ions, one finds that this is radioactive due to mixing of the inactive Me with active Me from dissociation of the complex. The increase in specific radioactivity is an easily calculated function of the moles of added Me and of that present as such in the original solution. Consequently a measurement of this specific radioactivity decrease permits a calculation of the concentration of Me ions.

The addition of the radioactive Me will shift the equilibrium of the complex ion toward less dissociation. A basic assumption is that mixing of the radioactive and inactive Me precedes this shift in the equilibrium.

Bjerrum[2] has demonstrated that, in the case of many coördination complexes, the formation of the complexes will take place in stepwise fashion, so that in the acid-induced dissociation of MeA_x the species MeA_{x-1}, MeA_{x-2}, . . ., as well as Me may be present. If these intermediate complexes are present as a sizeable fraction of the total complexed Me in the equilibrium solution, their presence will complicate the interpretation of the data and the calculation of the dissociation constant. For some complex ions this difficulty obviously will not enter. For other cases, however, it may be necessary to investigate this intermediate complex formation problem before the method can be safely applied.

Specific illustrations of the application of this technique are given in the next sections.

Dissociation Constant of Ferroin

The dissociation of this complex of ferrous ion and orthophenanthroline, $FePh_3^{++}$, has been studied by Lee, Kolthoff and Leussing[3a] who report a

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[1] (a) Work carried out in part under the auspices of the Atomic Energy Commission. (b) Department of Chemistry, Cornell University, Ithaca, N. Y.

[2] J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).

[3] (a) T. S. Lee, I. M. Kolthoff and D. L. Leussing, THIS JOURNAL, **70**, 2348 (1948); (b) I. M. Kolthoff, D. L. Leussing and T. S. Lee, *ibid.*, **72**, 2173 (1950).

K_d value of 5×10^{-22}. These authors have also shown[3b] that the intermediate complexes, $FePh^{++}$ and $FePh_2^{++}$, are present only in very small amounts unless excess ferrous ion is present. The ionization constant of the acid, HPh^+, has been shown to be 1.1×10^{-5}. The work of Ruben and Kamen[4] and unpublished work in this Laboratory show that the exchange of added radioactive ferrous ion with the ferroin complex is quite slow. Thus the necessary information for an application of the radioactive indicator method is available. The K_d values resulting from its application can be compared with the value obtained by Kolthoff and co-workers.

Experimental.—The specific procedure in this case differed slightly from that outlined earlier in general form. To equilibrated solutions of radioactive ferroin a large excess of a ferrous ion solution was added to serve as a hold-back carrier for the dissociated radioactive ferrous ions. The amount of the latter, rather than the specific activity, was then determined by a radioactivity count of the ferrous ions after separation.

A stock solution of radioactive ferroin was prepared by mixing a very slight excess of orthophenanthroline monohydrate with ferric sulfate solution containing Fe^{55} and Fe^{59} obtained from Oak Ridge. This mixture was reduced to ferroin by treatment with hydroxylamine sulfate and sulfur dioxide and finally diluted to a molarity of 0.025. Ten-ml. portions of this solution were mixed with known quantities of 1.00 normal sulfuric acid, diluted with water to a known final volume, and allowed to stand at 25° for two or more days in order to attain equilibrium dissociation of the ferroin. Each of these mixtures was then mixed with 20 ml. of approximately 0.6 molar inactive ferrous ion solution, after which the ferroin was removed by precipitation with excess cadmium tetraiodide ion solution. The filtrate from this precipitation contained all of the free ferrous ion; its volume was adjusted to 50 ml., and its radioactivity was measured with a solution counter of fixed geometry. For a comparison standard a 10-ml. portion of the initial ferroin solution was diluted to 50 ml. and its radioactivity was measured in the same counter.

Results.—Table I gives the total concentrations of sulfuric acid and ferroin in the equilibrated solutions and the corrected counting rate for the final ferrous solutions. The observed counting rates were corrected by an experimentally determined factor of 1.18 to compensate for the difference in density between the ferrous solutions and the standard ferroin solution. The values of the fractional dissociation α are calculated from the equation

$$\alpha = \frac{\text{corrected counting rate for separated ferrous solution}}{\text{counting rate for standard ferroin solution}}$$

This identification of ratio of counts with fractional dissociation is valid because the same amount of radioactive ferroin was present in the standard solution as was in all of the original solutions and because the ratio of moles of added ferrous ion carrier to moles of active ferrous ion from dissociation was always in excess of 100 to 1. The latter insured that at least 99% of the dissociated active ferrous ion was separated along with the inactive carrier.

Table I

Dissociation Constant of Ferroin at 25°

Ferroin standard is 27.34 counts/sec., net; concentration units are moles/liter.

Initial concn. H_2SO_4	$(FePh_3^{++})_0$ $\times 10^2$	Cor. Fe^{++} counts/ sec.	α	(H^+)	$\gamma_{H^+}/\gamma_{HPh^+}$	K_d $\times 10^{22}$
0.400	0.50	11.9	0.434	0.429	1.5	10.8
.300	1.00	4.82	.177	.327	1.35	5.1
.250	0.50	7.31	.268	.275	1.3	6.9
.250	0.25	11.1	.405	.275	1.3	5.5
.100	1.00	2.55	.0935	.120	1.15	11.3
.050	0.50	2.53	.0925	.0635	1.1	10.7
.050	0.25	3.87	.142	.0632	1.1	8.4

The reaction which occurs in the acidified solution of ferroin is

$$FePh_3^{++} + 3H^+ = Fe^{++} + 3HPh^+$$

For the calculation of K_d let $(FePh_3^{++})_0$ be the total concentration of ferroin in the original solution. Then for this original solution

$$(Fe^{++}) = \alpha(FePh_3^{++})_0;\ (FePh_3^{++}) = (1 - \alpha)(FePh_3^{++})_0$$

The dissociation constant of HPh^+ is

$$K_A = 1.1 \times 10^{-5} = \frac{(H^+)\gamma_{H^+}(Ph)\gamma_{Ph}}{(HPh^+)\gamma_{HPh^+}}$$

Thus

$$3(Fe^{++}) = (Ph) + (HPh^+) = (Ph)\left[1 + \frac{(H^+)\gamma_{H^+}\gamma_{Ph}}{\gamma_{HPh^+}\, 1.1 \times 10^{-5}}\right]$$

$$(Ph) = \frac{3\alpha(FePh_3^{++})_0}{F} \text{ where } F = 1 + \frac{(H^+)\gamma_{H^+}\gamma_{Ph}}{\gamma_{HPh^+}\, 1.1 \times 10^{-5}}$$

$$K_d = \frac{(Fe^{++})(Ph)^3\gamma_{Fe^{++}}\gamma^3{}_{Ph}}{(FePh_3^{++})\gamma_{FePh_3^{++}}}$$

$$= \frac{(Fe^{++})(Ph)^3}{(FePh_3^{++})} \text{ assuming } \gamma_{Ph} = 1 \text{ and } \gamma_{Fe^{++}} = \gamma_{FePh_3^{++}}$$

$$= \frac{27\alpha^4(FePh_3^{++})_0^3}{(1 - \alpha)F^3}$$

From the measured values of α one can thus obtain values of K_d since $(FePh_3^{++})_0$ is known and F is calculable.

In computing F, values of the ratio $\gamma_{H^+}/\gamma_{HPh^+}$ were interpolated from the data given by Lee, *et al.*,[3] and γ_{Ph} was assumed to be unity. The hydrogen ion concentrations were computed using values given by Klotz and Eckert[5] for the apparent second dissociation constant of sulfuric acid as a function of ionic strength.

Table I gives the observed data and calculated K_d values.

The average value of K_d is 8×10^{-22}. If one calculates (H^+) by consideration of individual ion activity coefficients in the same manner as was done by Kolthoff and co-workers[3] the average value of K_d is lowered to 7×10^{-22}. This is a satisfactory check with the value of 5×10^{-22} given by these workers, particularly since the experimental conditions are rather different.

Dissociation Constant of the $NiEdt^=$ Complex

Ethylenediaminetetraacetic acid forms stable complex ions with a large number of di- and trivalent metal ions including nickelous.[6] The nickel complex, abbreviated as $NiEdt^=$, is not precipitated by dimethylglyoxime, sodium hydroxide or ammonium sulfide and at *p*H values above one it undergoes exchange with added nickel ion only slowly.[7]

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(4) S. Ruben, M. Kamen, M. Allen and P. Nahinsky, This Journal, **64**, 2297 (1942).

(5) I. M. Klotz and C. F. Eckert, This Journal, **64**, 1878 (1942).

(6) H. Brintzinger, H. Thiele and U. Muller, *Z. anorg. allg. Chem.*, **249**, 113 (1942).

(7) F. A. Long, S. Jones, M. Burke, Brookhaven Conference Report # 2, Upton, N. Y., December 1, 1948.

Titration experiments show that the first ionization of H_2NiEdt is strong but the second is somewhat weak; at 25° the second ionization constant in 0.1 molar potassium chloride is $K_{A_2} = 1 \times 10^{-3}$.

Values of the four successive ionization constants of ethylenediaminetetraacetic acid at 20° were reported by Schwartzenbach[8] to be $pK_1 = 2.00$; $pK_2 = 2.67$; $pK_3 = 6.16$; $pK_4 = 10.26$. These values are concentration ionization constants for solutions of the acid in 0.1 molar potassium chloride.

The procedure used to determine K_d for this complex is similar in principle to the previous example. However, the radioactive indicator used here, Ni^{63}, gives such soft radiation (0.063 mev.) that solution counting cannot be used, and other procedures, described below, are followed.

Experimental.—A stock solution of 0.046 molar $NiEdt^-$ containing Ni^{63} obtained from Oak Ridge was prepared and adjusted to a pH value of 10. For each determination of K_d a 5-ml. portion of this solution was mixed with a measured amount of 1.00 normal hydrochloric acid and enough potassium chloride to give a final ionic strength of 0.1 and was then diluted with water to a known final volume. This solution was allowed to equilibrate at 20° for at least a day. The solution was then quickly mixed with 10 ml. of a 0.045 molar solution of inactive nickel chloride. From the resulting mixture four aliquots were removed at measured times after mixing. The nickel ion in these aliquots was precipitated as the hydroxide, using excess sodium hydroxide, and filtered off. The nickel from each precipitate was dissolved and eventually plated as the metal on copper disks. The radioactivity of the four nickel samples was determined in a windowless counter. For all samples the nickel plate was effectively infinitely thick and of constant area so that the net counting rate was directly proportional to the specific activity of the nickel.

The fraction of exchange, x, for each sample is given by the ratio of the specific activity of the nickel to that of a sample from nickel which has reached exchange equlibrium, *i.e.*

$$x_t = S_t/S_\infty$$

Plots of log $(1 - x_t)$ against time were made and an extrapolation to zero time gave values of the "instantaneous exchange," the exchange due to mixing of the dissociated Ni^{++} ions from the $NiEdt^-$ with the inactive nickel chloride. This fraction, called x_0 in subsequent discussion, was determined to within ±0.03 for all experiments. The observed values of x_0 are, however, slightly larger than the true x_0 values because even at high pH where dissociation does not occur there is a small amount of instantaneous exchange, probably due to a slight coprecipitation of active $NiEdt^-$ by the nickel hydroxide. From data at high pH we conclude that the observed x_0 values are high by approximately 0.025. The corrected values in Table II are simply the observed values minus this amount.

TABLE II

DISSOCIATION CONSTANT OF $NiEdt^-$, 20°

$(NiEdt^-)_0 = 0.00093\ M;\ B/A = 1.93$

Initial molarity HCl	Cor. x_0	α	(H^+), mole/l.	$K_d \times 10^{19}$
0.100	0.405	0.310	0.0982	1.00
.080	.355	.266	.0784	1.38
.060	.233	.165	.0586	1.04
.040	.142	.097	.0388	1.07
.020	.046	.031	.0190	0.73
			Average	1×10^{-19}

Results.—Let $(NiEdt^-)_0$ be the total concentration of complex ion in the original solution and let α be the fractional dissociation of this. Let A be the total moles of nickel in the original solution and B be the total moles of nickel in the added nickel chloride solution. From consideration of the specific radioactivity of the nickelous ion after mixing, the relationship between x_0 and α is

$$\alpha = \frac{x_0 B}{A(1 - x_0) + B}$$

Further, using the pK values listed earlier, in an equilibrated complex ion solution

$$\begin{aligned}(Ni^{++}) &= (Edt^{=}) + (HEdt^{=}) + (H_2Edt^-) + \\ &\qquad (H_3Edt^-) + (H_4Edt) \\ &= (Edt^{=})\ [1 + (H^+)10^{10.26} + (H^+)^2 10^{16.42} + \\ &\qquad (H^+)^3 10^{19.09} + (H^+)^4 10^{21.09}] \\ &\equiv (Edt^{=})\ F \\ (Ni^{++}) &= \alpha(NiEdt^-)_0 \\ (NiEdt^-) &= (1 - \alpha)(NiEdt^-)_0/[1 + (H^+)/K_{A_2}] \\ (Edt^{=}) &= (Ni^{++})/F = \alpha(NiEdt^-)_0/F\end{aligned}$$

Thus

$$K_d = \frac{(Ni^{++})(Edt^{=})}{(NiEdt^-)} = \frac{\alpha^2\ (NiEdt^-)_0}{(1 - \alpha)F}[1 + (H^+)/K_{A_2}]$$

where K_d is a concentration equilibrium constant. The last factor in brackets enters because of the weakness of the acid $HNiEdt^-$ and shows that the value of K_d depends not only on the values of the ionization constants for H_4Edt (through F) but also on the value of K_{A_2}. The absolute accuracy of K_d therefore depends directly on a precise knowledge of these acidity constants.

Table II gives the observed data and calculated K_d values at 20° and an ionic strength of 0.1. These experiments indicate that K_d is approximately constant over a five fold change in acidity. Other experiments not listed show that the K_d values are independent of the $(NiEdt^-)_0$ concentration and of the ratio B/A.

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(8) G. Schwartzenbach and H. Ackermann, *Helv. Chim. Acta*, **30**, 1798 (1947).