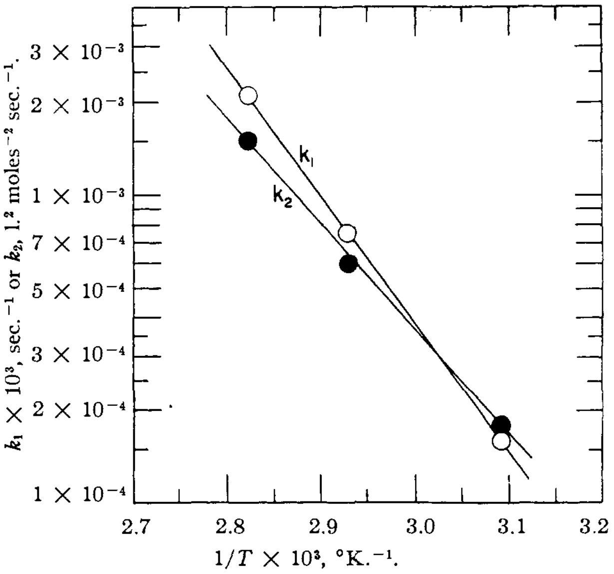


Fig. 1.—The temperature dependence of the specific rate constants.

The Mechanisms.—A mechanism which is consistent with the observed first-order path is represented by the slow equilibrium

$$SbCl_5 = SbCl_3 + Cl_2 \qquad (3)$$

The third-order path is consistent with the mechanism represented by equations 4, 5 and 6

$$2SbCl_5 = Sb_2Cl_{10} \text{ (rapid equilibrium)} \qquad (4)$$

$$Sb_2Cl_{10} + Sb^*Cl_3 = Sb^*Sb_2Cl_{13} \text{ (rapid equilibrium, activated complex)} \qquad (5)$$

$$Sb^*Sb_2Cl_{13} \longrightarrow SbCl_3 + Sb^*SbCl_{10} \text{ (rate-determining step)} \qquad (6)$$

The dimerization of antimony pentachloride is a reasonable possibility in light of the evidence for the existence of compounds of the type $SbCl_5 \cdot MCl_5$, where M may be either phosphorus or arsenic.[13] A possible structure for the activated complex is shown in Fig. 2 wherein the three antimony atoms occupy identical positions.

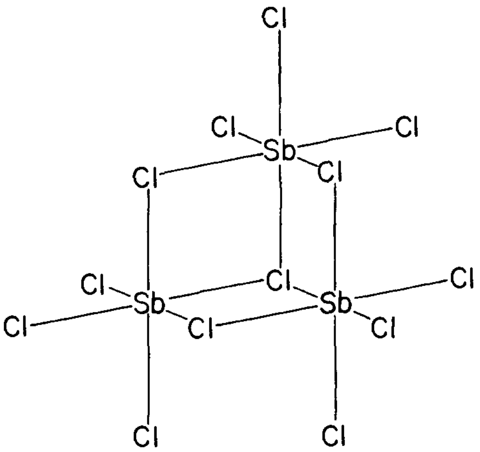


Fig. 2.—Proposed structure for termolecular activated complex.

Acknowledgment.—The authors wish to express their appreciation to Dr. R. W. Spence, Mr. J. E. Sattizahn and Mr. G. W. Knobeloch of the Los Alamos Scientific Laboratory for irradiating the samples of antimony trichloride.

ALBUQUERQUE, N. MEX.

---

[13] (a) V. Gutmann, *Monatsh.*, **82**, 473 (1951); (b) W. E. Thorneycroft, "Textbook of Inorganic Chemistry," Vol. VI, Part V, Edited by J. N. Friend, Charles Griffin and Co., London, 1936, p. 73.

[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY OF CLARK UNIVERSITY]

Thermodynamics of Metal Chelate Formation. V. Nitrilotriacetic Acid[1]

BY VINCENT L. HUGHES AND ARTHUR E. MARTELL[2]

RECEIVED OCTOBER 5, 1955

Potentials of cells consisting of hydrogen and silver–silver chloride electrodes have been measured in buffer solutions containing acid salts of nitrilotriacetic acid at various ionic strengths. The e.m.f. data obtained were extrapolated to infinite dilution with the aid of the Debye–Hückel activity coefficient relationship, and the thermodynamic acid dissociation constants were evaluated. Similar measurements made in the presence of Mn(II), Mg(II), Ca(II) and Ba(II) ions were used for the determination of the corresponding thermodynamic metal chelate stability constants. The standard free energy changes for the reactions at 0, 10, 20 and 30° were calculated, and the corresponding values of $\Delta H°$ and $\Delta S°$ applying over this temperature range are reported. The results are interpreted on the basis of recent theories of metal chelate formation in aqueous solution.

In order to provide more data for testing the significance of the entropy effect as a factor in the stability of metal chelate compounds,[3] the thermodynamic measurements reported previously for ethylenediaminetetraacetate chelates[4] have been extended in the present research to metal chelate compounds of nitrilotriacetic acid. Although the latter ligand provides fewer coördinating groups than does the anion of ethylenediaminetetraacetic acid, it nevertheless has a remarkable affinity for even the more basic divalent ions. Therefore it seems quite probable that relatively large entropy effects would contribute to the stability of metal–nitrilotriacetate chelates, as has been found to be

---

[1] This research was supported by the U. S. Navy Office of Naval Research under Contract Nonr-596(00). Abstracted from a dissertation submitted by Vincent Hughes to the Faculty of Clark University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Department of Chemistry, Clark University, Worcester, Mass.

[3] (a) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, p. 151; (b) G. Schwarzenbach, *Helv. Chim. Acta*, **35**, 2345 (1952).

[4] (a) F. F. Carini and A. E. Martell, THIS JOURNAL, **75**, 4810 (1953); (b) **76**, 2153 (1954).

true of the alkaline earth ethylenediaminetetraacetates.

The only chelate stability constants previously reported for nitrilotriacetic acid were measured at one temperature, 20°, and at a constant ionic strength of 0.10. Hence it is not possible to determine enthalpy and entropy changes from the "concentration" constants available for this ligand. In the present work, thermodynamic stability, or formation, constants are determined in order to provide more accurate values of enthalpy and entropy changes associated with formation of the metal chelate from the ligand and metal ions. Also, since the stabilities of the metal chelates are somewhat lower than those of ethylenediaminetetraacetic acid, it is possible in the present work to extend the potentiometric measurements to one of the more basic transition metals—Mn(II). Therefore the metal ions selected for this investigation are Mn(II), Ca(II), Mg(II) and Ba(II).

Experimental

The method employed for the determination of thermodynamic acid dissociation constants is similar in principle to the procedure described previously.[3] The cells employed contained no liquid junction and may be described by the following general type

$$\text{Pt–H}_2,\ \text{KCl}(m_1),\ \text{K}_n\text{H}_{3-n}\text{A}(m_2),\ \text{K}_{n+1}\text{H}_{2-n}\text{A}(m_3),\ \text{AgCl–Ag} \qquad (\text{I})$$

where H_3A represents nitrilotriacetic acid. The buffer solutions employed for the determination of K_1, K_2 and K_3, the first, second and third acid dissociation constants, correspond to values of $n = 0$, 1 and 2, respectively, in the general cell described above. The electromotive forces of each of these three cells were measured at 0, 10, 20, 30 and, in the case of K_1 and K_2 at 40°. Values for 0° were evaluated by extrapolation of measurements made at a slightly higher temperature.

Since the first two acid forms of nitrilotriacetic acid are strongly dissociated in aqueous solution and the corresponding dissociation constants do not differ greatly, it is better to employ the simple mono-potassium salt, KH_2A, rather than a mixture of the free acid and this salt, as the buffer solution. Thus the buffer solution employed in cell I involves only two concentrations, that of $HK_2A(m_2)$ and of $KCl(m_1)$.

The cell employed in the determination of metal chelate stability constants differs somewhat in the nature of the solutes and has the general form

$$\text{Pt–H}_2,\ \text{MCl}_2(m_1),\ \text{K}_2\text{HA}(m_2),\ \text{K}_3\text{A}(m_3),\ \text{AgCl–Ag} \qquad (\text{II})$$

where M represents the bivalent metal ions of Mn(II), Mg(II), Ca(II) and Ba(II).

The solutions employed in cell I were made up such that they initially contained the buffer ratios given below. This is the term $m_{\text{H}_i\text{A}}/m_{\text{H}_{i-1}\text{A}}$, which is determined by the concentration of the two anions in the solution. In the first two cases, no attempt was made to adjust further the ratio to the initial one. Literature data indicated that for the first and second acid constants involving carboxyl groups, no improvement in the extrapolation function or change in the intercept resulted.[5] In the last case, however, adjustment was made at each temperature and a constant ratio maintained, since higher terms were more likely to enter, and did enter, into the extrapolation function.

Materials and Measurements.—The nitrilotriacetic acid was obtained through the courtesy of Versenes, Inc., Framingham, Mass. It was further purified by successive recrystallizations from distilled water. The apparatus employed for e.m.f. measurements, the methods employed for the preparation of electrodes and the purification of reagents, and the experimental glass cell are the same as were previously described.[4] For each e.m.f. measurement a number of platinum and silver-silver chloride electrodes were employed as a check on the condition of the electrodes. The electromotive force values obtained for both cells were found to be reproducible to ± 0.05 mv. In most cases 5 hours was sufficient to obtain reproducible readings, which were found to remain constant a number of days. The temperature of the experimental solution was maintained constant within ±0.01°.

Calculations

All extrapolations were made on the basis of equations obtained by suitable substitution in the general equation for the e.m.f. of a cell consisting of hydrogen and silver–silver chloride electrodes and containing hydrogen and chloride ions. If a, m and represent activity, molal concentration and activity coefficient, respectively, the final expression for the thermodynamic constant K_1 becomes

$$pK_i = p\text{wH} + \log \frac{m_{\text{H}_i\text{A}}}{m_{\text{H}_{i-1}\text{A}}} + \log \frac{f_{\text{H}_i\text{A}} f_{\text{Cl}^-}}{f_{\text{H}_{i-1}\text{A}}} \qquad (1)$$

where pwH represents the function $(E - E^0)F/2.303\,RT + \log m_{\text{Cl}^-}$, according to usual practice.

The first and second terms on the right-hand of equation 1 involve only measured quantities. The third term is evaluated from the Debye–Hückel relationship

$$-\log f_i = \frac{AZ_i^2 \cdot \mu^{1/2}}{1 + Ba_i^* \mu^{1/2}} + \beta m_i \qquad (2)$$

The values of A and B have been given by Manov, *et al.*,[6] and the other terms have their usual meaning. All terms in equation 2 can be readily obtained, with the exception of a^*, which was arbitrarily chosen to give a minimum slope to the extrapolation function. It was found that only one value was necessary at the various temperatures to keep the slope of the extrapolation to infinite dilution reasonably low. In the case of K_3, slight curvature in the plots was eliminated by adding the term $-\beta\mu^3/3$ with $\beta = 3.50$. The evaluation of the terms other than the constants on the right-hand side of equation 1 was carried out in the following manner.

pK_3.—The third acid dissociation constant was obtained from e.m.f. measurements containing K_3A and K_2HA as the buffer solution. Because of the high pH of these solutions, it was necessary to take into consideration the hydrolysis of the very basic anion, A^{-3}.

Thus the equation employed in the extrapolation is

$$pK_3 = p\text{wH} + \log \frac{m_1 + m_{\text{OH}^-}}{m_2 - m_{\text{OH}^-}} + \frac{4A\mu^{1/2}}{1 + a^*B\mu^{1/2}} \qquad (3)$$

The molalities were adjusted throughout the measurements to maintain the ratio $m_1{:}m_2{:}m_3$ at the constant value 5.025:0.31:0.69.

pK_2.—The second acid dissociation constant was evaluated from the e.m.f. values of cell I containing KH_2A and K_2HA as the buffering substances. In addition to the equilibrium between these two substances, it is necessary to take into account the extensive dissociation of the H_2A^- anion. In this case the equation used for the extrapolation of e.m.f. data takes the following form

$$pK_2 = p\text{wH} - \log \frac{m_2 + m_{\text{H}^+}}{m_1 - m_{\text{H}^+}} + \frac{2A\mu^{1/2}}{1 + a^*B\mu^{1/2}} \qquad (4)$$

Here also, the experimental solutions were adjusted

---

(5) J. R. Bates and G. Pinching, THIS JOURNAL, **71**, 1274 (1949).

(6) G. Manov, R. Bates, W. Hamer and S. Acree, *ibid.*, **65**, 1765 (1943).

so that the molality ratio $m_1:m_2:m_3$ would have a constant value of 2.55:0.809:0.191.

pK$_1$.—The first acid dissociation constant was calculated from the product constant K_1K_2, which was determined by the method of Bates[7] for two overlapping dissociation reactions.

The extrapolation function is

$$\frac{1}{2}\,pK_1K_2 = p\text{wH} - \frac{1}{2}\log\frac{m_{\text{HA}^{-2}}}{m_{\text{H}_2\text{A}}} + 3/2\,\frac{A\mu^{1/2}}{1 + a^*B\mu^{1/2}} \quad (5)$$

The molality ratio $m_1:m_2$ was maintained constant at 2.52:1.00 throughout the measurements. The ratio $m_{\text{HA}^{-2}}/m_{\text{H}_2\text{A}}$ is obtained by successive approximations. In principle the method involves the assumption of a reasonable value for K_1. Then from the previously-determined value of K_2, and the activity coefficient of the medium, concentration constants are determined and the values of $m_{\text{HA}^{-2}}$ and $m_{\text{H}_2\text{A}}$ may thus be calculated for each ionic strength. The extrapolation is then carried out and the value of pK_1K_2 thus determined is used to calculate a better value of K_1. When the value of K_1 obtained by extrapolation is the same as the one chosen to evaluate the concentration quotient, the correct value has been obtained.

Metal Chelate Constants.—The buffer systems employed in cell II contained the ligand anions HA^{-2}, A^{-3} and a bivalent metal ion. The following equilibria are involved

$$\text{HA}^{-2} \rightleftharpoons \text{A}^{-3} + \text{H}^+ \quad K_3 = \frac{a_{\text{H}^+}a_{\text{A}^{-3}}}{a_{\text{HA}^{-2}}}$$

$$\text{M}^{+2} + \text{A}^{-3} \rightleftharpoons \text{MA}^{-1} \quad K_\text{M} = \frac{a_{\text{MA}^{-1}}}{a_{\text{M}^{+2}} \times a_{\text{A}^{-3}}}$$

The product of K_3 and K_M is the desired function

$$K_3K_\text{M} = \frac{a_{\text{MA}^{-1}}a_{\text{H}^+}}{a_{\text{M}^{+2}}a_{\text{HA}^{-2}}}$$

When this is substituted in the general extrapolation expression, the following relationship is obtained

$$\log K_\text{M} = pK_3 - p\text{wH} + \log\frac{m_\text{MA}}{m_{\text{M}^{+2}}m_{\text{HA}^{-2}}} + \frac{8A\mu^{1/2}}{1 + a^*B\mu^{1/2}} + \beta\mu \quad (6)$$

Since the *p*H values of all the solutions investigated were below 7, the concentration quotient was evaluated with the relationships

$$m_{\text{MA}^-} = m_3 + m_{\text{H}^+}$$

$$m_{\text{M}^{+2}} = m_1 - m_3 - m_{\text{H}^+}$$

$$m_{\text{HA}^{-2}} = \frac{m_2 - m_{\text{H}^+}}{1 + \dfrac{m_{\text{H}^+}}{K^{1/2}}}$$

where K is the concentration constant corresponding to the ionic strength of the solution. The buffer ratios $m_\text{MA}/(m_{\text{M}^{+2}})\,(m_\text{HA})\,(m_{\text{Cl}^-})$ were maintained constant throughout the investigation by the addition of acid or base to the solution. The values employed were 38.8, 200, 111 and 69.0 for Mn, Mg, Ca and Ba, respectively.

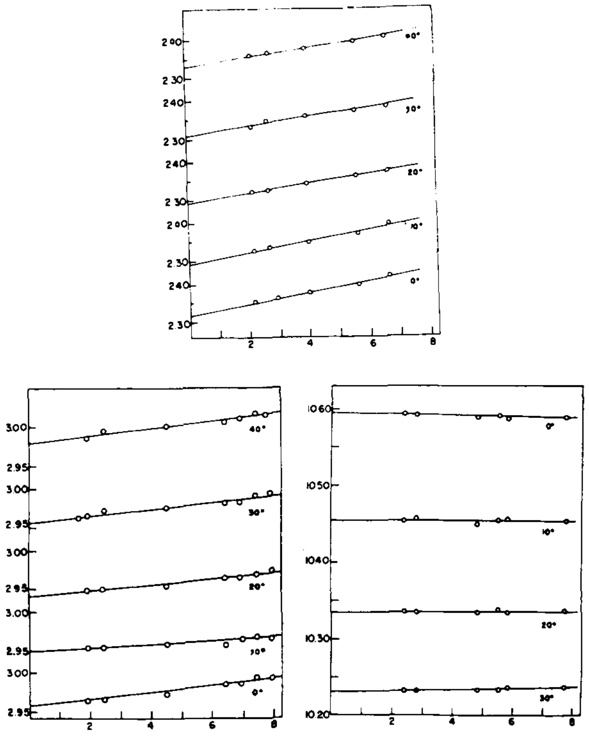


Fig. 1.—Extrapolation of e.m.f. data of cell I to infinite dilution: upper curve, $^1/_2pK_1K_2$ *vs.* $\mu \times 10^2$; lower left, pK_2 *vs.* $\mu \times 10^2$; lower right, pK_3 *vs.* $\mu \times 10^2$.

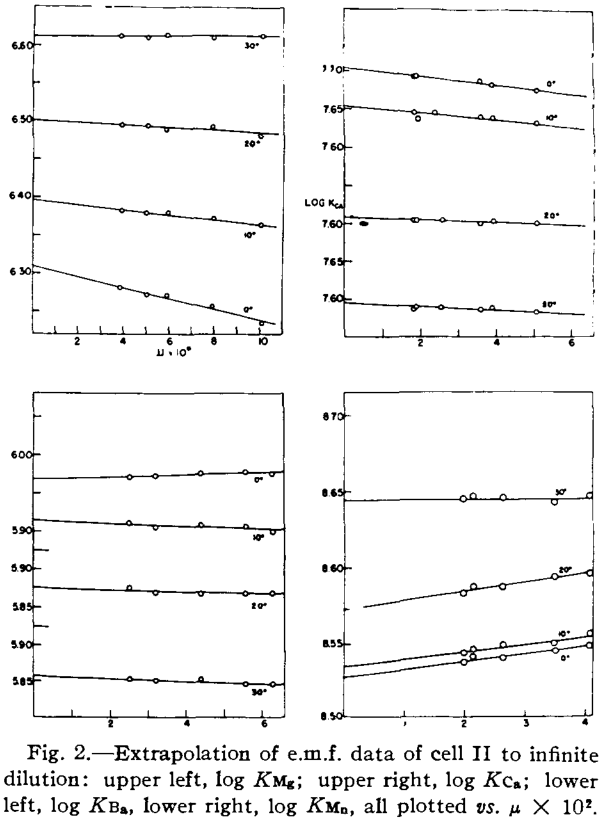


Fig. 2.—Extrapolation of e.m.f. data of cell II to infinite dilution: upper left, log K_Mg; upper right, log K_Ca; lower left, log K_Ba, lower right, log K_Mn, all plotted *vs.* $\mu \times 10^2$.

The extrapolations of the three functions developed above for the determination of acid dissociation constants are given practically in Fig. 1, and the extrapolation of e.m.f. data of cell II are given in Fig. 2 for each of the four metals involved. The values of the parameters, a^*, which were used in these extrapolations are 4.0 for all acid dissociation constants, and 1.25, 2.5, 4.0 and 1.25 for K_Mn,

---

(7) R. Bates, THIS JOURNAL, **70**, 1579 (1948).

K_{Mg}, K_{Ca} and K_{Ba}, respectively. The value 4.0 was used for the constant B in the calculation of the metal chelate formation constants.

The standard thermodynamic quantities ΔF^0, ΔH^0 and ΔS^0 associated with each of the chemical reactions investigated were calculated by means of the relationships

$$\Delta F^0 = -2.303RT \log K \quad (7)$$

$$\Delta H^0 = \frac{2.303RT_1T_2 (\log K_2 - \log K_1)}{T_2 - T_1} \quad (8)$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta F^0}{T} \quad (9)$$

The equilibrium constants calculated by means of equations 3–6, and the thermodynamic changes associated with the dissociation and chelate formation reactions, calculated by means of equations 7–9, are given in Tables I and II.

TABLE I

THERMODYNAMIC CHANGES FOR DISSOCIATION OF NITRILOTRIACETIC ACID

t, °C.	pK_3	$+\Delta F^0$, kcal./mole	$+\Delta H^0$, kcal./mole	$-\Delta S^0$, e.u./mole
30	10.23_0	14.23	4.05	33.6
20	10.33_4	13.89	4.40	32.4
10	10.45_4	13.55	4.80	30.9
0	10.59_4	13.28	5.20	29.6
	pK_2			
40	2.97_8	4.27	−1.1	17.2
30	2.95_6	4.10	−0.8	16.1
20	2.94_0	3.95	−0	13.5
10	2.94_8	3.83	+0.3	12.5
0	2.95_3	3.70	+0.4	12.1
	pK_1			
40	1.68_6	2.42	−1.75	12.3
30	1.66	2.31	−0.75	9.5
20	1.65	2.22	−0.25	8.4
10	1.65	2.14	+0.25	7.3
0	1.68_7	2.11	+2.0	2.1

TABLE II

THERMODYNAMIC CHANGES ASSOCIATED WITH COMBINATION OF NITRILOTRIACETATE AND METAL IONS

t, °C.	log K_M	$-\Delta F^0$, kcal./mole	$-\Delta H^0$, kcal./mole	$+\Delta S$, e.u./mole
Reaction: $Mn^{+2} + A^{-3} \rightarrow MnA^-$				
30	8.64_4	11.98	−3.5	51.1
20	8.57_3	11.49	−2.0	46.0
10	8.53_4	11.05	−0.8	41.9
0	8.52_7	10.67	~0	39.1
Reaction: $Mg^{+2} + A^{-3} \rightarrow MgA^-$				
30	6.61_2	9.167	−4.8	46.0
20	6.50_0	8.714	−4.3	44.3
10	6.39_6	8.282	−3.4	41.2
0	6.31_0	7.88	−2.5	38.0
Reaction: $Ca^{+2} + A^{-3} \rightarrow CaA^-$				
30	7.59_5	10.52	~0	34.6
20	7.60_8	10.21	1.0	31.4
10	7.65_2	9.90	1.7	29.0
0	7.70_4	9.64	2.1	27.5
Reaction: $Ba^{+2} + A^{-3} \rightarrow BaA^-$				
30	5.58_7	8.12	0.50	25.1
20	5.87_5	7.88	1.20	22.8
10	5.91_4	7.66	1.70	21.0
0	5.96_8	7.45_5	2.25	19.1

Discussion

Acid Dissociation Constants.—All of the acid dissociation constants reported in Table III show a non-linear variation as a function of temperature, and the enthalpy change thus varies with temperature. For the first and second dissociations, there is a minimum in pK for the temperature range investigated. This property has been observed for most weak acids, and many examples of such behavior have been given by Harned and Owen.[8] A satisfactory interpretation of this phenomenon seems to be that offered by Gurney,[9] whereby the quantum-mechanical binding energy (exchange forces) is decreased with an increase of temperature as a result of an increase of potential energy of the binding electrons. On the other hand the electrostatic binding energy increases with temperature as a consequence of the decreasing dielectric constant of the medium. In the case of carboxyl groups the latter effect is strong enough to counterbalance the former. Since the dielectric constant change is a function of molar volume, and decreases more rapidly at higher temperature, a minimum in pK (*i.e.*, a maximum in K) is observed. Although there is no corresponding minimum in pK_3, which involves the binding of a proton to a basic nitrogen atom, it is probable that the same factors operate in this case as well.

The difference between the first and second acid dissociation constants is perhaps more than would ordinarily be expected in view of the similarity of the dissociating groups. On the basis of statistical considerations alone, a difference of 0.5 in pK would be predicted. This is, however, only a small part of the observed difference of 1.3 pK units. The statistical factor would show up in the entropy term. It is seen from the data of Table I that all of the difference in these dissociation constants is attributable to entropy factors, and the reason for the greater-than-predicted difference in dissociation constant therefore has to do with structural and charge characteristics of the amino acid species involved.

The third acid dissociation constant is much weaker than the corresponding constant of glycine[10] ($pK_2 = 9.78$ at $\mu = 0$ and 25°). The increased basicity of the nitrogen atom in nitrilotriacetic acid is apparently a consequence of the inductive effect of the three attached acetate anions. It is further noted that the thermodynamic constants reported in this paper are larger than the concentration constants K_1' and K_2' ($pK_1 = 1.9$, $pK_2 = 2.49$) and smaller than the concentration constant K_3 ($pK_3 = 9.73$) reported by Schwarzenbach, *et al.*,[11] for 0.10 M potassium chloride solution at 20°.

Stability Constants.—The thermodynamic chelate stability constants listed in Table II are in all cases considerably higher than the concentration constants determined by Schwarzenbach, *et al.*[11,12]

---

[8] H. Harned and B. Owen, "The Physical Chemistry of Electrolytic Solutions," Second Edition, Reinhold Publ. Corp., New York, N. Y., 1950.

[9] R. W. Gurney, "Ionic Processes," McGraw-Hill Book Co., New York, N. Y., 1954.

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

[11] G. Schwarzenbach, Ackermann and Ruckstuhl, *Helv. Chim. Acta*, **32**, 1175 (1949).

[12] G. Schwarzenbach and E. Freitag, *ibid.*, **34**, 1492 (1951).

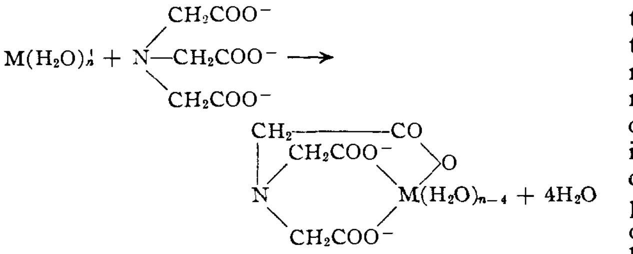
at 20° and 0.10 ionic strength. The relationship between the thermodynamic and concentration constants is

$$K_M = K_M' \frac{f_{MA^-}}{f_{M^{+2}}f_{A^{-3}}}$$

Since the activity coefficient factor should always be considerably greater than one, in view of the rather considerable charges of the ions in the denominator of the expression, the observed differences at ionic strengths 0 and 0.1 are in the direction predicted by the above equation.

Perhaps the most significant and interesting characteristic of the thermodynamic data in Table II is the generalization that all the enthalpy changes associated with metal chelate formation are very low, and that most of the driving force for the metal chelate formation reaction is an entropy effect. Thus it may be stated that the formation of nitrilotriacetate chelates of the more basic divalent metal ions is similar to the corresponding reactions of the ethylenediaminetetraacetate anion, and is in agreement with the entropy concept[3] of the stability of chelate rings.

The plots illustrated in Fig. 3 indicate that the entropy increases listed in Table II vary in an approximately linear manner with the value of e^2/r of the metal ion and the sum of the first and second ionization potentials of the metal. Since the partial molar entropies of the metal ions also depend on e^2/r, it seems that the factors which influence the entropy of the aquo metal ion influence in the same manner the entropy change which occurs in the formation of the nitrilotriacetate chelate. All of the reactions studied in this investigation may be formulated in the same manner



Since all the metal ions investigated have a coördination number of 4 or more, this tetradentate ligand probably displaces four of the coördinated water molecules from the hydration sphere of the metal ion. Consequently the main differences in the series of reactions investigated occur in the initial and final states of the species containing the metal. It is therefore possible to state that the variation of entropies of the metal chelates of the nitrilotriacetate anion is a linear function of the entropies of the aquo metal ions and of the value of e^2/r of these ions. Further, it can be stated that the slope of this function, $(S_{M_1A^-} - S_{M_2A^-})/(e^2/r_1 - e^2/r_2)$, is greater (*i.e.*, more positive) for the metal chelate compounds than for the aquo metal ions. Thus the chelating agent may be considered to have a leveling influence on the large negative entropy of the aquo metal ion and that the effect is greater on the ions with the most negative entropy (greatest value of e^2/r). This is a result of the fact that the donor atoms of the ligand are more polarizable than the aquated water molecules.

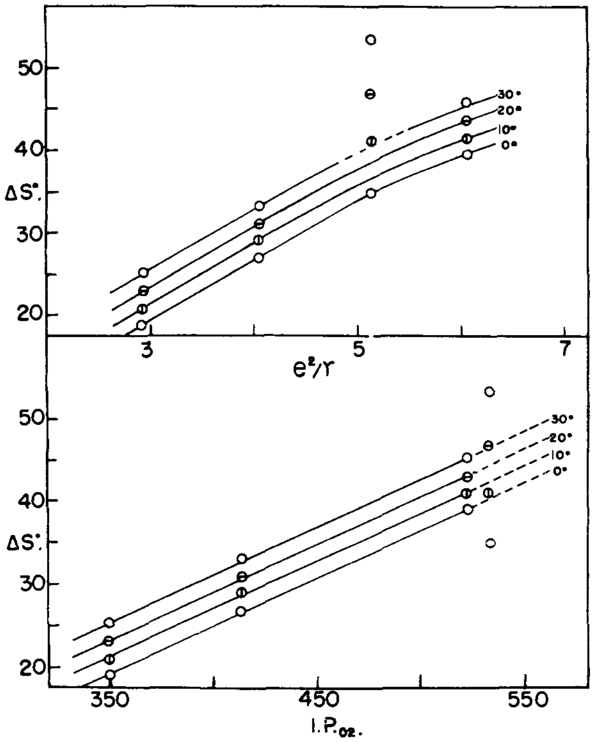


Fig. 3.—Correlation of ΔS° of metal chelate formation with ratio of electronic charge squared to ionic radius, e^2/r, and with the sum of the first and second ionization potentials I_{02}.

A very interesting comparison may be made between the entropy changes in the formation of nitrilotriacetate chelates and those of ethylenediaminetetraacetate anion. In the latter case the maximum entropy increase in the alkaline earth series occurs with the Ca(II) ion, while there is a regular increase in entropy values of the nitrilotriacetate chelates from Ba(II) to Mg(II). The difference in pattern is probably a consequence of the lower coördination requirement of Mg^{++}, which is believed to have a coördination number of about four, whereas the larger alkaline earth ions have coördination numbers of at least six. Therefore when Ba^{++} and Ca^{++} combine with the ethylenediaminetraacetate anion, approximately six water molecules are displaced from the coördination sphere of each metal ion, resulting in a considerable entropy increase which varies directly with e^2/r. In the case of Mg^{++}, however, the fact that only four aquo ions are displaced more than makes up for the still larger value of e^2/r with the result that the entropy increase is less. On the other hand the nitrilotriacetate anion is only tetradentate, so that the difference in coördination number of members of the alkaline earth series has little influence (all the reactions are exactly analogous), and a linear variation of entropy with e^2/r is found for the whole series.

The correlations illustrated in Fig. 3 indicate that the entropy values obtained for the formation of the Mn(II) chelate are somewhat anomalous. In addition to displacement of most of the Mn(II) values from the linear relationships which hold for the alkaline earths, the variation of ΔS^0 with temperature is also abnormally large. The reason for the unique behavior of Mn(II) in this case is not apparent.

WORCESTER, MASS.

[CONTRIBUTION FROM THE CHEMICAL INSTITUTE, NAGOYA UNIVERSITY]

Stability of Zinc and Cadmium Complexes with 2,2'-Bipyridine and 1,10-Phenanthroline

BY KAZUO YAMASAKI AND MOTOO YASUDA

RECEIVED AUGUST 18, 1955

The stability constants of zinc and cadmium complexes with 2,2'-bipyridine and 1,10-phenanthroline were determined by the *p*H titration method at 25°. The stepwise stability constants log k_1, log k_2 and log k_3 and the over-all constant log K for Cd- and Zn-bipyridine complexes were found to be 4.5, 3.5, 2.5, 10.5 and 5.4, 4.4, 3.5, 13.3, respectively. The values of log k_2 and log k_3 for Cd- and Zn-phenanthroline complexes were 5.2, 4.2 and 5.9, 4.8, respectively.

Stability constants of bivalent metal complexes of 2,2'-bipyridine[1] and 1,10-phenanthroline[2] have been reported by several authors. The ferrous complex,[3] in particular, has been studied because of its importance from the standpoint of analytical chemistry. During spectrochemical studies of several bipyridine and phenanthroline complexes[4] we have determined the stability constants of zinc and cadmium complexes with bipyridine and phenanthroline by the titration method of Bjerrum,[5] and compared them with data previously determined by other methods.

Experimental

Method and Apparatus.—By means of potentiometric *p*H determinations the acid dissociation constants of bipyridine and phenanthroline were determined in 0.1 M potassium nitrate solution at 25°. Fifty ml. of 0.001 M ligand solution was titrated with standard nitric acid solution. Similar measurements were then made on solutions in which the metal being investigated was maintained at a concentration of about 2-5 × 10^{-4} M and that of the ligand 5-10 × 10^{-4} M. In all cases a very large excess of KNO_3 over all other ionic species present was added to maintain the ionic strength at about 0.1. A glass electrode combined with a thermionic amplifier was used. The *p*H values in duplicate titrations agreed within 0.01 *p*H unit.

Materials.—2,2'-Bipyridine and 1,10-phenanthroline employed were reagents prepared by the Osaka Government Industrial Research Institute and G. F. Smith Co., U.S.A., respectively. Nitrates of both metals were analytical grade.

Results

The acid dissociation constants determined are: bipyridine, $-\log k = 4.44$; phenanthroline, 4.92. The $-\log k$ value reported by Krumholz[6] at 25° and ionic strength of 0.33 is 4.43 for bipyridine. The $-\log k$ value for phenanthroline determined by Lee, *et al.*,[3] under the same conditions as ours is 4.91.

The data for bipyridine and phenanthroline complexes are given in Table I. The first formation constant, k_1, of the phenanthroline complexes could not be determined for both metals; only k_2 and k_3 were determined. This difficulty occurs because the mixed solution of metal ion, ligand and nitric acid behaves as a strong acid.

TABLE I

Complex	log k_1	log k_2	log k_3	log K	Author
Cd-bipyridine	4.5	3.5	2.5	10.5	Present study
	..	...	...	10.47	Douglas, *et al.*[1]
Zn-bipyridine	5.4	4.4	3.5	13.3	Present study
Cd-phenanthroline	..	5.2	4.2	.....	Present study
	..	...	...	15.20	Douglas, *et al.*[1]
Zn-phenanthroline	..	5.9	4.8	.....	Present study
	6.43	~5.8	~4.8	~17.0	Kolthoff, *et al.*[2]

The values obtained here agree well with those of other authors determined by different methods.

Acknowledgments.—The expense of the present study was defrayed by Grant-in-aid for Fundamental Scientific Research from Ministry of Education.

CHIKUSA, NAGOYA, JAPAN

---

(1) B. E. Douglas, H. A. Laitinen and J. C. Bailar, Jr., THIS JOURNAL, **72**, 2484 (1950); E. I. Onstott and H. A. Laitinen, *ibid.*, **72**, 4724 (1950).

(2) I. M. Kolthoff, D. L. Leussing and T. S. Lee, *ibid.*, **73**, 390 (1950).

(3) E. P. Dwyer and H. A. McKenzie, *Proc. Roy. Soc. N. S. Wales*, **81**, 97 (1947); T. S. Lee, I. M. Kolthoff and D. L. Leussing, THIS JOURNAL, **70**, 2348 (1948); J. H. Baxendale and P. George, *Nature*, **162**, 777 (1948); **163**, 725 (1949); P. Krumholz, THIS JOURNAL, **71**, 3654 (1949); *Anal. acad. Brasil. cienc.*, **22**, 263 (1950); C. M. Cook, Jr., and F. A. Long, THIS JOURNAL, **73**, 4119 (1951).

(4) K. Yamasaki, *Bull. Chem. Soc. Japan*, **12**, 390 (1937); **14**, 538 (1938); **15**, 130, 461 (1940); K. Yamasaki and M. Yasuda, *Proc. Japan Academy*, **29**, 337 (1953).

(5) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

(6) P. Krumholz, *Nature*, **163**, 724 (1949).