tion and greater water structure-breaking), unless the cation is so small and highly charged as to cause appreciable interaction with the iodide ion (through a water molecule) and so lower significantly the activity coefficient of the iodide salt. Among the alkali metals this would be most important with LiI and least with CsI, and so, the activity coefficients of LiI and $LiClO_4$ should be most similar, that of NaI should be significantly greater than that of $NaClO_4$ and as one descends the alkali family to the cesium salts, where localized hydrolysis effects are negligible, the predicted order of activity coefficients should become more markedly that determined by hydration and water structure-breaking effects alone, namely, $F > Cl > Br > I > ClO_4$. Experimental data are available only for the acids and the lithium and sodium salts, but they do show the predicted behavior (Table I).

Since the dipositive alkaline earth ions as a group are more highly hydrated than the unipositive alkali metal cations, the rise in activity coefficients with increasing concentration should be more marked, and, experimentally, this is so with a larger spread in the values of the activity coefficients of a particular halide from Mg to Ba than from Na to Cs. But the localized hydrolysis effect should also be enhanced due to the greater fields of the alkaline earth cations, and so the activity coefficient order $I>Br>Cl$ should also be more marked; and it is, see Table I. As with the alkalies, this effect should decrease as one descends the family to the larger and less polarizing cations, but with the highly polarizing dipositive ions, no reversal to the order expected of independent halide ions in solution occurs, even at barium, although there is a trend in that direction. This trend toward the order $F>Cl>Br>I>ClO_4$ is more obvious if one compares the iodide and perchlorate salts. With magnesium, the localized hydrolysis effect is so important, even with the iodide, that the activity coefficients of MgI_2 are below those of $Mg(ClO_4)_2$. With calcium the decrease in the activity coefficients of the iodide salt due to this effect is smaller and $\gamma_\pm$ for CaI_2 and $Ca(ClO_4)_2$ are similar. With strontium and barium iodides the effect becomes unimportant, and the order $I > ClO_4$ becomes increasingly marked.

The effect of localized hydrolysis should be still more important with small tripositive cations, and so, if no actual complex ion formation occurs, the order $I>Br>Cl$ should be expected there, too, with the activity coefficients of the perchlorates becoming perhaps larger than those of the iodides, at least for small cations. There are few experimental data with which to compare, but in the case of the rare earth chlorides and bromides whose activity coefficients have been measured up to about $0.03m$,[21] the order $Br>Cl$ is apparent.

In summary it is seen that the idea of an interaction between oppositely charged ions through the intermediary of a water molecule is a reasonable one even for the anions of acids normally considered strong, and this leads to a decrease in the mean activity coefficient of the ions. This effect, which depends upon the polarizing power of the cation on the water molecule (proton repulsion) and upon the proton accepting ability of the anion, can explain, then, the anomalous anion order of the activity coefficients of the alkaline earth and of most of the alkali metal halides, and the reversal of this order with the rubidium and cesium halides. The activity coefficients of the perchlorate salts (and presumably of other large, relatively unhydrated and non-associating ions) are in agreement with what would be expected from the effects discussed in this paper of water structure-breaking (a decrease in $\gamma_\pm$ with an increase in the size of the ion), and those ions where the charge is localized at one part of a hydrophobic structure, as with the normal carboxylate anions, will show the opposite behavior because of their water structure-tightening effect.

(21) F. H. Spedding, P. E. Porter and J. M. Wright, THIS JOURNAL, **74**, 2781 (1952); F. H. Spedding and I. S. Yaffe, *ibid.*, **74**, 4751 (1952).

ITHACA, N. Y.

[CONTRIBUTION FROM THE NICHOLS LABORATORY, NEW YORK UNIVERSITY]

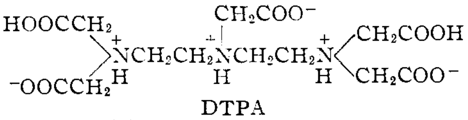
The Acid Dissociation Constants of Diethylenetriaminepentaacetic Acid and the Stability Constants of Some of its Metal Chelates[1]

BY EDWARD J. DURHAM AND DANIEL P. RYSKIEWICH[2]

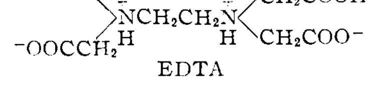
RECEIVED MARCH 26, 1958

The acid dissociation constants of diethylenetriaminepentaacetic acid, H_5Y, and the stability constants of its chelates with Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2}, Mn^{+2}, Fe^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2} and Cd^{+2} were determined at 20° and an ionic strength of 0.10. The existence of a stable monohydrogen chelate species, MHY^{-2}, and the usual chelate, MY^{-3}, is illustrated. No bimetallic chelate is formed. The *p*H dependence of chelate formation is quantitatively described by means of *p*M, % MHY^{-2} and % MY^{-3} *versus* *p*H plots.

The chelating properties of diethylenetriaminepentaacetic acid, DTPA, are of interest in view of its structural relationship to the well known chelating agent ethylenediaminetetraacetic acid, EDTA.



DTPA



EDTA

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(1) Abstracted from a dissertation submitted by Daniel P. Ryskiewich to the Faculty of New York University in partial fulfillment of requirements for the degree of Doctor of Philosophy.

(2) Geigy Chemical Corp., Ardsley, N. Y.

Only the acid dissociation constants[3–5] and some alkaline earth chelate stability constants[5,6] of DTPA have been reported previously. The possible ability of this chelating agent to form bimetallic chelates has been suggested.[4] Due to the increased polydentate character of DTPA a stable monohydrogen chelate is formed but its importance has not been recognized.

It was of interest, therefore, to conduct a more extensive investigation of the chelating properties of DTPA with the alkaline earths and some heavy metal ions.

Experimental

Materials.—Solid DTPA[7] was recrystallized several times from hot water and dried at 110°. A 0.001 *M* solution was standardized by direct titration with carbonate-free potassium hydroxide and by a second titration in the presence of a bivalent metal ion.

A 0.005 *M* solution of triaminotriethylamine trihydrochloride,[7] used in the determination of the heavy metal chelate stability constants, was standardized by titration in the presence of a slight excess of cadmium ions.

Approximately 0.033 *M* metal ion solutions were prepared from the corresponding J. T. Baker Analyzed Reagent chlorides. They were analyzed for metal content by the Schwarzenbach procedure[8] and for chloride content by the Volhard method.

A 0.1 *M* carbonate-free potassium hydroxide solution was prepared by the interaction of silver oxide and potassium chloride.[9]

Three buffers having *p*H values of 1.10, 4.00 and 9.22 at 20° were prepared according to recommendations of the National Bureau of Standards.[10] A fourth buffer having a *p*H value of 7.02 was prepared from a Beckman "*p*H 7 Buffer" stock solution according to their directions.

Freshly boiled distilled water was used in the preparation of all solutions.

Apparatus and Procedure.—A Beckman Model G *p*H meter, in conjunction with commercial glass and calomel extension electrodes, was used to measure *p*H values. The vessels were 250-ml. tall form Pyrex beakers equipped with tight fitting #11.5 rubber stoppers with holes to accommodate the electrodes, gas inlet and outlet tubes and a buret.

The procedure of Schwarzenbach and Ackermann[11] was followed to determine the successive acid dissociation constants of DTPA and the stability constants of its alkaline earth chelates. This procedure involves titrating the amino acid alone and in 1:1 and 15:1 molar ratios of metal ion to amino acid.

To determine the heavy metal chelate constants the exchange method developed by Schwarzenbach and Freitag,[12] involving the introduction of another chelating agent triaminotriethylamine trihydrochloride, H_3X^{+3}, and a second metal ion, was employed. Different amounts of carbonate-free potassium hydroxide solution were added to six solutions containing equimolar amounts of DTPA, H_3X^{+3}, the metal ion whose constants were to be determined and a 1:1 or 10:1 molar ratio of a second metal ion whose constants were known. Periodic *p*H measurements of the solutions were made until constant readings were obtained. Equilibrium was reached within approximately 4 hr. in all the systems with the exception of the Ni^{+2}–Ca^{+2} system which reached equilibrium in about four days.

Measurements were made at 20.0 ± 0.02°. The ionic strength was maintained at 0.10 by the addition of an appropriate amount of 1 *N* potassium chloride solution. The concentration of DTPA was approximately 6×10^{-4} *M*.

All experiments were performed under a nitrogen atmosphere with the exception of those systems containing Mn^{+2}, Fe^{+2} or Co^{+2}. In these systems a few drops of colloidal palladium were added and hydrogen was used as the inert atmosphere to maintain adequate reducing conditions.

Before each titration or exchange study the electrode system was standardized with the four buffers at bath temperature and rechecked after the completion of the experiment.

Calculations and Results.—The acid dissociation constants of DTPA, k_1, k_2, k_3, k_4 and k_5 were calculated by the method of Schwarzenbach.[11,13]

In the range $a = 0$ to $a = 3$, where "*a*" denotes moles of base added per mole of amino acid, no appreciable acidification effect occurs in the presence of an alkaline earth metal ion (Fig. 1), which indicates that chelation involves the trivalent anion, H_2Y^{-3}, of DTPA. In the titrations containing excess alkaline earth metal ion[14] the possible chelate species are, therefore, MHY^{-2}, MY^{-3} and M_2Y^{-1}, their respective stability constants being

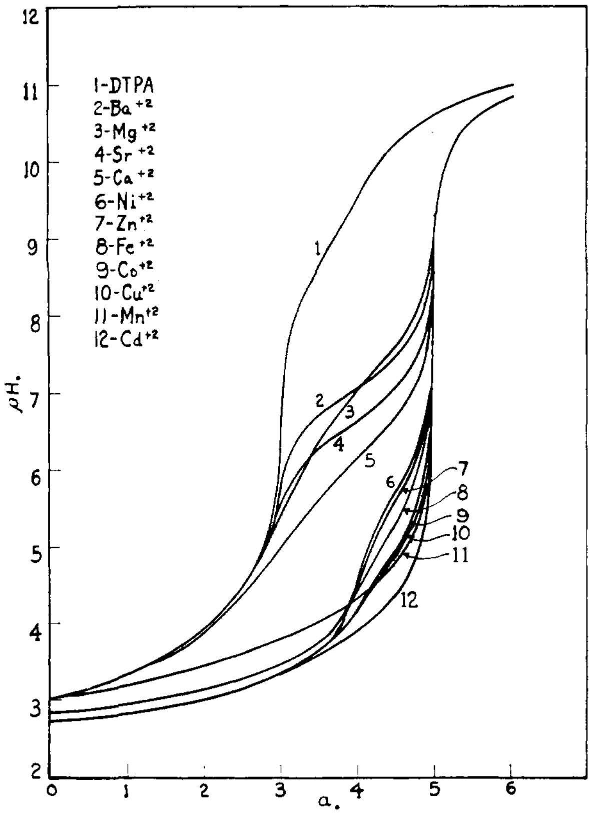

Fig. 1.—Equimolar DTPA-metal ion titration curves. Values of *p*H *vs.* "*a*," moles of KOH added per mole of DTPA.

$$K_{MHY} = (MHY^{-2})/(M^{+2})(HY^{-4})$$

$$K_{MY} = (MY^{-3})/(M^{+2})(Y^{-5})$$

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[3] H. Kroll, G. Pinching and F. Butler, Abst. 122nd Amer. Chem. Soc. Meeting, Atlantic City, N. J., Sept. 14–19, 6p (1952).

[4] A. E. Frost, *Nature*, **178**, 322 (1956).

[5] E. Wanninen, *Suomen Kemistilehti*, **B28**, 146 (1955).

[6] E. Wanninen, *ibid.*, **B29**, 184 (1956).

[7] Obtained from the Geigy Chemical Corp.

[8] G. Schwarzenbach, "Die Komplexometrische Titration," Ferdinand Enke, Stuttgart, Germany, 1955, p. 21.

[9] G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, **31**, 339 (1948).

[10] R. G. Bates, "Electrometric *p*H Determinations," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 87, 118.

[11] G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **31**, 1029 (1948).

[12] G. Schwarzenbach and E. Freitag, *ibid.*, **34**, 1503 (1951).

[13] G. Schwarzenbach, H. Willi and R. Bach, *ibid.*, **30**, 1303 (1947).

[14] The titration curves of systems having 15:1 ratios of alkaline earth metal ion to DTPA are identical in shape to those of Fig. 1, the *p*H simply being displaced to lower values at corresponding "*a*" values.

and

$$K_{M_2Y} = (M_2Y^-)/(M^{+2})(MY^{-3})$$

where parentheses indicate molar concentrations. Following the procedure of Schwarzenbach, K_{MHY} and another constant

$$K' = K^H_{MY} + (M^{+2})K^H_{M_2Y} \quad (1)$$

are calculated, where K^H_{MY} and $K^H_{M_2Y}$ are the equilibrium constants of the reactions

$$MHY^{-2} \rightleftarrows MY^{-3} + H^+ \quad (2)$$

and

$$MHY^{-2} + M^{+2} \rightleftarrows M_2Y^- + H^+ \quad (3)$$

It is seen readily from (1) that K' equals the acidity constant K^H_{MY} of the monohydrogen chelate when no bimetallic chelate is formed, *i.e.*, when $K^H_{M_2Y}$ is small. In titrations of equimolar mixtures of DTPA and alkaline earth metal ion the equilibrium (3) can be disregarded and the acidity constant K^H_{MY} then can be calculated as shown by Schwarzenbach. The pK' values in Table I, calculated from the 15:1 metal ion to amino acid titration data, can be compared to the pK^H_{MY} values calculated from the equimolar titration data. These values are identical within experimental error, *i.e.*, $K' = K^H_{MY}$ and none or a negligible amount of M_2Y^- forms in the presence of excess alkaline earth metal ion. The chelate stability constant, K_{MY}, then can be calculated from

$$K_{MY} = K'K_{MHY}/k_5 \quad (4)$$

TABLE I

ACID DISSOCIATION CONSTANTS AND ALKALINE EARTH CHELATE STABILITY CONSTANTS

Cation	pk_1	pk_2	pk_3	pk_4	pk_5
H^+	2.08	2.41	4.26	8.60	10.55
M^{+2}	log K_{MHY}	pK'	pK^H_{MY}	log K_{MY}	
Mg^{+2}	5.59	7.11	7.09	9.03	
Ca^{+2}	6.17	6.09	5.99	10.63	
Sr^{+2}	4.78	5.65	5.69	9.68	
Ba^{+2}	3.77	5.69	5.55	8.63	

The basis of the method for the determination of the stability constants of the other bivalent metal ions involves the introduction of another chelating agent, H_3X^{+3}, and a second metal ion, M_s^{+2}, which is strongly bound by DTPA but not by the polyamine salt. The alkaline earth ions, which form no chelates with triaminotriethylamine trihydrochloride, and Mn^{+2} which forms only a weak chelate, are especially suited for use as the second metal ion.

In a system containing equimolar amounts of DTPA, H_3X^{+3}, M^{+2} and 1:1 or 10:1 molar ratios of second metal ion to DTPA, the equilibrium of interest at "*a*" values between 6 and 7 is

$$H_3X^{+3} + MY^{-3} + M_s^{+2} \rightleftarrows MX^{+2} + M_sY^{-3} + 3H^+ \quad (5)$$

with an equilibrium constant

$$K_e = (M_sY^{-3})(MX^{+2})(H^+)^3/(MY^{-3})(H_3X^{+3})(M_s^{+2}) = K_{MX}K_{M_sY}K_{H_3X}/K_{MY} \quad (6)$$

where K_{H_3X} is the product, $K_1K_2K_3$, of the acid dissociation constants of H_3X^{+3} and K_{MX} is the stability constant of the heavy metal–amine chelate.

The following material balance equations were used for the calculation of K_e from the experimental "*a*" and *p*H values.

$$c = (DTPA)_t = (MY^{-3}) + (M_sY^{-3}) + (M_sHY^{-2}) \quad (7a)$$

$$c = (H_3X^{+3})_t = (MX^{+2}) + \alpha(H_3X^{+3}) \quad (7b)$$

$$c = (M^{+2})_t = (MX^{+2}) + (MY^{-3}) \quad (7c)$$

$$c \text{ or } 10c = (M_s^{+2})_t = (M_sY^{-3}) + (M_sHY^{-2}) + (M_s^{+2}) \quad (7d)$$

$$g = (8 - a)c - (H^+) + (OH^-) = \beta(H_3X^{+3}) + (M_sHY^{-2}) \quad (7e)$$

The subscript "*t*" is used to represent total molar concentrations and "*g*" represents the total amount of titratable acid hydrogen. Also

$$\alpha = 1 + K_1/(H^+) + K_1K_2/(H^+)^2 + K_1K_2K_3/(H^+)^3$$
$$\beta = 3 + 2K_1/(H^+) + K_1K_2/(H^+)^2$$

From (7a-7e) and $K^H_{M_sY}$

$$(M_sHY^{-2}) = \frac{c - \alpha(H_3X^{+3})}{\gamma} \quad (8)$$

where

$$\gamma = 1 + \frac{K^H_{M_sY}}{(H^+)}$$

Substituting (8) into (7e) and rearranging yields

$$(H_3X^{+3}) = \frac{g - c/\gamma}{\beta - \alpha/\gamma} \quad (9)$$

This concentration term is solved for the different experimental "*a*" and *p*H values, then introduced into (7a-7e), (8) and (9) to determine the other concentration terms. These quantities then are introduced into (6) for the calculation of K_e and finally K_{MY}. The results are given in Table II.

TABLE II

HEAVY METAL CHELATE STABILITY CONSTANTS

M^{+2}	M_s^{+2} [a]	pK_e	log K_{MY}
Cu	Ca	20.04	21.03
Cu	Mg	21.63	21.02
Cd	Ca	24.44	18.93
Cd	Mn	19.94	15.13[b]
Cu	Mn	15.60	21.09 (21.05)
Co	Ca	23.87	18.87
Co	Mn	19.55	19.04
Fe	Ca	25.54	16.55
Fe	Mn	21.17	16.66
Zn	Ca	21.32	18.17
Zn	Mn	17.01	18.35 (18.28)
Ni	Ca	23.22	20.21

[a] The ratio M_s^{+2}/M^{+2} was 1 in systems containing Mn^{+2} and 10 in all the other systems. [b] This is the value of K_{MnY} calculated using the value log K_{CdY} = 18.93.

The preceding heavy metal chelate stability constants have been calculated by assuming that the amount of heavy metal hydrogen chelate, MHY^{-2}, present was negligible since the stability constants K_{MHY} and K^H_{MY} were not known. Also, for the same reason, the manganese hydrogen chelate had to be neglected when manganese was used as the second metal ion. However, using the preliminary K_{MY} values of Table II it was possible to calculate these constants from data for the equimolar DTPA–metal ion titrations.

Between $a = 4$ and $a = 5$

$$c = (DTPA)_t = (MHY^{-2}) + (MY^{-3}) + x(Y^{-5}) \quad (10a)$$

$$c = (\mathrm{M}^{+2})_t = (\mathrm{MHY}^{-2}) + (\mathrm{MY}^{-3}) + (\mathrm{M}^{+2}) = (\mathrm{MHY}^{-2}) + (\mathrm{MY}^{-3})\left[1 + \frac{1}{K_{\mathrm{MY}}(\mathrm{Y}^{-5})}\right] \quad (10\mathrm{b})$$

$$g = (5 - a)c - (\mathrm{H}^+) = (\mathrm{MHY}^{-2}) + y(\mathrm{Y}^{-5}) \quad (10\mathrm{c})$$

where

$$x = (\mathrm{H}^+)^5/k_1k_2k_3k_4k_5 + (\mathrm{H}^+)^4/k_2k_3k_4k_5 + (\mathrm{H}^+)^3/k_3k_4k_5 + (\mathrm{H}^+)^2/k_4k_5 + (\mathrm{H}^+)/k_5 + 1$$

and

$$y = 5(\mathrm{H}^+)^5/k_1k_2k_3k_4k_5 + 4(\mathrm{H}^+)^4/k_2k_3k_4k_5 + 3(\mathrm{H}^+)^3/k_3k_4k_5 + 2(\mathrm{H}^+)^2/k_4k_5 + (\mathrm{H}^+)/k_5$$

From (10_a), (10b) and K_{MY}

$$(\mathrm{MY}^{-3}) = xK_{\mathrm{MY}}(\mathrm{Y}^{-5})^2 = \frac{c - (\mathrm{MHY}^{-2})}{1 + \frac{1}{K_{\mathrm{MY}}(\mathrm{Y}^{-5})}} \quad (11)$$

From (10c)

$$(\mathrm{MHY}^{-2}) = g - y(\mathrm{Y}^{-5}) \quad (12)$$

Substituting (12) into (11) and rearranging yields

$$xK_{\mathrm{MY}}(\mathrm{Y}^{-5})^2 + (x - y)(\mathrm{Y}^{-5}) + (g - c) = 0 \quad (13)$$

which can be solved for (Y^{-5}), permitting the calculation of all other concentration terms and leading lutimately to the determination of K_{MHY} and then $K^{\mathrm{H}}_{\mathrm{MY}}$ through

$$K^{\mathrm{H}}_{\mathrm{MY}} = K_{\mathrm{MY}}k_5/K_{\mathrm{MHY}} \quad (14)$$

The results are presented in Table III.

TABLE III

HEAVY METAL HYDROGEN CHELATE CONSTANTS

M^{+2}	$\log K_{\mathrm{MHY}}$	$pK^{\mathrm{H}}_{\mathrm{MY}}$
Cu	15.27	4.79
Cd	12.48	4.09
Mn	9.00	4.42
Co	13.30	4.81
Fe	11.28	5.17
Zn	13.08	5.46
Ni	15.25	5.59

Once these values of K_{MHY} were known new values for K_{MY} could be calculated from the previous data, now taking (MHY^{-2}) and/or (MnHY^{-2}) into account. It was found that the results were identical with those of Table II with the exception of the Cu^{+2}–Mn^{+2} and Zn^{+2}–Mn^{+2} systems, *i.e.*, (MHY^{-2}) and (MnHY^{-2}) were negligible in all the other systems. The recalculated constants for these systems are given in Table II in parentheses. These corrected values for K_{MY} are seen to agree more closely with those of the corresponding systems containing Ca^{+2} as the second metal ion.

Discussion

Previously reported DTPA constants are listed in Table IV.

The corresponding constants in Table I agree very well with those of Frost[4] and Wanninen[5,6] with the exception of $\log K_{\mathrm{CaY}}$. This discrepancy is due to the fact that the monohydrogen chelate was not considered by Wanninen in that particular determination. The acid dissociation modes of DTPA have been described previously.[4,5]

The unusual shapes and relative positions of the metal–DTPA titration curves are of importance in a discussion of the metal chelate constants. It is a well known fact that, the greater the tendency for a metal ion to combine with an amino acid, the greater the drop in pH. This generally observed property is used qualitatively to determine the relative tendencies of metal ions to combine with a given reagent. If the titration curves of Fig. 1 are considered, it would seem, for example, that the order of stability of the heavy metal chelates of DTPA was $\mathrm{Ni}^{+2} < \mathrm{Zn}^{+2} < \mathrm{Fe}^{+2} < \mathrm{Co}^{+2} < \mathrm{Cu}^{+2} < \mathrm{Mn}^{+2} < \mathrm{Cd}^{+2}$ which is, of course, not the case. This unusual behavior of DTPA readily can be explained when one realizes that two chelates are being formed, one a monohydrogen species which is a relatively weak acid in most cases.

TABLE IV

PREVIOUSLY REPORTED DTPA CONSTANTS

Cation	pk_1	pk_2	pk_3	pk_4	pk_5	Ref.
H^+	1.90	2.70	4.42	10.62	12.59	3
	1.79	2.56	4.42	8.76	10.42	4
	1.86	2.79	4.29	8.61	10.48	5
M^{+2}		$\log K_{\mathrm{MHY}}$		$\log K_{\mathrm{MY}}$		
Mg^{+2}		5.71		9.34		6
Ca^{+2}				9.98		5
Sr^{+2}				9.48		5
Ba^{+2}		3.64		8.78		6

In general, on a qualitative basis, the relative positions of all the curves up to about $a = 4$ will depend primarily on the stability of the hydrogen chelate, MHY^{-2}, —the more stable this chelate, the lower will be the pH because of greater interaction with the ligand. The slope of the portion of the curve between $a = 4$ and $a = 5$ will depend on the difference $\log K_{\mathrm{MY}} - \log K_{\mathrm{MHY}}$, *i.e.*, on the ratio $K_{\mathrm{MY}}/K_{\mathrm{MHY}}$ which is directly related to the acid dissociation constant of the hydrogen chelate $K^{\mathrm{H}}_{\mathrm{MY}}$ through (14).

When K_{MHY} and K_{MY} are both low, as is the case with the alkaline earth ions, the titration curves are identical to that of DTPA alone up to about $a = 3$, indicating that chelation begins with the species $\mathrm{H_2Y^{-3}}$. With Sr^{+2} and Ba^{+2} only a very small amount of MHY^{-2} will form since K_{MHY} is low and $K_{\mathrm{MY}} >> K_{\mathrm{MHY}}$. The shapes of their curves therefore will depend almost exclusively on the formation of the MY^{-3} chelate with the simultaneous liberation of two protons, resulting in a relatively flat buffer region between $a = 3$ and $a = 5$. Since Sr^{+2} forms the stronger chelates its titration curve is below the Ba^{+2} curve. The Mg^{+2} and Ca^{+2} titration curves are below the Sr^{+2} and Ba^{+2} curves at low "a" values because of the greater stability of the hydrogen chelate. However, as the titration progresses and more MY^{-3} is being formed the curves rise sharply because of the low acidity of MHY^{-2} as indicated by higher $pK^{\mathrm{H}}_{\mathrm{MY}}$ values, the Mg^{+2} system so much so that it intersects the Sr^{+2} and Ba^{+2} curves.

When both K_{MHY} and K_{MY} are high, as in the case of the heavy metal systems, chelation occurs to such an extent that the pH is much lower than that of DTPA alone, even at "a" values below 3. The relative position of each curve is seen to follow the order of decrease in $pK^{\mathrm{H}}_{\mathrm{MY}}$ in the range $a = 4$ to $a = 5$ where the conversion of MHY^{-2} to MY^{-3} is taking place.

The quantitative relationship of the concentrations of the two chelates present in a solution at various pH values serves to illustrate the points discussed above. Figures 2, 3 and 4 are plots of the percentages of MHY^{-2} and MY^{-3} simultaneously present at various *p*H values in equimolar metal ion–DTPA systems at a concentration of 1×10^{-3} *M*. These values are determined readily from the experimentally determined values of the various constants.

The instabilities of the hydrogen chelates of Sr^{+2} and Ba^{+2} are readily apparent since their maximum concentrations are only 9 and 3% of the total metal ion concentration, respectively. A much greater percentage of the metal ion is seen to be present as the hydrogen chelate at low *p*H values in the Ca^{+2} and Mg^{+2} systems as was qualitatively deduced previously. The predominance of the hydrogen chelate at low *p*H values and its subsequent conversion to the MY^{-3} chelate with increase in *p*H in the heavy metal ion systems is self-evident.

Another way of describing the *p*H dependence of chelate formation is to plot *pM versus p*H curves where $pM = -\log (M^{+2})$. The *p*M *versus p*H data of metal ion–DTPA systems having a total metal ion concentration of 10^{-2} *M* in the presence of a 100% molar excess of DTPA were calculated. The results are presented in Table V.

Results for some of the cations are presented in the form of *p*M *vs. p*H curves in Fig. 5 with com-

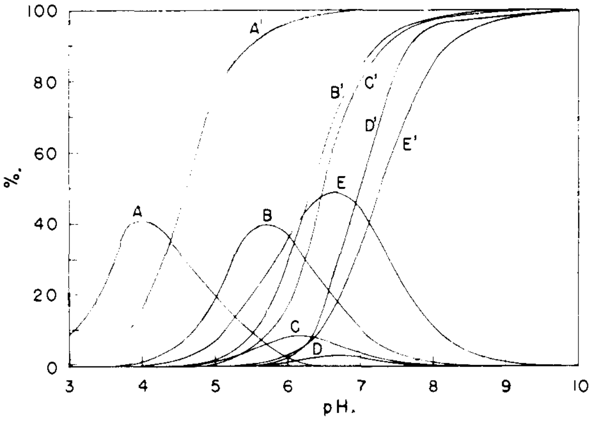

Fig. 2.—Per cent. MHY^{-2} and MY^{-3} as a function of *p*H: A = $MnHY^{-2}$; A' = MnY^{-3}; B = $CaHY^{-2}$; B' = CaY^{-3}; C = $SrHY^{-2}$; C' = SrY^{-3}; D = $BaHY^{-2}$; D' = BaY^{-3}; E = $MgHY^{-2}$; E' = MgY^{-3}; $(DTPA)_t = (M^{+2})_t = 1 \times 10^{-3}$.

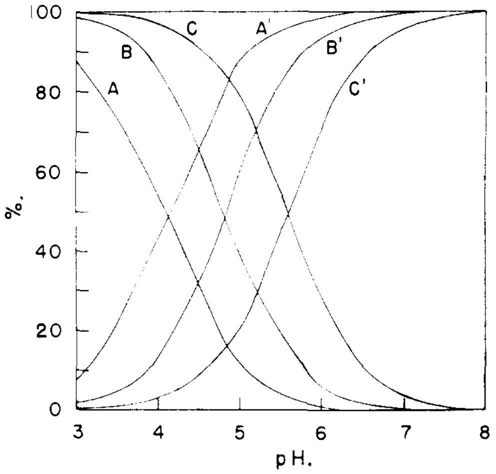

Fig. 3.—Per cent. MHY^{-2} and MY^{-3} as a function of *p*H: A = $CdHY^{-2}$; A' = CdY^{-3}; B = $CuHY^{-2}$; B' = CuY^{-3}; C = $NiHY^{-2}$; C' = NiY^{-3}; $(DTPA)_t = (M^{+2})_t = 1 \times 10^{-3}$.

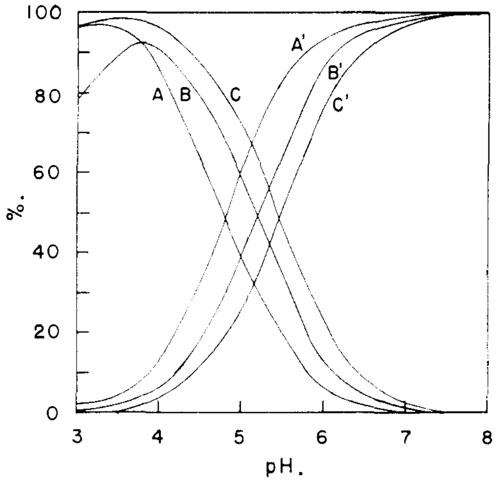

Fig. 4.—Per cent. MHY^{-2} and MY^{-3} as a function of *p*H: A = $CoHY^{-2}$; A' = CoY^{-3}; B = $FeHY^{-2}$; B' = FeY^{-3}; C = $ZnHY^{-2}$; C' = ZnY^{-3}; $(DTPA)_t = (M^{+2})_t = 1 \times 10^{-3}$.

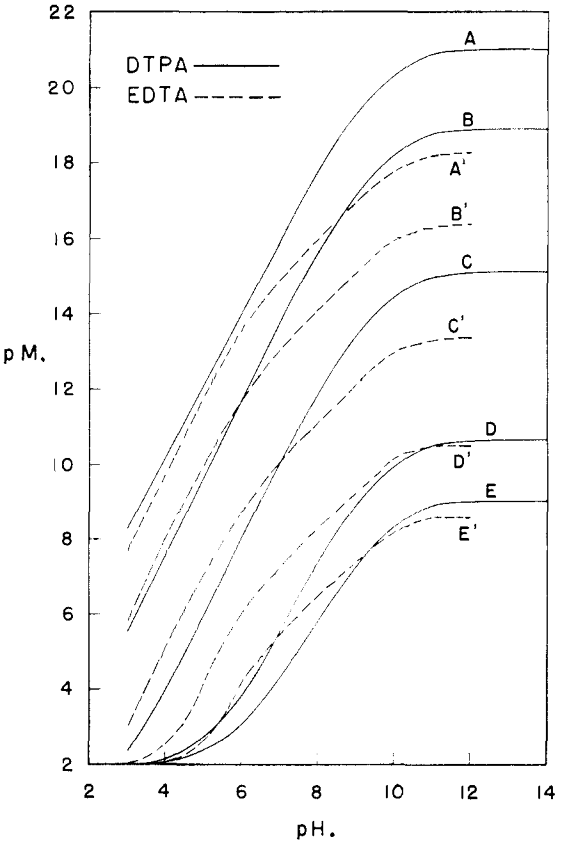

Fig. 5.—*p*M as a function of *p*H: A and A' = Cu^{+2}; B and B' = Cd^{+2}; C and C' = Mn^{+2}; D and D' = Ca^{+2}; E and E' = Mg^{+2}; $(\text{Chelating agent})_t = 2 \times 10^{-2}$, $(M^{+2})_t = 1 \times 10^{-2}$.

TABLE V

pM *versus* pH DATA

$(M^{+2}) = 1 \times 10^{-2}\,M \quad (DTPA) = 2 \times 10^{-2}\,M$

pH	Ca^{+2}	Mg^{+2}	Sr^{+2}	Ba^{+2}	Cu^{+2}	Ni^{+2}	Co^{+2}	Zn^{+2}	Cd^{+2}	Fe^{+2}	Mn^{+}
3.0	2.00	2.00	2.00	2.00	8.29	8.26	6.32	6.09	5.52	4.30	2.40
4.0	2.09	2.03	2.00	2.00	10.28	10.20	8.31	8.04	7.68	6.25	4.09
5.0	2.71	2.33	2.11	2.01	12.01	11.68	10.04	9.53	9.76	7.84	5.86
6.0	3.83	3.09	2.82	2.23	13.90	13.19	11.91	11.12	11.78	9.57	7.99
7.0	5.52	4.23	4.54	3.31	15.87	15.07	13.89	13.02	13.77	11.51	9.97
8.0	7.39	5.83	6.43	5.38	17.78	16.97	15.80	14.92	15.69	13.42	11.89
9.0	8.93	7.33	7.98	6.92	19.33	18.51	17.34	16.46	17.23	14.96	13.43
10.0	9.96	8.36	9.01	7.96	20.36	19.54	18.37	17.50	18.26	15.99	14.46
11.0	10.50	8.90	9.55	8.50	20.90	20.08	18.91	18.03	18.80	16.53	15.00
12.0	10.62	9.01	9.66	8.62	21.01	20.20	19.03	18.15	18.92	16.65	15.12
13.0	10.63	9.03	9.68	8.63	21.03	20.21	19.04	18.16	18.93	16.66	15.13
14.0	10.63	9.03	9.68	8.63	21.03	20.21	19.04	18.17	18.93	16.66	15.13

parable data for EDTA.[15] It is immediately evident that DTPA is a more effective chelating than EDTA at high pH values due to the greater stability of the MY^{-3} chelate. However, at lower pH values, due to the influence of the less stable hydrogen chelate, DTPA is in some cases less effective, *e.g.*, in the Ca^{+2} and Mg^{+2} systems.

Chelates of the type M_2Y^- are not formed to any extent since it has been shown that pK^{H}_{MY} is independent of the concentration of metal ion.

If ligand–metal binding in the hydrogen chelates involved only one terminal iminodiacetic acid group the stability would be of the same order of magnitude as the chelates of iminodiacetic acid or methyliminodiacetic acid. However, the chelates are very much more stable indicating a greater degree of ring formation. Several possibilities also exist for the binding in the MY^{-3} chelates; however, no definite choice can be made as to the actual structures from these data alone.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OSAKA UNIVERSITY AND THE OSAKA MUNICIPAL TECHNICAL RESEARCH INSTITUTE]

Infrared Spectra of Metallic Complexes. V. The Infrared Spectra of Nitro and Nitrito Complexes[1]

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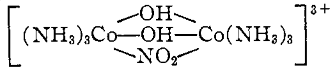
The infrared spectra of nitro and nitrito complexes have been measured in the 5000 ∼ 400 cm.$^{-1}$ region. The normal coördinate treatment of the $[Pt(NO_2)_4]^{2-}$ ion has been carried out to give complete assignments. The following conclusions have been obtained: (1) in a series of nitro complexes of various central metals, the metal–nitrogen bond becomes stronger progressively in the order of $[Ni(NO_2)_6]^{4-} < [Co(NO_2)_6]^{3-} < [Pt(NO_2)_4]^{2-}$; (2) the spectra of nitroammine complexes can be correlated with the structure more easily in the KBr region than in the NaCl region; (3) the structure of the nitro bridge in  $\left[(NH_3)_3Co\begin{matrix}-OH-\\-OH-\\-NO_2-\end{matrix}Co(NH_3)_3\right]^{3+}$ ion can be determined by the infrared study; (4) $[Cr(NH_3)_5NO_2]^{2+}$ is spectroscopically shown to be a nitrito and not a nitro complex.

Introduction

Recently Beattie and Tyrrell[3] studied the infrared spectra of a series of nitroammine complexes, $[Co(NH_3)_{6-n}(NO_2)_n]^{(3-n)+}$ in the 5000∼650 cm.$^{-1}$ region, and attempted to correlate the stereoisomerism and the number of nitro groups with the infrared spectra. It was found, however, that the spectra were too complicated to allow band assignment because the absorptions due to nitro and ammine groups overlap each other. Faust and Quagliano[4] also compared the infrared spectra of *trans*- and *cis*-$[Co(NH_3)_4(NO_2)_2]Cl$. However, no substantial difference was observed between these two isomers, although the latter exhibits a more complicated spectrum than the former in the 7∼8μ region.

It is expected that a study of the infrared spectra of these nitroammine complexes below 650 cm.$^{-1}$ will afford more information, since the Co–NH_3 and Co–NO_2 stretching modes as well as the wagging, rocking and twisting modes of the nitro group appear in this region, and the overlapping of the nitro and ammine bands may possibly be avoided.

The infrared spectra of ammine complexes have already been studied extensively by Powell and Sheppard,[5] and Mizushima, *et al.*[6] In order to

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