of M^+ are about 0.5 e.v. with an unusual situation of 1.5 volt deviation in the Cr^+ ion. Consequently the errors in the determination of the absolute value of appearance potentials are magnified by the difficulty in calibration. An alternative to the use of rare gas calibration is the assumption that, in $C_{10}H_{10}Ni$, for example, the sum of the ionization potential of Ni and the thermochemically determined bond dissociation energy is equal to the appearance potential of Ni^+. This gives a value 0.7 e.v. lower than obtained using a Kr calibration. This still gives poor internal consistency in the iron case with an estimated bond energy higher than obtained from the thermochemical data.

Results obtained for metal–ring bond energies by subtracting ionization potentials of the free metal atom from the appearance potential of the corresponding ion from $C_{10}H_{10}M$ indicates weaker bonding in $C_{10}H_{10}Mg$, $C_{10}H_{10}Mn$ and $C_{10}H_{10}Ni$. The values for the compounds of Fe, Co, Cr and V are higher but in view of the uncertainties these can be considered only as showing a trend indicating stronger bonding. Subtraction of the estimated bond energy from appearance potentials of $C_5H_5M^+$ ions gives an upper limit for the ionization potential of the C_5H_5M radical. If these potentials are compared with ionization potentials of the respective metal atoms a similar correlation is made separating ionization mechanisms for C_5H_5Mg, C_5H_5Mn and C_5H_5V radicals into one category with potentials 0.7 and 1.5 volts above the atomic ionization potentials and remaining ions with potentials ranging from 2.4 to 32. e.v. higher. Higher ionization potentials indicate ionization mechanisms involving removal of electrons either from the C_5H_5 ring or from ring–metal bonds rather than loss of electrons from non-bonding metal orbitals.

Consideration of ionization mechanisms leads to the row in Table III containing molecular ionization potentials. In the Mg, Cr, Mn and V compounds these values are all close to free metal ionization potentials. Differences of approximately 0.6 and 0.9 e.v. below atomic ionization potential are observed in Ni and Fe, respectively, with Co lower by the largest amount, 1.7 e.v. The experimental data on molecular ionization potentials are probably least subject to error of all the appearance potentials. Some qualitative arguments may be suggested for the low $C_{10}H_{10}Co^+$ value on the basis of a closed electronic configuration for the positive ion.

[CONTRIBUTION FROM THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Chelation of Copper(II) with Polyacrylic and Polymethacrylic Acid

BY A. M. KOTLIAR[1] AND H. MORAWETZ

RECEIVED JANUARY 6, 1955

The binding of copper(II) ion by poly(acrylic acid) and poly(methacrylic acid) was investigated by comparing titration data, absorption spectra and dialysis equilbria. The extent of copper(II) binding cannot be calculated from the titration shift without assuming the nature of the chelate formed. Spectroscopic evidence indicates the persistence of a single chelate, containing probably four carboxylates bound to a copper(II) ion, over a wide range of conditions. Dialysis equilibrium measurements can be made with dilute polymer solutions and high polymer/copper(II) ratios and they yield a detailed picture of the dependence of chelation on electrostatic factors, polymer concentration and the density of ligand groups in the individual macromolecule.

The interaction of polyions with monovalent counter-ions has been thoroughly investigated in recent years and an excellent review of the work has been published by Doty and Ehrlich.[2] Much less is known about the behavior of polymeric acids in the presence of multivalent cations, where both electrostatic interactions and specific complex formation have to be taken into account. A previous communication from this Laboratory[3] dealt with the binding of alkaline earth ions by hydrolyzed maleic anhydride copolymers, a particularly simple case, since there is no uncertainty about the nature of the chelate complex.

This paper deals with the chelation of copper(II) by poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA). The procedure outlined previously[3] for the interpretation of the *p*H shift produced by a cation in terms of complex formation with a polymeric acid does not yield unambiguous results if the number of ligands bound is unknown and the titration data were therefore supplemented with a direct determination of copper(II) binding by dialysis equilibrium and spectroscopic studies of the nature of the chelate complex.[4]

Results and Discussion

When (PMA) is titrated in 1 *N* potassium nitrate, a pronounced shift to lower *p*H values is observed on addition of small concentrations of copper(II) ion (Table I). This was ascribed to complex formation, since similar concentrations of alkaline earth ions produce no shift in the titration curve of PMA in strong salt solution.

To interpret titration shifts brought about by a chelating ion, the procedure introduced by Bjerrum[5] has to be modified in accordance with polyelectrolyte theory. We shall assume that the electrical free energy of dissociation ΔF_{el}[6] of the carboxyl groups on the polymeric chain is independent of the number of bound metal ions as long as z, the average negative charge per carboxyl group is held con-

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(1) Abstracted from the 1955 Ph.D. thesis of A. M. Kotliar, Monsanto Chemical Co. Fellow, 1952–1954.

(2) P. Doty and G. Ehrlich, *Ann. Rev. Phys. Chem.*, 111 (1952).

(3) H. Morawetz, A. M. Kotliar and H. Mark, *J. Phys. Chem.*, **58**, 19 (1954).

(4) Copper(II) chelation by PAA was also studied recently by H. P. Gregor, L. B. Luttinger and E. M. Loebl (*J. Phys. Chem.*, **59**, 34 (1955)) using potentiometric titration and by F. T. Wall and S. J. Gill (*ibid.*, **58**, 1128 (1954)) using titration, spectroscopy and polarographic data.

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

(6) A. Katchalsky and J. Gillis, *Rec. trav. chim.*, **68**, 879 (1949).

stant. For a degree of neutralization α, we have then the relations

$$A = (\mathrm{HA}) + (\mathrm{A}^-) + (\mathrm{X}) \quad (1)$$

$$\mathrm{A}(1 - \alpha) = (\mathrm{HA}) + (\mathrm{H}^+) - (\mathrm{OH}^-) \quad (2)$$

$$\frac{(\mathrm{H}^+)(\mathrm{A}^-)}{(\mathrm{HA})} = K_\mathrm{a} = K_\mathrm{a}{}^\circ \exp(-\Delta F_\mathrm{el}/RT) = f(z) \quad (3)$$

where A is the stoichiometric carboxyl concentration, (HA), (A^-) and (X) denoting concentrations of un-ionized, ionized and complexed carboxyl. For divalent cations forming chelates with an average of n carboxylate groups

$$z = \frac{1}{A}\left[(\mathrm{A}^-) + \frac{n-2}{n}(\mathrm{X})\right] \quad (4)$$

and equations 1–4 can be combined to

$$\frac{2f(z)}{nzA + (2-n)[A\alpha + (\mathrm{H}^+) - (\mathrm{OH}^-)]} = \frac{(\mathrm{H}^+)}{A(1-\alpha) - (\mathrm{H}^+) + (\mathrm{OH}^-)} \quad (5)$$

The functions $f(z)$ for PAA and PMA in salt free and 1 M $\mathrm{KNO_3}$ solutions are plotted in Fig. 1. The effective acidity of the carboxyl groups decreases, in general, with increasing charge of the polymer, except for the apparent increase in the dissociation constant of PMA on addition of small amounts of base. This anomaly may be related to the increase in the effective local dielectric constant accompanying the initial expansion of the bulky PMA chain.

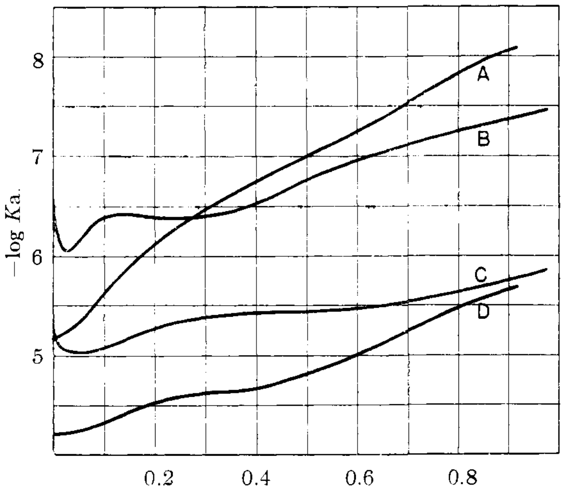

Fig. 1.—Dependence of the effective ionization constants of PAA and PMA on the charge density of the polyion: A, PAA, no salt; B, PMA, no salt; C, PMA, 1 M $\mathrm{KNO_3}$; D, PAA, 1 M $\mathrm{KNO_3}$.

Equation 5 cannot be solved without assuming a value of n. Using values of $n = 2$, 3 or 4 in conjunction with the titration data in Table I leads to estimates of copper binding represented on Fig. 2. Although phase separation occurs over most of the titration range in the presence of copper(II) ion, the interpretation of the titration shift is believed to remain valid, since at high counter-ion concentrations ΔF_el should be the same in swollen gels as in solution.

The association equilibria of a cation M with n ligand groups X are usually characterized by formation constants of the form $K_\mathrm{f} = (\mathrm{MX}_n)/(\mathrm{M})(\mathrm{X})^n$. This approach is obviously not applicable when we deal with polymers carrying large numbers of ligands. Thus, if copper(II) ion is added to a dilute solution of PMA or PAA, only the association with the first carboxylate should depend on the over-all carboxylate concentration in the solution. Once the copper ion is bound to a polyion, any further carboxylate binding will depend only on the number and spatial distribution of ligand groups in this one chain molecule. Chelation with two neighboring carboxylates would result in an eight-membered ring and such chelate rings are rare on account of the steric strain involved,[7] but larger rings have a high probability in view of the high carboxyl concentration in the swollen polymer coil.

TABLE I

EFFECT OF COPPER(II) ION ON THE TITRATION OF 0.0196 N PMA IN 1 N $\mathrm{KNO_3}$ AT 25°

α	pH Blank	pH 0.0023 M copper(II)	α	pH Blank	pH 0.0023 M Copper(II)
0.068	3.99	3.67	0.267	4.96	4.40
.100	4.19	3.79	.300	5.06	4.56
.167	4.55	4.02	.333	5.13	4.69
.200	4.70	4.15	.400	5.26	4.92
.233	4.84	4.27	.467	5.38	5.13

TABLE II

DIALYSIS EQUILIBRIUM OF 10^{-4} M COPPER(II) WITH 0.017 N PMA AND PAA AT 27.8°

Polymer	α	$10^4(\mathrm{H}^+)$	$\mathrm{Cu_b}/(\mathrm{Cu}^{++})$
PMA	0.14	42	5.9
PMA	.21	21	11.4
PMA	.28	12	14.6
PMA	.35	6.9	26
PMA	.42	5.0	38
PMA	.49	3.7	59
PAA	.28	63	8.1
PAA	.35	41	16.2
PAA	.42	23	33
PAA	.49	14	55
PAA	.56	8.5	103

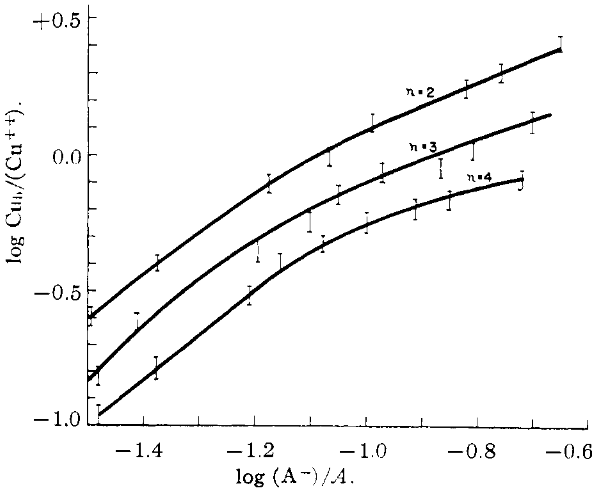

Fig. 2.—Copper(II) binding of PMA calculated from titration data; 0.0196 N PMA, 0.0023 M copper(II).

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[7] A. E. Martell and M. Calvin, "Chemistry of Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, p. 138.

Spectroscopic measurements are particularly well suited for the clarification of the nature of copper association complexes. Klotz and Fiess have shown that the absorption maximum shifts from 770 to 750 and 730 mμ as copper(II) ion binds one, two and three acetate groups.[8] The spectra of PMA solutions of different *p*H values containing copper(II) are shown in Fig. 3 and it may be seen that although the extinction coefficient is *p*H dependent, the location of the absorption maximum is not. A comparison of this maximum (about 700 mμ) with that of the copper(II) acetate complexes indicates the formation of copper(II) complexes with four carboxylates of the polyion over a wide range of conditions.

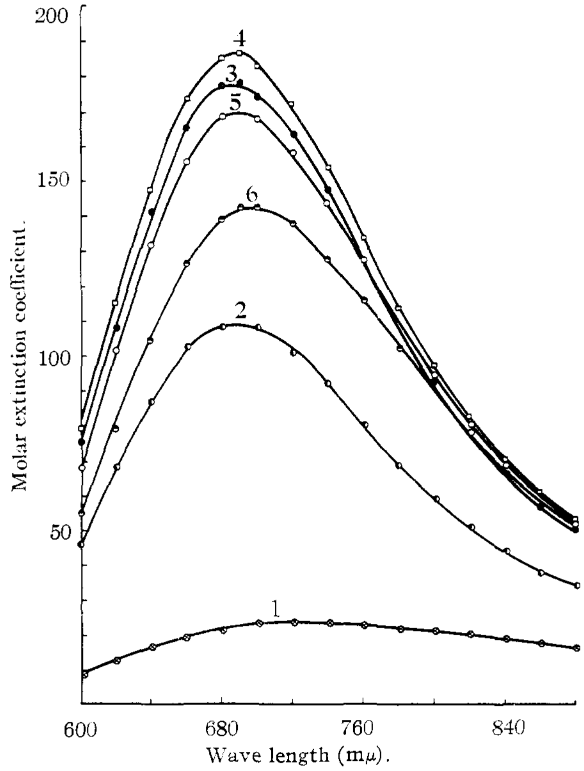

Fig. 3.—Spectra of 0.002 *M* copper(II) ion in 0.0242 *N* PMA: 1, *p*H 3.9; 2, *p*H 4.5; 3, *p*H 5.1; 4, *p*H 5.4; 5, *p*H 5.9; 6, *p*H 6.5.

Dialysis equilibria may be determined accurately in dilute polymeric acid solutions containing a high carboxyl/copper ratio. In this way an unambiguous measure of copper(II) binding is possible with the chain molecules acting independently of each other and with little interference between the regions of a poly-ion participating in the chelation of different copper(II) ions. The copper association equilibrium can then be expressed as

$$\frac{\mathrm{Cu_b}}{(\mathrm{Cu^{++}})} = Ag(z) \qquad (6)$$

where $\mathrm{Cu_b}$ is the concentration of bound copper and the function $g(z)$ expresses the dependence of the copper(II) affinity of an isolated polymer molecule on its state of ionization. For 0.0131 *N* PMA at a degree of neutralization $\alpha = 0.62$, the ratio $\mathrm{Cu_b}/(\mathrm{Cu^{++}})$ was found to be 60.8 and 53.1 with $3 \times 10^{-4}M$ and $6 \times 10^{-4}M$ copper(II), respectively, indicating that there is, indeed, little interference between the chelate groups of the poly-ion in this range of copper(II) concentration. This is no longer true for the lower carboxyl/copper ratios used in the titration studies and Fig. 2 shows that $\mathrm{Cu_b}/(\mathrm{Cu^{++}})$ is always less than unity if the copper (II) ion is assumed to chelate with four carboxyl groups.

Data obtained by varying the polymer concentration at constant degree of neutralization showed that equation 6 is obeyed by PAA, while for PMA the ratio of bound and free copper(II) is proportional to $A^{0.65}$ indicating a significant interaction of the macromolecules. The dependence of $\mathrm{Cu_b}/(\mathrm{Cu^{++}})$ on the degree of neutralization of the two polymeric acids is given in Table II.

The increasing copper binding with increasing polymer ionization is in part a consequence of the electrical free energy of copper–polyion association $\Delta F'_{\mathrm{el}}$, so that we may define an "intrinsic copper(II) association function" $g°(z)$ by

$$g(z) = g°(z) \exp\left(-\Delta F'_{\mathrm{el}}/RT\right) \qquad (7)$$

The electrical free energies of proton dissociation and copper(II) association are related by $-\Delta F'_{\mathrm{el}} = 2\Delta F_{\mathrm{el}}$ and a combination of equations 3, 6 and 7 gives

$$g°(z) = \frac{\mathrm{Cu_b}}{(\mathrm{Cu^{++}})A}\left(\frac{K_a}{K_a°}\right)^2 \qquad (8)$$

The magnitudes of $K_a°$ were estimated as 6.4×10^{-5} and $1.1 + 10^{-5}$ for PAA and PMA, respectively, in 1 *N* potassium nitrate solution. The range of *z* over which the results were significant was limited on one hand by copper(II)–hydroxyl association above *p*H 6 (indicated by a decrease in the optical density of the solutions) and on the other hand by precipitation of the PAA in the presence of small amounts of copper(II) at low degrees of neutralization.

In a 0.013 *N*, 62% neutralized PMA solution containing $3 \times 10^{-4}M$ copper(II), a reduction of the $\mathrm{KNO_3}$ concentration from 1 to 0.5 *M* increased $g°(z)$ from 410 to 480. This small change could be due to a variation in activity coefficients and the result indicates that there is little, if any, competition of potassium ion with copper(II) ion for the polyion.

The function $g°(z)$ is independent of the concentration of PAA but varies with the concentration of PMA. The results (Fig. 4) show that $g°(z)/z$ remains approximately constant for PAA while it

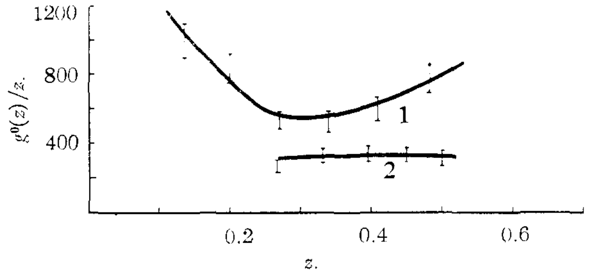

Fig. 4.—Intrinsic copper(II) association function $g^0(z)$; concentration of polymeric acids 0.017 *N*; 1 PMA; 2 PAA.

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[8] I. M. Klotz and A. F. Fiess, *J. Phys. Colloid Chem.*, **54**, 18 (1950).

exhibits a pronounced minimum around $z = 0.3$ for the PMA solutions. The treatment used attributes the observed variation in the apparent acid dissociation constant to electrostatic effects and neglects the possible role of hydrogen bonding, which plays a role in the dissociation equilibria of some dibasic acids.[9] The calculated electrical free energies of polyion–copper(II) association may thus be too high and a detailed interpretation of the behavior of $g^\circ(z)$ is not justified at this time.

Acknowledgment.—This study was supported by a grant of the Monsanto Chemical Company.

Experimental

Polymeric Acids.—Acrylic acid (Goodrich) and methacrylic acid (Rohm and Haas) were distilled under nitrogen at reduced pressure. The polymerization of 20 g. of monomer in 160 ml. of butanone containing 60 mg. of azo-bis-isobutyronitrile was carried out at 60° to 80–85% conversion. The polymer gel was washed with acetone and ether, dissolved in water, dialyzed and freeze-dried. The carboxyl content determined by titration was within 2% of the calculated value. The intrinsic viscosities in 2 *N* NaOH at 30° were 1.07 for PMA (corresponding to D.P. of 1600[10]) and 0.65 for PAA.

Titration.—*p*H was determined with a Cambridge Instrument Co. research model *p*H meter with external shielded electrodes. During titration, solutions were held at 25 ± 0.1°, stirred and protected from CO_2 by a stream of nitrogen. Four minutes had to be allowed after each addition of base to obtain equilibrium. The shift in the titration curves of polymeric acids caused by the addition of copper(II) ion was determined in the presence of 1 molar potassium nitrate, so that the change in the ionic atmosphere due to the divalent cations could be neglected.

Absorption Spectra.—A Beckman quartz spectrophotometer model DU was used with 1-cm. Corex cells. Spectra were measured at a temperature of 25 ± 0.5°.

Dialysis Equilibria.—Cellulose casing was washed for 48 hours with repeated changes of glass distilled water. The polymers used were dialyzed with the same stock membrane for 2 weeks against daily changes of distilled water, before use in dialysis experiments. A cellulose casing sack containing 20 ml. of polymer solution was equilibrated for 6–7 days at 28.7 + 0.02° with 50 ml. of 1 *N* KNO_3 containing small concentrations of copper(II). The acidified dialyzate was extracted with dithizone solution in carbon tetrachloride and the copper(II) concentration determined spectrophotometrically.[11] Results are reported only for conditions which did not lead to phase separation. Blank runs in which no polymer was present in the dialysis sack showed negligible errors in the copper(II) determination.

BROOKLYN, N. Y.

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(9) D. H. McDaniel and H. C. Brown, *Science*, **118**, 370 (1953).

(10) A. Katchalsky and H. Eisenberg, *J. Polymer Sci.*, **6**, 145 (1951).

(11) F. B. Sandell, "Colorimetric Determination of Traces of Metals," Second edition, Interscience Publishers, Inc., New York, N. Y., 1950.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

Metallo Complexes of Tetrametaphosphate[1a]

BY ROBERT J. GROSS AND JOHN W. GRYDER[1b]

RECEIVED MARCH 5, 1955

The association constants for the ions formed between tetrametaphosphate and Na^+, Cu^{++} and Ni^{++} ions have been measured by a potentiometric procedure. At 30 ± 0.05° and at a volume ionic strength maintained at 1.00 with tetramethylammonium nitrate, values for the association constants for $NaP_4O_{12}^{-3}$, $CuP_4O_{12}^{-2}$, $Cu(P_4O_{12})_2^{-6}$, $NiP_4O_{12}^{-2}$, $Ni(P_4O_{12})_2^{-6}$ were found to be 6.5 ± 0.1, $1.52 \pm 0.03 \times 10^3$, $44 \pm 5 \times 10^3$, $4.3 \pm 0.2 \times 10^2$, and $3 \pm 1 \times 10^3$, respectively.

Introduction

The chemistry of the condensed phosphates has been studied for many years, but little quantitative information has been obtained.[2,3] Monk and coworkers have determined the dissociation constants for a number of metallo complexes of tri- and tetrametaphosphate by a conductometric procedure.[4] However, the nature of the assumptions necessary in the employment of conductivity measurements for the determination of equilibrium constants of species involving large charges are such that an independent check is advisable. Other factors which prompted this work were the contradictory results on other phases of metaphosphate chemistry reported in the literature and the possibility of impurities in metaphosphate preparations.

Materials and Methods

Sodium tetrametaphosphate was prepared and purified as described in a previous publication.[5] Stock solutions of copper and nickel nitrates were prepared from the C.P. salts. The copper was determined by an iodometric procedure[6] and the nickel determined gravimetrically as the dimethyl glyoximate.[7] Tetramethylammonium nitrate was prepared from Matheson, Coleman and Bell tetramethylammonium bromide by metathesis with $AgNO_3$ and was recrystallized until no test for excess silver or bromide ions was obtained. The sodium nitrate was the C.P. salt dried in a vacuum desiccator. The tetramethylammonium tetrametaphosphate was prepared by metathesis of silver tetrametaphosphate with tetramethylammonium bromide. The resulting solution gave negative tests for bromide and silver and was analyzed by hydrolysis of the metaphosphate to orthophosphate which was determined colorimetrically.[8]

The two-phase copper amalgam[9] was prepared by electrolyzing a 0.5 *f* solution[10] of $CuSO_4$, slightly acidified with H_2SO_4, between a mercury cathode and an electrolytic Cu

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(1) (a) Based on a dissertation submitted by R. J. Gross in partial fulfillment of the requirements for the degree of Doctor of Philosophy. This work was supported in part by Grant G-3604(C) National Institutes of Health, Department of Health, Education and Welfare. (b) Person to whom inquiries should be addressed.

(2) B. Topley, *Quart. Rev.*, **3**, 345 (1949).

(3) D. M. Yost and H. Russell, "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, pp. 210–224.

(4) C. B. Monk and C. W. Davies, *J. Chem. Soc.*, 417 (1949); H. W. Jones, C. B. Monk and C. W. Davies, *ibid.*, 2693 (1949); H. W. Jones and C. B. Monk, *ibid.*, 3475 (1950); C. B. Monk, *ibid.*, 1317 (1952).

(5) D. L. Barney and J. W. Gryder, THIS JOURNAL, **77**, 3195 (1955).

(6) E. H. Swift, "Introductory Quantitative Analysis," pages 208–209, Prentice-Hall, Inc., New York, N. Y., 1950, pp. 208–209.

(7) W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929, pp. 315–317.

(8) O. H. Lowry and J. A. Lopez, *J. Biol. Chem.*, **162**, 421 (1946).

(9) R. F. Nielson and D. J. Brown, THIS JOURNAL, **49**, 2423 (1927).

(10) Concentration will be expressed in volume formality, *f*, the number of formula weights per liter of solution.