

exhibits a pronounced minimum around  $\alpha = 0.3$  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.<sup>9</sup> The calculated electrical free energies of polyion-copper(II) association may thus be too high and a detailed interpretation of the behavior of  $g^\circ(\alpha)$  is not justified at this time.

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### 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<sup>10</sup>) and 0.65 for PAA.

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

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

**Titration.**—pH was determined with a Cambridge Instrument Co. research model pH meter with external shielded electrodes. During titration, solutions were held at 25 ± 0.1°, stirred and protected from CO<sub>2</sub> 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<sub>3</sub> containing small concentrations of copper(II). The acidified dialyzate was extracted with dithizone solution in carbon tetrachloride and the copper(II) concentration determined spectrophotometrically.<sup>11</sup> 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.

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

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## Metallo Complexes of Tetrametaphosphate<sup>1a</sup>

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The association constants for the ions formed between tetrametaphosphate and Na<sup>+</sup>, Cu<sup>++</sup> and Ni<sup>++</sup> 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<sub>4</sub>O<sub>12</sub><sup>-3</sup>, CuP<sub>4</sub>O<sub>12</sub><sup>-2</sup>, Cu(P<sub>4</sub>O<sub>12</sub>)<sub>2</sub><sup>-6</sup>, NiP<sub>4</sub>O<sub>12</sub><sup>-2</sup>, Ni(P<sub>4</sub>O<sub>12</sub>)<sub>2</sub><sup>-6</sup> were found to be 6.5 ± 0.1, 1.52 ± 0.03 × 10<sup>3</sup>, 44 ± 5 × 10<sup>3</sup>, 4.3 ± 0.2 × 10<sup>2</sup>, and 3 ± 1 × 10<sup>2</sup>, respectively.

### Introduction

The chemistry of the condensed phosphates has been studied for many years, but little quantitative information has been obtained.<sup>2,3</sup> Monk and co-workers have determined the dissociation constants for a number of metallo complexes of tri- and tetrametaphosphate by a conductometric procedure.<sup>4</sup> 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.

(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).

### Materials and Methods

Sodium tetrametaphosphate was prepared and purified as described in a previous publication.<sup>5</sup> Stock solutions of copper and nickel nitrates were prepared from the C.P. salts. The copper was determined by an iodometric procedure<sup>6</sup> and the nickel determined gravimetrically as the dimethyl glyoximate.<sup>7</sup> Tetramethylammonium nitrate was prepared from Matheson, Coleman and Bell tetramethylammonium bromide by metathesis with AgNO<sub>3</sub> 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.<sup>8</sup>

The two-phase copper amalgam<sup>9</sup> was prepared by electrolyzing a 0.5 *f* solution<sup>10</sup> of CuSO<sub>4</sub>, slightly acidified with H<sub>2</sub>SO<sub>4</sub>, between a mercury cathode and an electrolytic Cu

(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.

anode. The current density was 5 amp. per square decimeter of Hg surface.

The concentration cell employed was a modified H cell, so adapted that Airco Seaford Nitrogen could be bubbled through the solutions in both arms simultaneously. The cell was made from two four-inch test-tubes with capillary side arms connected by a three-way T stopcock. A Leeds and Northrup type K<sub>2</sub> potentiometer and Number 2500 galvanometer were employed for the voltage measurements.

#### Experimental

The concentration cells in each measurement had the same amount of added cation in both arms of the H cell and in addition one side contained added sodium or tetramethylammonium tetrametaphosphate. The total volume ionic strength was adjusted to the same value (usually 1.00) with tetramethylammonium nitrate. All solutions were prepared from the pure salts and the diluted stock solutions of copper or nickel nitrate just before they were added to the cells to avoid hydrolysis of the tetrametaphosphate. The comparison solution was prepared from a 5-ml. aliquot of the diluted cation stock solution and sufficient tetramethylammonium nitrate was added to give the appropriate ionic strength. This solution was diluted to 10 ml. in a volumetric flask with distilled water and 5 ml. of the diluted solution added to one arm of the cell. The metaphosphate containing solution was prepared in the same fashion, with the exception that it contained sodium metaphosphate and a correspondingly smaller amount of tetramethylammonium nitrate. In the experiments to determine sodium ion dependence, NaNO<sub>3</sub> was substituted for some of the tetramethylammonium nitrate in both solutions.

After the solutions had been added to the cell, the stopcock was opened and N<sub>2</sub> bubbled through the solutions for ten minutes while the cell and its contents were submerged in a constant temperature water-bath maintained at 30 ± 0.05°. The stopcock was closed and copper amalgam added to both arms. Contact to the amalgam was made with platinum wires sealed in glass. The N<sub>2</sub> bubbling was continued for a few more minutes and the liquid junction made. Potentiometric readings were continued for one hour or more, the readings generally becoming constant after ten minutes.

#### Results

**Copper and Sodium Tetrametaphosphate Complexes.**—The observed potential differences for experiments involving copper and sodium tetrametaphosphate complexes are presented in Table I. It is evident that increasing the ratio of metaphosphate to copper causes an increase in the e.m.f. corresponding to a decrease in free copper ion concentration, whereas an increase in total sodium ion concentration at constant copper and meta-

phosphate causes a decrease in e.m.f. corresponding to an increase in free copper ion concentration. The best fit of the data was obtained by assuming the presence of the species NaP<sub>4</sub>O<sub>12</sub><sup>-3</sup>, CuP<sub>4</sub>O<sub>12</sub><sup>-2</sup>, and Cu(P<sub>4</sub>O<sub>12</sub>)<sub>2</sub><sup>-6</sup> and the absence of appreciable amounts of Na<sub>2</sub>(P<sub>4</sub>O<sub>12</sub>)<sup>-2</sup>, NaCuP<sub>4</sub>O<sub>12</sub> or Cu<sub>2</sub>P<sub>4</sub>O<sub>12</sub>.

TABLE I

Ionic strength maintained at 1.00 volume formality with tetramethylammonium nitrate.

(Cu <sup>++</sup> ) × 10 <sup>3</sup> , <i>f</i>	(P <sub>4</sub> O <sub>12</sub> <sup>-4</sup> ) × 10 <sup>3</sup> , <i>f</i>	(Na <sup>+</sup> ) × 10 <sup>3</sup> , <i>f</i>	E.m.f., mv.
2.575	2.646	10.58	12.15
2.575	2.562	50.25	10.65
2.575	2.620	60.48	10.71
2.575	2.562	74.55	9.94
2.575	2.562	110.25	9.51
2.575	5.125	20.50	21.29
2.575	10.25	41.00	31.96
2.575	10.25	41.00	32.11
2.575	10.23	60.96	30.93
2.575	10.24	80.96	29.57
2.575	20.50	82.00	41.63
2.575	2.225	0	10.44
2.575	4.450	0	20.07
2.575	8.900	0	31.70
2.575	17.80	0	42.78

If we consider only the first six experiments in Table I, it can be assumed that in the presence of the low total concentration of tetrametaphosphate no Cu(P<sub>4</sub>O<sub>12</sub>)<sub>2</sub><sup>-6</sup> is present. Assuming only Cu(P<sub>4</sub>O<sub>12</sub>)<sup>-2</sup> and Na(P<sub>4</sub>O<sub>12</sub>)<sup>-3</sup> to be present, we have the following relationships, where α is the association constant for Na(P<sub>4</sub>O<sub>12</sub>)<sup>-3</sup>, β<sub>1</sub> is the association constant for Cu(P<sub>4</sub>O<sub>12</sub>)<sup>-2</sup>, Cu<sub>T</sub> is total copper ion concentration, Cu is free copper ion concentration, P<sub>T</sub> is total metaphosphate concentration, P is free metaphosphate concentration, and Na is free sodium ion concentration.

$$Cu_T = Cu + \beta_1(Cu)(P) \quad (1)$$

$$P_T = P + \beta_1(Cu)(P) + \alpha(Na)(P) \quad (2)$$

Eliminating P from eq. 1 and 2 and rearranging we find

$$F(Cu) \equiv (P_T - Cu_T + Cu)(Cu)/(Cu_T - Cu) = (1 + \alpha Na)/\beta_1$$

Since Na<sub>T</sub>, the total sodium ion concentration, is greater than P<sub>T</sub> in the six experiments under consideration, and since the change in e.m.f. with varying Na<sub>T</sub> is relatively small at constant Cu<sub>T</sub> and P<sub>T</sub>, it is apparent that most of the sodium ion is uncomplexed and that Na<sub>T</sub> is approximately equal to Na. A plot of F(Cu) vs. Na<sub>T</sub> should, therefore, be a straight line with an intercept of 1/β<sub>1</sub> and a slope of α/β<sub>1</sub>. This graph is given in Fig. 1 and is seen to be in good agreement with the theory. A least squares treatment minimizing the function [F(Cu) - (1/β<sub>1</sub>)(1 + αNa)]<sup>2</sup>/[F(Cu)]<sup>2</sup> with respect to α and β<sub>1</sub> was made and gave α = 6.5 and β<sub>1</sub> = 1.51 × 10<sup>3</sup>.

The straight line in Fig. 1 eliminates the possibility of appreciable quantities of Na<sub>2</sub>(P<sub>4</sub>O<sub>12</sub>)<sup>-2</sup>, NaCu(P<sub>4</sub>O<sub>12</sub>)<sup>-</sup> or Cu<sub>2</sub>P<sub>4</sub>O<sub>12</sub> as is indicated by the following arguments. If Na<sub>2</sub>(P<sub>4</sub>O<sub>12</sub>)<sup>-2</sup> were present, eq. 2 would contain an additional term, α'(Na)<sup>2</sup>(P), and one would obtain by the methods employed

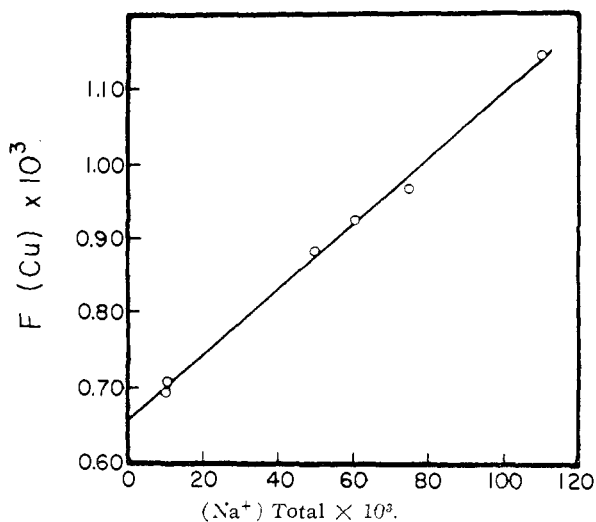


Fig. 1.

before  $F(\text{Cu}) = [1 + \alpha(\text{Na}) + \alpha'(\text{Na})^2]/\beta_1$ . Since there is no indication of a quadratic dependence in Fig. 1, we may assume that there is no appreciable amount of  $\text{Na}_2\text{P}_4\text{O}_{12}^{2-}$  present under the conditions of the experiment.

If  $\text{NaCuP}_4\text{O}_{12}^-$  formed either by  $\text{Na}^+$  reacting with  $\text{CuP}_4\text{O}_{12}^{2-}$  or  $\text{Cu}^{++}$  reacting with  $\text{NaP}_4\text{O}_{12}^{3-}$ , eq. 1 and 2 would contain an additional term of the form  $\alpha''\beta_1(\text{Na})(\text{Cu})(\text{P})$  and one would obtain

$$F(\text{Cu}) = (1 + \alpha\text{Na})/\beta_1(1 + \alpha''\text{Na})$$

For the graph of  $F(\text{Cu})$  vs.  $\text{Na}$  to be a straight line,  $\alpha''$  must be much less than  $\alpha$  and therefore no appreciable amount of  $\text{NaCuP}_4\text{O}_{12}^-$  can be present.

If  $\text{Cu}_2\text{P}_4\text{O}_{12}$  were present, eq. 1 would contain an additional term  $2\beta'(\text{Cu})^2(\text{P})$ , and eq. 2 would contain a term  $\beta'(\text{Cu})^2\text{P}$ . Solving as before we find

$$F(\text{Cu}) = [1 + \alpha\text{Na} - \beta'(\text{Cu})^2]/(\beta_1 + 2\beta'\text{Cu})$$

Since  $\text{Cu}$  increases as  $\text{Na}$  increases,  $F(\text{Cu})$  would be concave downward. This is not the case and therefore it appears that no appreciable quantity of  $\text{Cu}_2\text{P}_4\text{O}_{12}$  is formed.

In the absence of any sodium ion, the complex species present are  $\text{Cu}(\text{P}_4\text{O}_{12})^{2-}$  and  $\text{Cu}(\text{P}_4\text{O}_{12})_2^{6-}$ . We can then write

$$\text{Cu}_T = \text{Cu} + \beta_1(\text{Cu})(\text{P}) + \beta_2(\text{Cu})(\text{P})^2 \quad (3)$$

$$\text{P}_T = \text{P} + \beta_1(\text{Cu})(\text{P}) + 2\beta_2(\text{Cu})(\text{P})^2 \quad (4)$$

where  $\beta_2$  is the association constant for the  $\text{Cu}(\text{P}_4\text{O}_{12})_2^{6-}$  ion. Eliminating  $\text{P}$  and rearranging we obtain

$$(\text{Cu}_T - \text{Cu})/\text{Cu} = \beta_1\text{P}_T - \beta_1^2\text{Cu}(\text{P}_T + \text{Cu} - \text{Cu}_T) + 2\beta_2[\text{P}_T + 2(\text{Cu} - \text{Cu}_T)]^2$$

Applying a least squares treatment to this expression, we find for the experiments using tetramethylammonium tetrametaphosphate, the last four lines of Table I, the values  $\beta_1 = 1.53 \times 10^3$  and  $\beta_2 = 12.4 \times 10^3$ . This value for  $\beta_1$  is in good agreement with that calculated above. In the presence of sodium, eq. 4 would have an additional term,  $\alpha(\text{Na})(\text{P})$ , and we obtain

$$(\text{Cu}_T - \text{Cu})/\text{Cu} = \{\beta_1(\text{P}_T + \text{Na}\alpha) - \beta_1^2\text{Cu}[\text{P}_T + \text{Cu} - \text{Cu}_T] + \beta_2[\text{P}_T + 2(\text{Cu} - \text{Cu}_T)]^2\}/[1 + 2\alpha\text{Na} + \alpha^2\text{Na}^2]$$

Using the value of  $\alpha$  obtained above, 6.5, and performing a least squares treatment with all the data in Table I except the last four experiments, we obtain  $\beta_1 = 1.515 \times 10^3$  and  $\beta_2 = 43.9 \times 10^3$ . Again the agreement of  $\beta_1$  is excellent. The agreement between the values for  $\beta_2$  calculated from the different sets of data is not good. However, the preparation of the tetramethylammonium tetrametaphosphate was difficult and a slight error in its concentration would affect the value of  $\beta_2$  markedly. The important point is that a  $\text{Cu}(\text{P}_4\text{O}_{12})_2^{6-}$  species is necessary to explain the data in the absence of sodium as well as in its presence. Estimating probable error, the values of the constants are  $\alpha = 6.5 \pm 0.1$ ,  $\beta_1 = 1.51 \pm 0.03 \times 10^3$  and  $\beta_2 = 44 \pm 5 \times 10^3$ . These constants will fit all the experimental points to within 2%.

**Nickel Tetrametaphosphate Complexes.**—The nickel constants were determined by a procedure involving the displacement of copper from its

complexes by nickel. The data for the determination of the nickel constants are presented in Table II.

TABLE II

Ionic strength maintained at 1.00 volume formality with tetramethylammonium nitrate. Total copper iron concentration equals  $2.575 \times 10^{-3}f$ .

$(\text{Ni}^{++}) \times 10^3, f$	$(\text{P}_4\text{O}_{12}^{4-}) \times 10^3, f$	E.m.f., mv.	$(\text{Ni}^{++}) \times 10^3, f$	$(\text{P}_4\text{O}_{12}^{4-}) \times 10^3, f$	E.m.f., mv.
2.570	5.125	17.36	10.28	10.23	19.95
5.140	5.125	14.30	20.56	10.23	13.56
10.28	5.125	10.13	30.84	10.23	10.36
20.56	5.125	6.91	2.570	15.38	35.23
30.84	5.125	5.17	5.140	15.38	32.47
2.570	10.25	28.86	10.28	15.38	27.75
5.140	10.23	25.61	5.140	17.94	35.17
			5.140	20.50	37.61
			20.56	20.50	26.05

Using eq. 3 and 4, the measured e.m.f., the total copper added, and the values for the constants determined above, it is possible to calculate the concentration of free metaphosphate and the total concentration of metaphosphate not bound by copper or sodium. Assuming that the only nickel species are  $\text{NiP}_4\text{O}_{12}^{2-}$  and  $\text{Ni}(\text{P}_4\text{O}_{12})_2^{6-}$  and employing the method of Bjerrum<sup>11</sup> for the determination of stepwise association of a ligand with a metal ion, we can define

$$\bar{n} \equiv (\text{P}_T' - \text{P})/\text{Ni}_T = (\gamma_1\text{P} + 2\gamma_2\text{P}^2)/1 + \gamma_1(\text{P}) + \gamma_2(\text{P})^2 \quad (5)$$

where  $\bar{n}$  is the average number of ligands per nickel,  $\text{P}_T'$  is the metaphosphate not complexed with  $\text{Cu}$  or  $\text{Na}$ ,  $\text{Ni}_T$  is total nickel, and  $\gamma_1$  and  $\gamma_2$  are the association constants for  $\text{NiP}_4\text{O}_{12}^{2-}$  and  $\text{Ni}(\text{P}_4\text{O}_{12})_2^{6-}$ , respectively. Rearranging eq. 5 we have

$$\bar{n} = \gamma_1(1 - \bar{n})(\text{P}) + \gamma_2(2 - \bar{n})(\text{P})^2$$

Minimizing the function  $[\bar{n} - \gamma_1(1 - \bar{n})(\text{P}) - \gamma_2(2 - \bar{n})(\text{P})^2]/\bar{n}^2$  with respect to  $\gamma_1$  and  $\gamma_2$  for the data in Table II, we obtain  $\gamma_1 = 4.25 \times 10^2$  and  $\gamma_2 = 2.72 \times 10^3$ . Figure 2 shows a graph of experimental  $\bar{n}$  vs. free metaphosphate and the calculated curve using the values of  $\gamma_1$  and  $\gamma_2$  obtained above. Considering the indirect method for determining the constants, the agreement is good and indicates that the values obtained for the copper complexes are also valid. The value for  $\gamma_2$  is very uncertain since it varies over a wide range when  $\alpha$ ,  $\beta_1$  or  $\beta_2$  is changed. However,  $\gamma_1$  is relatively independent of variations in the copper or sodium constants and is therefore more accurately determined. The good agreement between observed and calculated values for large ratios of  $\text{Ni}_T$  to  $\text{P}_T$  indicate that there is no appreciable quantity of  $\text{Ni}_2\text{P}_4\text{O}_{12}$  formed. Estimating probable error, the best values for the constants are  $\gamma_1 = 4.3 \pm 0.2 \times 10^2$  and  $\gamma_2 = 3 \pm 1 \times 10^3$ .

**Effect of Ionic Strength.**—Four experiments in which the total ionic strength was varied keeping total copper and total metaphosphate essentially constant are shown in Table III. Since the metaphosphate concentration varied,  $F(\text{Cu})$  defined

(11) J. C. Sullivan and J. C. Hindman, *THIS JOURNAL*, **74**, 6091 (1952).

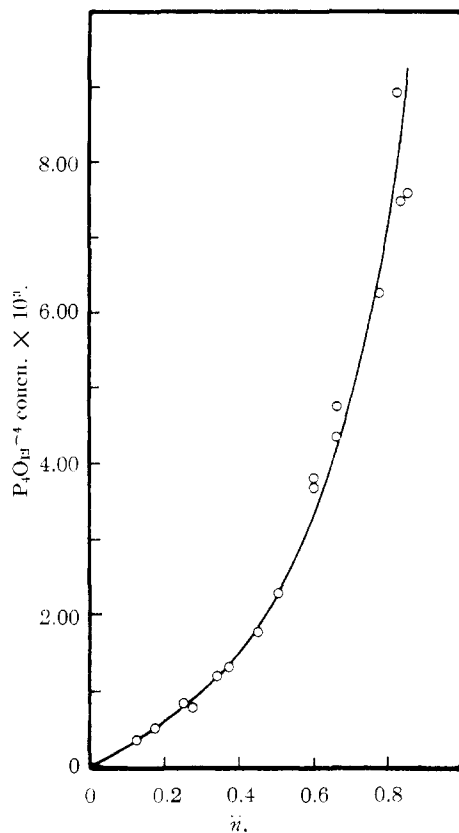


Fig. 2.

above is also given. It is evident that the results are not critical to changes of ionic strength in the region employed in this investigation. In addition, it is reasonable to assume that there is no sizeable liquid junction potential because of the large concentration of indifferent electrolyte and the fact that there is no large change with total ionic strength which should affect the junction potential as well as the activity coefficients.

TABLE III

Total copper ion concentration equals  $2.575 \times 10^{-3} f$ .

Ionic strength	$(P_4O_{12}^{-4}) \times 10^3, f$	E.m.f., Mv.	$F(Cu) \times 10^4$
1.00	2.646	12.15	7.10
0.80	2.562	11.88	6.85
0.60	2.646	12.44	6.54
0.40	2.562	12.78	5.65

### Discussion

The species found to exist in solutions containing  $Na^+$ ,  $Ni^{++}$ ,  $Cu^{++}$  and  $P_4O_{12}^{-4}$  are not in agreement with those assumed by Monk and co-workers.<sup>4</sup> Monk, *et al.*, assumed species of the type  $NaMP_4O_{12}^{-1}$  and  $M_2P_4O_{12}$  both of which are inconsistent with the results reported here. However, the conductivity method involves the necessity of assuming which species are present and reasonable values for the mobilities of these species based on analogy and then the determination of the best fit of the experimental data by evaluating the equilibrium constants assumed to be operative. The difficulties and resultant uncertainties of the method have been discussed by Harned and

Owen.<sup>12</sup> The advantage of the method is that dilute solutions are employed and thermodynamic constants are obtained. The potentiometric method necessitates relatively high concentrations of ions and therefore cannot give thermodynamic constants, unless activity coefficients have been determined, but has the advantage that it is not necessary to guess which species are present in the solution. Both the present work and that of Monk, *et al.*, indicate that the principal species present is  $MP_4O_{12}^{-}$ . However, the association constant reported by Monk for nickel tetrametaphosphate is approximately 200 times larger than that found here. The difference could be due to one or more of the following reasons: (1) the incorrect assumptions concerning the species present resulted in false constants; (2) the activity coefficients are such that the thermodynamic constant and the concentration constant differ by a factor of 200; (3) impurities in the metaphosphate used by Monk, *et al.*, resulted in false constants.

Reasons (1) and (2) are undoubtedly operative. Monk found an association constant of  $7.7 \times 10^4$  for  $CaP_4O_{12}^{-}$  from the effect of sodium tetrametaphosphate on the solubility of  $Ca(IO_3)_2$  when he neglected the formation of  $NaCaP_4O_{12}^{-}$  and a value of  $2.3 \times 10^9$  determined by conductivity. This would indicate that the errors in the conductivity treatment are such that the association constant would appear to be too large. On the other hand, one would expect the activity effects to be such that the concentration constant would be smaller than the thermodynamic constant. Any impurity of tripolyphosphate or pyrophosphate would increase the observed constants.<sup>13</sup> In particular potentiometric data on a partially purified sample of sodium tetrametaphosphate prepared in this Laboratory and later shown to contain polyphosphate indicated a much larger association constant.

It is of interest to compare the constants obtained in the present investigations with those observed for copper pyrophosphate<sup>9</sup> also obtained at an ionic strength of 1.00. The association constants for  $CuP_2O_7^{-2}$  and  $Cu(P_2O_7)_2^{-6}$  are  $5 \times 10^{10}$  and  $2.5 \times 10^{14}$ , respectively. The pyrophosphate constants were obtained in a solution containing large amounts of  $NaNO_3$  and therefore are probably too small since  $NaP_2O_7^{-3}$  was neglected.

The ring metaphosphates in contradistinction to the straight chain polyphosphates are seen to be relatively poor complexing agents. They are also well known to form stronger acids as is indicated by the titration curves with strong base.<sup>5</sup> Both of these facts are undoubtedly due to the large separation of negative charges in the metaphosphates relative to the concentration of negative charge on two oxygen atoms attached to a single phosphorus atom in the polyphosphates.

**Acknowledgment.**—One of the authors (R.J.G.) wishes to acknowledge a grant-in-aid from the Hynson, Westcott and Dunning Research Fund.

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(12) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, pp. 145-148.

(13) J. I. Watters and A. Aaron, *THIS JOURNAL*, **75**, 611 (1953).