p-xylene disproportionates far more readily than either *o*- or *m*-xylene. The three-compound kinetic equations presented earlier are not valid when disproportionation occurs.

Although the *p*-xylene trajectory deviates seriously when no diluent is used, the fact that $k_{po} = 0$ in toluene solution indicates that the isomerization of *p*-xylene in toluene solution is intramolecular. If *p*-xylene alkylated toluene, it is doubtful that k_{po} would equal zero. The postulate that *p*-xylene will readily alkylate itself, but not toluene, is consistent with the fact that toluene is less susceptible to electrophilic substitution than *p*-xylene.[13]

The agreement of the *o*-xylene–*p*-xylene isomerization compositions with the theoretical trajectory in spite of extensive disproportionation suggests that the disproportionation reaction is largely the alkylation of the *o*-xylene by the *p*-xylene.

The dramatically higher ratio of disproportion rate to isomerization rate for *p*-xylene as compared to *o*-xylene or *m*-xylene is quite surprising since *p*-xylene is the least readily substituted isomer. Thus, *p*-xylene appears to have a great tendency to act as an alkylating agent.

Experimental

To a solution of 663 g. (7.2 moles) of toluene and 85 g. (0.8 mole) of xylene maintained at 50° in 2-l. 3-necked creased flask, equipped with a gas inlet tube, a thermometer, a stirrer and a $CaCl_2$ drying tube, was added 53 g. (0.4 mole) of Baker and Adams resublimed anhydrous $AlCl_3$. Hydrogen chloride was passed through the stirred reaction mixture for 10 minutes. At specific times 50-ml. samples were withdrawn from the reaction mixture, washed with water and dried over $CaSO_4$. The samples were then analyzed by vapor phase chromatography[14] using a 10 ft. column at 90° packed with 30% di-(2-ethylhexyl) sebacate and 70% 30-60 mesh Celite. The V.P.C. unit was connected through a Brown Recorder to an Instron two counter automatic integrator. One area for *m*- and *p*-xylenes and one area for *o*-xylene were obtained. The analyses were repeated until analyses differing no greater than 1% were obtained. Since an equivalent amount of *p*-xylene produced an area 1.053 times that for *o*-xylene and an equivalent amount of *m*-xylene produced an area 1.022 times that for *o*-xylene, it was necessary to use the differential infrared analyses for *m*- and *p*-xylene to adjust the *m*-, *p*-xylene areas so that the *o*-xylene analyses could be calculated.

The isomerizations of xylene without toluene were carried out as above, except that 424 g. (4.0 moles) of xylene and 133 g. (1.0 moles) of $AlCl_3$ were added to a one-l. flask, and only 10-ml. samples were taken. The samples were analyzed by infrared analysis.

Acknowledgment.—The authors are indebted to D. S. Erley of the Dow Spectroscopy Department for the infrared data.

MIDLAND, MICHIGAN

---

[13] F. E. Condon, THIS JOURNAL, **74**, 2528 (1952); H. C. Brown and J. D. Brady, *ibid.*, **74**, 3570 (1952).

[14] R. S. Gohlke, *Anal. Chem.*, **29**, 1723 (1957).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS, THE STATE UNIVERSITY]

Counterion Binding by Polyelectrolytes. II. The Determination of the Binding of Univalent Cations by Long-chain Polyphosphates from Conductivity and Electrophoresis Data[1]

BY ULRICH P. STRAUSS AND SYDNEY BLUESTONE

RECEIVED APRIL 23, 1959

The conductivities of long-chain lithium, sodium, potassium and tetramethylammonium polyphosphate samples were measured in 0.2 M solutions of the bromides of the corresponding cations at 0°. The equivalent conductance of each polyphosphate was independent of the polyphosphate concentration. By combining the equivalent conductance data with the corresponding electrophoretic mobilities, the degree of ionization, i, of each of the polyphosphates was calculated by means of the Kohlrausch equation. The resulting values of i were proportional to the values of the electrophoretic mobility. These experimental results are consistent with the interpretation that the polyphosphate chains are free draining, that relaxation effects are negligible and that the friction coefficient of the polymer is not affected by the nature of the bound counterion within the range of counterion sizes employed in this investigation.

In several recent papers, theories concerning the electrophoretic mobility[2,3] and the electrical conductivity[4] of polyelectrolytes in solutions containing a simple electrolyte have been developed. Experimental results conforming qualitatively to the electrophoresis theory have also been reported.[5] If the polyelectrolyte chains are free-draining, u, the electrophoretic mobility, is given by the expression

$$u = e/f \qquad (1)$$

where e and f are the effective charge and friction constant, respectively, of a monomer unit.[2,3] This result has been used in the first paper of this series to estimate the degree of ionization of polyphosphates in solutions of tetramethylammonium (TMA^+) and alkali metal bromides.[6] The validity of eq. 1 depends on the absence of relaxation effects. Such relaxation effects have been considered insignificant both on theoretical[2] and experimental[5] grounds. On the other hand, Longworth and Hermans[7] have theorized relaxation effects to explain qualitatively observed deviations of their experimental conductivity results from the

---

[1] This investigation was supported by a grant from the United States Atomic Energy Commission under Contract AT(30-1)1018. The results presented in this paper will be contained in a thesis to be presented by S. Bluestone to Rutgers, The State University, in partial fulfillment of the requirements for the Ph.D. degree.

[2] J. Th. G. Overbeek and D. Stigter, *Rec. trav. chim.*, **75**, 543 (1956).

[3] J. J. Hermans and H. Fujita, *Koninkl. Ned. Akad. Wetenshap, Proc.*, *B***58**, 182 (1955).

[4] H. Fujita and J. J. Hermans, *ibid.*, *B***58**, 188 (1955).

[5] N. Nagasawa, A. Soda and I. Kagawa, *J. Polymer Sci.*, **31**, 439 (1958).

[6] U. P. Strauss, D. Woodside and P. Wineman, *J. Phys. Chem.*, **61**, 1353 (1957).

[7] R. Longworth and J. J. Hermans, *J. Polymer Sci.*, **26**, 47 (1957).

original theory,[4] even though the deviations could have been explained equally well in terms of counterion binding.

It is therefore of interest to test the validity of eq. 1 by experimental means. If one assumes free draining and neglects relaxation effects, the theoretical treatments[2–4] imply the relation (2) between

$$\Lambda_p = i(\mathfrak{F}u + \lambda_c) \qquad (2)$$

Λ_p, the equivalent conductance,[8] and i, the degree of ionization of the polyelectrolyte in a solution containing a simple electrolyte with a common counterion. Here $\mathfrak{F}$ is the faraday and λ_c is the equivalent conductance of the counterion in the solution of simple electrolyte serving as the solvent. By suitable conductivity and electrophoresis measurements, i can thus be determined. If conditions are such that f remains constant, equation 1 predicts that u should be proportional to i, and the presence or absence of such a proportionality will serve as the desired validity test.

Since the necessary electrophoresis data were available from another investigation,[9] we have determined the conductance of lithium, sodium, potassium and tetramethylammonium polyphosphates in aqueous 0.2 M solutions of the respective bromides at 0°. The results and interpretation of these experiments are described in this paper.

Experimental

Materials.—The sodium polyphosphate used (our sample No. NaPP-B1) was a *Graham salt* prepared as previously described.[10] Its degree of polymerization (DP) was determined by an end-group titration method[11] to be 130. Tetramethylammonium polyphosphate (our sample No. TMA-PP-B1) was prepared by ion exchange from potassium *Kurrol salt*.[12] The sample contained 9.40% of water which remained after freeze-drying. The DP was determined from viscosity measurements in 0.35 N NaBr to be 7800. Soluble potassium polyphosphate (our sample No. KPP-W1) was prepared by P. Wineman by first dissolving a potassium *Kurrol salt* with an ion-exchange resin in the sodium form and then bringing the polymer back to the potassium form by ion exchange. Freeze-drying left a water content of 8.84% in the soluble KPP. Its DP as determined by viscosity in 0.35 N NaBr was 8000. The lithium polyphosphate used (our sample No. LiPP-B1) was prepared from LiH_2PO_4 by the same method that Graham salts are prepared from NaH_2PO_4.[10] Its DP was determined to be 102 by end-group titration.[11]

Conductance.—Alternating-current conductance measurements were made at 0° with a Shedlovsky type bridge.[13,14] The cell which contained bright platinum electrodes followed the general design of Jones and Bollinger[15,16] and had a cell constant of 11.805 ± 0.002.[17] Polarization effects were eliminated by extrapolating data obtained at 2000, 3000 and 4000 c.p.s. to infinite frequency. Conductivity water, prepared by passing distilled water through a mixed-bed ion-exchange resin, was used throughout. Its specific conductance ranged from 0.3 to 0.8 × 10^{-6} reciprocal ohms per cm. at 0°.

The concentrations of the solutions of simple electrolyte, serving as solvents, were determined by potentiometric titration for Br^- with $AgNO_3$. The polymer solutions were prepared by volumetric dilution of known weights of stock solutions. Each stock solution was prepared by weight. At least two such stock solutions were used for each run with a given solvent. The pH of the polymer solutions varied between 4.7 and 8.5, in which range it has no significant effect on the degree of ionization or the conductivity.

Results and Discussion

Calculation of Conductivity Results.—We calculate the equivalent conductance, Λ_p, of the polyphosphate by the equation

$$\Lambda_p = \frac{1000(\kappa_{ps} - \kappa_s)}{N_p} + m_s \times \frac{d\Lambda_s}{dm_s} \times \frac{(m_s - m_s')}{N_p} \qquad (3)$$

In the first term on the right-hand side, κ_{ps} and κ_s represent the specific conductivities of the salt solution with and without added polyphosphate, respectively, with N_p being the polyphosphate normality. The second term on the right-hand side is a correction factor to account for the effect of the added polyelectrolyte on the conductivity of the simple electrolyte. This effect is taken into account by considering the polyelectrolyte chain and its ionic atmosphere to compress the simple electrolyte from its stoichiometric molarity m_s to an effective higher molarity m_s' which is the molarity which would be observed in a typical Donnan membrane equilibrium experiment on the polymer-free side of the membrane. This electrolyte compression which has been discussed elsewhere[18] then causes a decrease in Λ_s, the equivalent conductance of the salt. The derivation of eq. 3 is given in the Appendix. The derivative was determined from data representing Λ_s as a function of m_s which were obtained either from the literature[19] or from our own measurements. The quantity $[(m_s - m_s')/N_p]$ was calculated from data of Strauss and Ander.[18] Since this quantity was independent of the polyphosphate concentration, the correction term in eq. 3 was also. The correction term represented about 6% of Λ_p in the TMA^+ case, 5% in the Na^+ case, 3% in the K^+ case and 7% in the Li^+ case.

The equivalent conductance of the polyphosphates in 0.2 M solutions of the various cation bromides are shown as a function of N_p in Fig. 1. It is seen that there is no systematic effect of the polymer normality on Λ_p in the concentration region investigated. Therefore, horizontal lines were drawn in all cases.

The values of Λ_p so obtained then were used to calculate i, the degree of ionization of the polyphosphate. The results of the calculation are shown in Table I. The first two columns give the nature and molarity of the aqueous electrolyte solution used as the solvent. The third and fourth columns contain the equivalent conductance and electrophoretic mobility[9] of the polyphosphate, respectively. In the fifth column the equivalent conductance of the simple electrolyte is presented. The transference number of the cation, t_c, is given in the next column. This quantity is obtained by

---

[8] Λ_p represents the equivalent conductance of the electroneutral polyelectrolyte, *i.e.*, the macro-ion and its equivalent of counterions.

[9] U. P. Strauss and P. D. Ross, THIS JOURNAL, **81**, 5295 (1959).

[10] U. P. Strauss, E. H. Smith and P. L. Wineman, *ibid.*, **75**, 3935 (1953).

[11] J. R. Van Wazer, *ibid.*, **72**, 647 (1950).

[12] R. K. Iler, *J. Phys. Chem.*, **56**, 1086 (1952).

[13] T. Shedlovsky, THIS JOURNAL, **52**, 1793 (1930).

[14] D. Edelson and R. M. Fuoss, *J. Chem. Ed.*, **27**, 610 (1950).

[15] G. Jones and G. M. Bollinger, THIS JOURNAL, **53**, 411 (1931).

[16] T. Shedlovsky in "Physical Methods of Organic Chemistry," Vol. I, A. Weissberger, ed., Interscience Publishers, Inc., New York, N. Y., 1949, p. 1666, Fig. 10.

[17] G. Jones and B. C. Bradshaw, THIS JOURNAL, **55**, 1780 (1933).

[18] U. P. Strauss and P. Ander, *ibid.*, **80**, 6496 (1958).

[19] "International Critical Tables," Vol. VI, McGraw-Hill Book Co., New York, N. Y., 1928, p. 235. Actually, for convenience, Λ_s *vs.* $\sqrt{m_s}$ plots were employed.

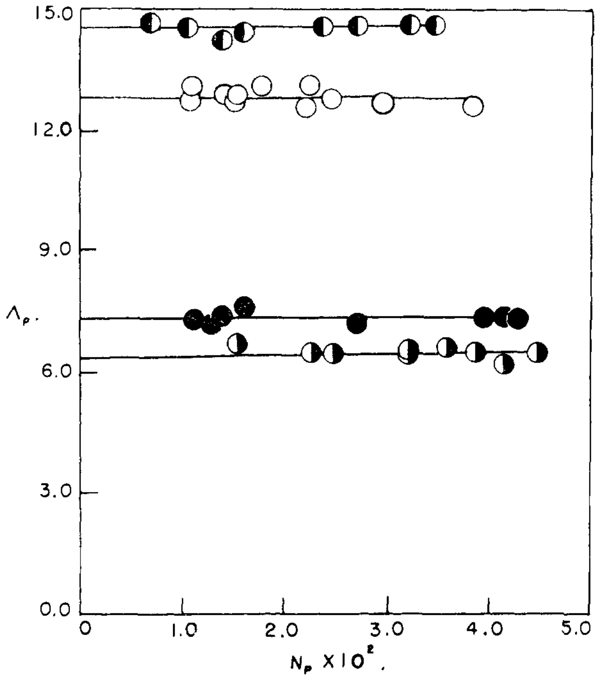

Fig. 1.—Equivalent conductance of long-chain polyphosphates in 0.2 N electrolyte solution as a function of the polymer concentration: ◑, LiPP(DP = 102) in LiBr; ●, NaPP(DP = 130) in NaBr; ○, KPP(DP = 8000) in KBr; ◐, TMAPP(DP = 7800) in TMABr.

dividing the limiting equivalent conductance of the cation by the limiting equivalent conductance of the simple electrolyte.[20] The quantity λ_c in the next column is then the product of Λ_s and t_c. The assumption involved in this procedure that t_c is independent of the electrolyte concentration is adequate for our purposes. The last column contains i, the degree of ionization of the polyphosphate, as calculated by eq. 2.

TABLE I

ELECTRICAL TRANSPORT DATA AND DEGREES OF IONIZATION OF POLYPHOSPHATES IN 0.2 M ELECTROLYTE SOLUTIONS AT 0°

Electrolyte	m_s	Λ_p	$u \times 10^{4\,a}$	Λ_s	t_c	λ_c	i
LiBr	0.203	6.51	1.23	51.1	0.313	16.0	0.233
NaBr	.199	7.35	1.14	57.2	.384	22.0	.223
KBr	.216	12.8	1.41	70.8	.488	34.6	.266
TMABr	.209	14.7	2.07	48.3	.362	17.5	.392

[a] From reference 9.

The dependence of i on u is represented graphically in Fig. 2. It is evident that the data lie on a straight line which passes through the origin and can be represented by the relation

$$i = u/(5.2 \times 10^{-4}) \qquad (4)$$

The proportionality between i and u provides strong experimental evidence for the constancy of the friction coefficient and for the validity of the hydrodynamic theories assuming free draining and the absence of relaxation effects[2-4] at 0.2 ionic strength.

The denominator on the right-hand side of equation 4 previously was predicted to be 3.2×10^{-4}, based on equation 1 and on the estimated size of a hypothetical spherical monomer unit.[6] The present result is of the right order of magnitude but indicates that the polyphosphate chain offers somewhat less friction to solvent flow than was anticipated on the basis of a geometrical bead model. A cylindrical segment model might prove more appropriate.

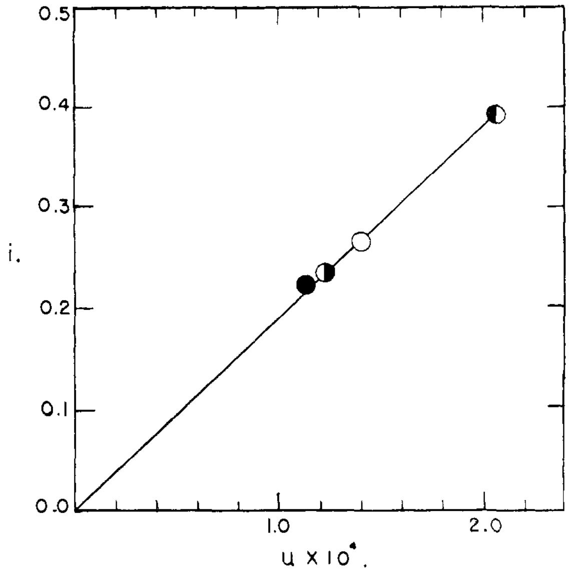

Fig. 2.—Relationship between degree of ionization and electrophoretic mobility of long-chain polyphosphates in 0.2 N cation bromide solutions: ◑, Li^+; ●, Na^+; ○, K^+; ◐, TMA^+.

Equation 4 furnishes a means of determining the degree of ionization of polyphosphates from the electrophoretic mobility alone. This possibility is especially useful for systems containing several cations where the Kohlrausch equation 2 is not directly applicable. However, one might expect the friction constant eventually to increase as the size of the bound cation is increased beyond a certain (as yet undetermined) point; therefore, eq. 4 should not be used for cations larger than TMA^+ without first testing its validity by combined electrophoresis and conductance measurements.

Appendix

Derivation of Equation 3.—The equivalent conductance of the polyphosphate is given by the equation.

$$\Lambda_p = \frac{1000(\kappa_{ps} - \kappa_{se})}{N_p} \qquad (3a)$$

where κ_{se} is the effective specific conductance of the electrolyte solution serving as the solvent, and the other symbols have been defined previously. From the discussion in the text it is clear that

$$\kappa_{se} = \kappa_s \left(\frac{\Lambda_{se}}{\Lambda_s}\right) \qquad (3b)$$

$$= \kappa_s - \kappa_s \left(\frac{\Lambda_s - \Lambda_{se}}{\Lambda_s}\right) \qquad (3c)$$

$$= \kappa_s - \frac{m_s}{1000}(\Lambda_s - \Lambda_{se}) \qquad (3d)$$

---

[20] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Academic Press, Inc., New York, N. Y., 1955, p. 454.

By means of a first-order power series expansion, we obtain

$$\Lambda_s - \Lambda_{se} = \left(\frac{d\Lambda_s}{dm_s}\right) \times (m_s - m_s') \qquad (3e)$$

where m_s' has been defined in the text as the effective electrolyte concentration. We then have

$$\kappa_{se} = \kappa_s - \frac{m_s}{1000} \times \left(\frac{d\Lambda_s}{dm_s}\right) \times (m_s - m_s') \qquad (3f)$$

By combining equations 3a and 3f, we obtain equation 3 as given in the text.

NEW BRUNSWICK, NEW JERSEY

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS, THE STATE UNIVERSITY]

Counterion Binding by Polyelectrolytes. III. Stability Constants for the Binding of Univalent Cations by PO_3^--Groups of Polyphosphates from Electrophoresis Measurements[1]

BY ULRICH P. STRAUSS AND PHILIP D. ROSS

RECEIVED APRIL 23, 1959

The degree of binding of alkali metal ions to long-chain polyphosphates has been determined by electrophoresis measurements at 0° in aqueous solutions maintained at 0.2 ionic strength with tetramethylammonium bromide. The method depends on an empirical calibration with Ca^{++}, Mg^{++} and Mn^{++}, which are essentially completely bound at divalent ion to polyphosphate normality ratios up to 0.5. If the alkali metal ions and the tetramethylammonium ions are considered as site-bound, the association of individual PO_3^--groups with the univalent cations follows the Law of Mass Action modified for the effects of the high potential near the polyelectrolyte chain, of the nearest neighbor interactions of adjacent PO_3^--groups and of the changes in the molecular dimensions. The binding constants decreased in the order of increasing crystal radii of the cations, namely, $Li^+ > Na^+ > K^+ > Cs^+ \approx (CH_3)_4N^+$.

In the first paper of this series, the effects of lithium, sodium, potassium and tetramethylammonium (TMA^+) ions on the electrophoretic mobility of long-chain polyphosphates were compared.[2] The results indicated that the alkali metal ions were more strongly bound to the polyphosphate than was the TMA^+. However, a meaningful quantitative comparison of the data was complicated by many factors, such as variations in the ionic environment and in the molecular dimensions of the polymer chain.

In the work described in this paper, considerable simplification was achieved by comparing the effects of small amounts of various alkali metal ions on the electrophoretic mobility of the polyphosphate chain in the presence of a large excess of TMABr. By keeping the total ionic strength of simple electrolyte at 0.2 *N*, the comparison could be made while the polymer chain was maintained in a relatively constant condition. With certain assumptions it also was found possible to determine the extent of binding quantitatively and to calculate binding constants. Such information contributes to an understanding of polyelectrolyte behavior and may also help to elucidate certain biological phenomena.

Experimental

The potassium polyphosphate employed was a Kurrol's salt (our sample No. H-2170W) with weight-average degree of polymerization P_w equal to 9,400.[3]

Electrophoretic mobilities were determined at 0° in a Perkin–Elmer Model 38 Tiselius apparatus by the method previously described.[4] Single sharp boundaries were obtained by slowly adding solvent from a glass tube with a fine capillary tip when bringing the boundaries into view. This improvement in the technique is due to M. Levy. In general, the ascending boundaries moved 1-5% faster than the descending boundaries. Average values of the mobilities are used throughout this paper. There was no effect of polyphosphate concentration on the mobility in the concentration range employed (0.01–0.02 *N*). The *p*H of all solutions was maintained between 6.2 and 7.5, in which range it did not affect the mobility.[2] Each solution of the potassium polyphosphate in 0.2 *N* TMABr was introduced into a Visking cellulose bag and dialyzed against several portions of this TMABr solution to eliminate the potassium ion. Then the dialysis was continued against several portions of the alkali metal bromide–TMABr solution against which the boundaries were to be formed.[5] Tumbling at 5° was employed to ensure the attainment of equilibrium. Dialysis for electrophoresis of the divalent counterions studied (Ca^{++}, Mg^{++} and Mn^{++}) was conducted by a slightly different technique. After the removal of the K^+, carried out as described above, a portion of the polyphosphate solution was pipetted into a new dialysis bag and an amount of divalent cation (M^{++}) bromide solution, calculated to give the desired degree of binding, was added from a micro-buret. The dialysis bag was sealed and immersed in a twenty-fold excess of 0.20 *M* TMABr. Equilibrium was obtained by tumbling for 24–36 hr. at 5°.[6]

Conductivity water prepared by passing distilled water through a mixed-bed ion-exchange resin and whose specific conductance ranged from 0.3 to 0.8×10^{-6} reciprocal ohms per cm. at 0° was used to make up all solutions employed in this investigation.

---

[1] The contents of this paper are contained in a thesis to be submitted by P. D. Ross to the Graduate School of Rutgers, The State University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. This investigation was supported by a grant from the United States Atomic Energy Commission under Contract AT(30-1)1018.

[2] U. P. Strauss, D. Woodside and P. Wineman, *J. Phys. Chem.*, **61**, 1353 (1957).

[3] This sample was prepared by R. Hubbard who also determined its P_w by viscometry. The sample was washed with water to remove any low molecular weight species as described by R. Pfanstiel and R. K. Iler, THIS JOURNAL, **74**, 6059 (1952).

[4] U. P. Strauss, N. L. Gershfeld and H. Spiera, *ibid.*, **76**, 5909 (1954).

[5] It was previously established that after three to four changes, the outside solution maintains its original composition.

[6] As a check in a few cases, both the inside and outside solutions were analyzed for Ca^{++} after completion of the dialysis. These analyses were carried out by flame photometry using the internal standard procedure. (L. L. Merritt, H. H. Willard and J. A. Dean, "Instrumental Methods of Analysis," D. Van Nostrand Co., New York, N. Y., 1951, pp. 79–83). All of the added Ca^{++} was found in the inside solutions containing the polyphosphate, while no Ca^{++} could be detected in the outside solutions. These analyses, which were carried out up to Ca^{++} to polyphosphate normality ratios of 0.3 and were accurate to ±0.02 in this quantity, lend support to the assumption of virtually complete binding of Ca^{++} in this range.