

Table II

Copper complex	g_{\perp} factors at 77°K. (± 0.0003)		
	Acetone	1-Chloro-naphthalene	Pyridine
Desoxophylloerythrin monomethyl ester	2.0616 ^a	2.0641 ^a	2.0752 ^a
Desoxophylloerythroetioporphyrin	2.0616 ^a	2.0641 ^a	2.0752 ^a
Etioporphyrin II	2.0616	2.0643	2.0756
Pyrroporphyrin XV monomethyl ester	2.0627	2.0643	2.0747
Mesoporphyrin IX dimethyl ester	2.0624	2.0646	2.0753
Phylloporphyrin XV monomethyl ester	2.0633	2.0653	2.0761
Deuterioporphyrin IX dimethyl ester	2.0621	2.0657	2.0756
Protoporphyrin IX	<i>b</i>	<i>b</i>	2.0761
Tetraphenylporphin	<i>b</i>	2.0658	2.0776
Pyropheophorbide <i>a</i> monomethyl ester	2.0618 ^a	2.0660	2.0776
Diacetyldeuterioporphyrin IX dimethyl ester	<i>c</i>	2.0668	2.0762 ^a
Chlorin <i>e</i> -6 trimethyl ester	<i>c</i>	2.0681 ^a	2.0835 ^a
Dinitrodeuterioporphyrin IX dimethyl ester	<i>c</i>	2.0718	2.0930 ^a

Silver complex	g factors at 77°K. (± 0.0003)				
	Acetone		1-Chloronaphthalene		Pyridine
	g_{\parallel}	g_{\perp}	g_{\parallel}	g_{\perp}	
Mesoporphyrin IX dimethyl ester	2.1065	2.0305	2.1075	2.0322	<i>c</i>
Etioporphyrin II	2.1060	2.0304	2.1066	2.0325	<i>c</i>
Deuterioporphyrin IX dimethyl ester	2.1040	2.0294	2.1070	2.0317	<i>c</i>
Diacetyldeuterioporphyrin IX dimethyl ester	<i>c</i>		<i>c</i>		<i>c</i>

^a Broadening. ^b Insoluble. ^c Complete broadening.

values, which accompanies a change in the solvent from castor oil to 1-chloronaphthalene, occurs on both the perpendicular and parallel sides of the spectrum. The arrangement of the molecular orbitals for these systems, therefore, must be one for which the B_{2g} orbital, to which d_{xy} of the metal contributes, is below that for the degenerate d_{xz} and d_{yz} levels. This arrangement was first proposed by Roberts and Koski for

copper etioporphyrin II^{3b} and more recently used to explain the spin resonance spectra of crystalline copper phthalocyanine.^{3d} A summary of the g values found is given in Table II.

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Volume Changes as a Criterion for Site Binding of Counterions by Polyelectrolytes¹

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Exploratory measurements have been made of the volume changes accompanying the interactions between various polyelectrolytes containing sulfonate, carboxylate, phosphonate, or phosphate groups and a number of alkali and alkaline earth metal ions. With one exception, all the polyanions showed effects large enough to implicate site binding as the cause. Various structural features of the polyelectrolytes, such as the nature and the spacing of the anionic groups, the degree of dissociation, and the cross linking, were found to have a pronounced influence

on the volume changes. The largest effects were observed with the long-chain polyphosphates. For the reaction $Li^+ + -PO_3^- \rightarrow -PO_3Li$, the volume increase ranged from 13 to 16 ml. per mole of participating lithium ion, depending on the over-all charge on the polyphosphate. In the case of analogous reactions of polyphosphate with sodium and magnesium ions, the corresponding ranges were 12.2 to 14.5 ml. per mole of Na^+ and 42 to 52 ml. per mole of Mg^{2+} . The method employed promises to be useful for studying the nature of site binding by polyelectrolytes and ion-exchange resins. Our results appear to be the most direct experimental evidence obtained so far for the role of the solvent postulated in theories dealing with cation sequences observed in a large variety of phenomena occurring in both synthetic and biological systems.

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The low osmotic activity of counterions in polyelectrolyte solutions is usually attributed to two types of "binding." One is the specific association between counterions and the fixed ionic groups of the macroion and is known as "site binding." The other is the effect of the large electrostatic field of the macroion on the dissociated ions in its vicinity and has been denoted by "ionic atmosphere binding."²⁻⁴

For a large number of polyelectrolyte systems and especially for the alkali metal salts of polyanions, there still appears to be some difference of opinion concerning the existence, the nature, and the extent of site binding. Rice, Nagasawa, and their co-workers could find no evidence for ion-pair formation either by Raman spectroscopy and nuclear magnetic resonance studies in solutions of polystyrenesulfonic acid^{5,6} or by activity coefficient determinations in solutions of short-chain polyethylenimine salts.⁷ On the basis of these studies they ruled out ion-pair formation at charged sites of polyions, though they did not exclude the possibility that the counterion distribution could have local maxima near peaks in the charge density on the polymer chain.^{6,7} This view received further support by the findings of Kotin and Nagasawa⁸ and of Alexandrowicz and Katchalsky⁹ that counterion distributions about a cylindrical macroion model, calculated from solutions of the Poisson-Boltzmann equation, could account for potentiometric titration and Donnan membrane equilibrium data obtained with a number of anionic polyelectrolytes entirely in terms of ionic atmosphere binding of the alkali metal counterions. However, more recently it was shown that the same theory could explain most of the same data equally well, if not better, if a portion of the anionic sites was postulated to form ion pairs with the alkali metal ions.⁴ Positive evidence for site binding came from observations of reversals of the normal binding order of alkali metal ions in potentiometric titrations of polycarboxylic acids^{10,11} and in membrane equilibrium and electrical transport studies of polyphosphates.¹²⁻¹⁵ Furthermore, with the polyphosphates specific effects of the alkali metal ions on molecular dimensions, second virial coefficients, and phase separation behavior were noted which appear to be explainable only by invoking site binding.^{12,16-18} More recently, very similar effects were also reported for DNA.¹⁹

(2) F. Oosawa, N. Imai, and I. Kagawa, *J. Polymer Sci.*, **13**, 93 (1954).

(3) H. Morawetz, *Fortschr. Hochpolymer. Forsch.*, **1**, 1 (1958).

(4) L. M. Gross and U. P. Strauss, Symposium on Electrolyte Solutions, Electrochemical Society, Toronto, 1964, in press.

(5) S. Lapanje and S. A. Rice, *J. Am. Chem. Soc.*, **83**, 496 (1961).

(6) L. Kotin and M. Nagasawa, *ibid.*, **83**, 1026 (1961).

(7) S. Lapanje, J. Haebig, H. T. Davis, and S. A. Rice, *ibid.*, **83**, 1590 (1961).

(8) L. Kotin and M. Nagasawa, *J. Chem. Phys.*, **36**, 873 (1962).

(9) Z. Alexandrowicz and A. Katchalsky, *J. Polymer Sci.*, **A1**, 3231 (1963).

(10) H. P. Gregor, L. B. Luttinger, and E. M. Loebel, *J. Am. Chem. Soc.*, **76**, 5879 (1954).

(11) H. P. Gregor and M. Frederick, *J. Polymer Sci.*, **23**, 451 (1957).

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

(13) U. P. Strauss and S. Bluestone, *J. Am. Chem. Soc.*, **81**, 5292 (1959).

(14) U. P. Strauss and P. D. Ross, *ibid.*, **81**, 5295, 5299 (1959).

(15) U. P. Strauss and A. Siegel, *J. Phys. Chem.*, **67**, 2683 (1963).

(16) U. P. Strauss and P. L. Wineman, *J. Am. Chem. Soc.*, **80**, 2366 (1958).

(17) P. D. Ross and U. P. Strauss, *ibid.*, **82**, 1311 (1960).

(18) U. P. Strauss and P. Ander, *J. Phys. Chem.*, **66**, 2235 (1962).

(19) P. D. Ross and R. L. Scruggs, *Biopolymers*, **2**, 79, 231 (1964).

Some of the evidence cited indicates that site binding is accompanied by the release of water molecules from the solvation shells of the participating species, and this phenomenon may serve as a useful criterion for characterizing site binding and for distinguishing it from ionic atmosphere binding which can be expected to leave the solvation shells intact. Since for many ions the hydration layer shows electrostriction effects, site binding may be accompanied by measurable volume increases. Such volume changes have been observed for the binding of hydrogen ions by both low and high molecular weight bases.^{20,21} We have therefore carried out exploratory dilatometry experiments involving the interactions of several alkali and alkaline earth metal ions with a number of polyanions.

Results and Discussion

Comparison of Gross Effects. Table I summarizes the results from the following type of experiment. Three milliliters of initial solution I containing 0.57×10^{-3} monomole of polyelectrolyte in the tetramethylammonium (TMA) form and having been brought to membrane equilibrium against a 0.2 N TMAcI solution is mixed with 1 ml. of initial solution II containing 0.19 mequiv. of metal chloride and 0.01 mequiv. of TMAcI. The resulting volume increase, Δv_t , is given in ml./equiv. of total metal ion. The polyanions used were polystyrenesulfonate (PStySO₃⁻), polyvinylsulfonate (PViSO₃⁻), polyacrylate (PViCOO⁻), polymethacrylate (PCH₃PViCOO⁻), singly and doubly charged polyvinylphosphonate (PViPO₃H⁻ and PViPO₃²⁻, respectively), polyphosphate (PPO₃⁻), and cross-linked polystyrenesulfonate (PStySO₃⁻, 8% DVB).

Table I. Comparison of Δv_t Values^a

	Li ⁺	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺
PStySO ₃ ⁻	0.9	1.2	1.5	2.1	2.9
PViSO ₃ ⁻	3.4	4.7	5.6	7.2	10.6
PViCO ₂ ⁻	4.5	4.1	3.9	11.7	17.3
PCH ₃ PViCO ₂ ⁻	2.9	3.1	3.0	9.2	13.7
PViPO ₃ H ⁻	6.8	5.9	5.3	15.8	22.2
PViPO ₃ ²⁻	9.6	9.4	7.7	19.6	24.7
PPO ₃ ⁻	11.3	11.0	9.6	24.4	25.5
PStySO ₃ ⁻ , 8% DVB	5.4	13.0

^a The Δv_t values are expressed in ml./equiv. of total metal ion present (see text).

Since in the absence of association or dissociation reactions similar mixing experiments with simple electrolytes rarely produce volume changes greater than 1 in these units,²² we may consider those data in Table I which significantly exceed this value an indication of specific cation-polyanion interactions.²³ If we ignore

(20) J. Rasper and W. Kauzmann, *J. Am. Chem. Soc.*, **84**, 1771 (1962).

(21) W. Kauzmann, A. Bodanzky, and J. Rasper, *ibid.*, **84**, 1777 (1962).

(22) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958, Chapter 8.

(23) While, in principle, conformation changes could also produce volume changes of the magnitude observed, we consider it extremely unlikely that with the flexible-coil type of polymers treated here such conformation changes occur. On the other hand, changes in the molecular dimensions which do occur¹⁶ are not likely to cause volume changes. Some experimental evidence for the correctness of the latter opinion is presented in the Experimental section.

a number of secondary effects to be discussed below, the Δv_t values may be related to Δv , the volume change expressed in ml./equiv. of bound metal ion by the relation

$$\Delta v_t = [(M)_b/(M)_t]\Delta v \quad (1)$$

where $(M)_b$ and $(M)_t$ are the normalities of bound and total metal ion, respectively, after mixing. In most cases treated here, no data are available to calculate $(M)_b$.²⁴ However, since the ratio in brackets is a measure of the amount of bound metal ion, and since Δv would be expected to increase with increasing tightness of binding, the quantity Δv_t should be a rather sensitive indicator of site binding and serve as a basis for comparison both among the polyanions and among the metal ions.

Several aspects of the experimental data support this expectation. First of all, there are large differences among the various polyelectrolytes. These differences cannot be due to ionic atmosphere binding since such binding depends predominantly on the linear charge density of the polyanions^{4,8,25} and, with the exception of the doubly charged polyvinylphosphonate, these charge densities are approximately the same for all the polyelectrolytes in Table I. Furthermore, whereas the Δv_t values are very large with the polyphosphates for which significant site binding has been demonstrated by other methods,¹²⁻¹⁸ they are very small with the polystyrenesulfonate for which site binding of hydrogen ion was undetectable by Raman spectroscopy and n.m.r. techniques.^{5,6}

Our results then indicate that site binding of alkali and alkaline earth metal ions takes place to varying degrees with the majority of commonly investigated polyelectrolytes. The differences among the polyanions may be due to a number of structural features. The importance of the anionic group can be seen from a comparison of the polyvinylsulfonate, the polyacrylate, and the singly charged polyvinylphosphonate. The phosphonate group gives much larger effects than the carboxylate and the sulfonate groups; furthermore, while with the sulfonate the effects increase with decreasing size of the hydrated alkali metal ions, with the other two groups this order is reversed. The fact that these alkali metal sequences find their exact parallel in the cation affinity order of loosely cross-linked ion-exchange resins²⁶ (i.e., for sulfonate resins the sequence in order of decreasing affinity is $K^+ > Na^+ > Li^+$,²⁷ while for carboxylate²⁸ and phosphonate²⁹ resins this order is reversed) is further evidence that our observed volume changes are caused by site binding. Similar cation sequences have also been observed in studies of membrane potentials,³⁰ of electrophoretic mobility of colloids,³¹ and of ion-transport phenom-

ena.³² These effects have been ascribed to a competition between water of hydration and anion for a position near a given cation and ultimately to the charge distributions, polarizabilities, and effective field strengths of the participating ions.³¹⁻³⁴ Our results furnish direct experimental evidence in support of the role attributed to the solvent by such theoretical explanations. Interpreted in the light of such theories, our data indicate that among the anionic groups studied here the phosphate and phosphonate groups have the highest and the sulfonate groups the lowest field strength in their immediate vicinities.

The much smaller volume changes observed with polystyrenesulfonate as compared with polyvinylsulfonate are very likely due to the differences in the spacing of the sulfonate groups, making cooperation of two adjacent groups in the binding of a cation more difficult in the case of the styrene polymer. Ascribing these effects instead to a delocalization of the negative charge of the sulfonate by the phenyl group seems unjustified in the light of the findings of Bell and co-workers that the sulfonate group is weakly electron attracting at short distances owing to a considerable positive charge on the sulfur atom.^{35,36} The smaller differences between the polyacrylate and polymethacrylate are probably also attributable to a greater likelihood of cooperation by nearby carboxylate groups in the case of the more flexible polyacrylate.

The expected effects of a charge increase of either the polyanion or the cation is observed by comparing the singly with the doubly charged polyvinylphosphonates on the one hand, and the alkali with the alkaline earth metal ions on the other. However, it is noteworthy that the polyphosphates whose groups are singly charged give a larger effect than the doubly charged polyvinylphosphonate. This difference may be due to the ease with which two adjacent phosphate groups may chelate a metal ion with the formation of a six-membered ring. Finally, the rather large effect of another structural feature, namely, cross linking, is seen by comparing the first and last rows of Table I.

Volume Changes per Equivalent of Bound Cation. For a few polyphosphate systems the degree of binding of metal ions has been measured, and thus Δv , the volume increase in ml./equiv. of bound metal ion, can be determined. The results of such determinations for Li^+ , Na^+ , and Mg^{2+} ions are given in Table II. Each initial solution I contained tetramethylammonium polyphosphate and was brought to membrane equilibrium against 0.2 N TMACl. Each initial solution II contained the appropriate metal chloride, and the total chloride normality was brought to 0.2 with TMACl. The amounts of solutions I and II and their polyphosphate and metal ion normalities, respectively, are given in columns 2 to 5. The final solution, obtained by

(24) For several of the polyphosphate systems such data are available, and Δv will be given below.

(25) The linear charge density is defined as the number of fixed electronic charges per unit contour length of the polyanion.

(26) F. Helfferich, "Ion Exchange," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 5.

(27) G. E. Boyd and B. A. Soldano, *Z. Elektrochem.*, **57**, 162 (1953).

(28) H. P. Gregor, M. J. Hamilton, R. J. Oza, and F. Bernstein, *J. Phys. Chem.*, **60**, 263 (1956).

(29) J. I. Bregman and Y. Murata, *J. Am. Chem. Soc.*, **74**, 1867 (1952).

(30) Reference 26, Chapter 8.

(31) H. G. Bungenberg de Jong in "Colloid Science," Vol. II, H. R. Kruyt, Ed., Elsevier Publishing Co., Inc., New York, N. Y., 1949, Chapter 9.

(32) G. Eisenman in "Symposium on Membrane Transport and Metabolism," Academic Press, New York, N. Y., 1961, pp. 163-179.

(33) G. Wiegner and H. Jenny, *Kolloid-Z.*, **42**, 268 (1927).

(34) G. N. Ling, "A Physical Theory of the Living State," Blaisdell, New York, N. Y., 1962.

(35) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, pp. 99-101.

(36) R. P. Bell and B. A. W. Collier, *Trans. Faraday Soc.*, **60**, 1087 (1964).

mixing solutions I and II, is described in the next three columns which contain the polyphosphate normality, the normality of free metal ion, $(M)_f$, and the degree of binding β , i.e., the fraction of phosphate groups neutralized by bound metal ions. The latter two quantities were calculated from membrane equilibrium

arise from site binding of alkali and alkaline earth metal ions by polyanions. We do not want to imply, however, that the site binding of these ions has covalent character. Explanations in terms of classical electrostatic interactions have been proposed which appear to be quite satisfactory.^{32,34} Neither do we wish to

Table II. Volume Changes per Equivalent of Bound Metal Ion

Metal ion in soln. II	Solution I ^a		Solution II ^a		Final solution ^a			Δv , ml./equiv.
	Vol., ml.	(PPO ₃ ⁻)	Vol., ml.	(M)	(PPO ₃ ⁻)	(M) _f × 10 ³	β	
Li ⁺	3.5	0.150	0.5	0.150	0.131	2.2	0.126	16.0
	3.5	0.188	0.5	0.188	0.165	2.3	0.129	15.9
	3.0	0.108	1.0	0.108	0.081	6.4	0.255	13.9
	3.0	0.150	1.0	0.150	0.113	7.3	0.268	13.8
	2.0	0.108	2.0	0.108	0.054	30.8	0.426	13.0
Na ⁺	2.0	0.150	2.0	0.150	0.075	40.5	0.462	13.0
	14.0	0.108	2.0	0.108	0.094	3.1	0.110	14.5
	3.5	0.188	0.5	0.188	0.165	3.5	0.122	14.3
	12.0	0.108	4.0	0.108	0.081	8.4	0.230	12.8
	3.0	0.188	1.0	0.188	0.141	10.6	0.258	13.1
	8.0	0.108	8.0	0.108	0.054	30.6	0.43	12.5
	2.0	0.188	2.0	0.188	0.094	46.0	0.51	12.0
Mg ²⁺	4.0	0.108	12.0	0.108	0.027	65.0	0.58	12.2
	3.5	0.132	0.5	0.101	0.116	<10 ⁻³	0.109	26.1
	3.0	0.132	1.0	0.101	0.099	0.004	0.255	25.4
	2.5	0.132	1.5	0.101	0.083	0.2	0.457	22.7
	2.0	0.132	2.0	0.101	0.066	10	0.61	21

^a For a complete description of these solutions see text.

data in the case of lithium and sodium ions,¹⁴ and from ion-exchange resin distribution results in the case of magnesium ion.¹⁵ In the final column is given Δv , obtained by the relation

$$\Delta v = 1000\Delta V/[V\beta(\text{PPO}_3^-)] \quad (2)$$

where ΔV and V are the measured volume change and the volume of the final solution, respectively. Two features of these results are noteworthy. One is that the Δv values are of the same magnitude as those reported for binding reactions between hydrogen ion and hydroxide or carboxylate ions.^{20,21} In fact, the volume changes per mole of bound magnesium which are twice the values given in Table II are apparently the largest such volume changes described so far. The other feature is that the Δv values decrease somewhat with increasing β . This effect has also been reported for polycarboxylate-hydrogen ion interactions and has been ascribed to a decrease of the electrostriction of the solvent around the polyanion as the charge on the latter decreases.²¹ An alternate interpretation is that the metal ions are more tightly bound at lower β with a consequent release of more water of solvation. The latter interpretation would imply that the nature of the binding reaction between a metal ion and a polyelectrolyte segment changes with the polyelectrolyte charge, and that the electrical free energy correction to the binding constant depends not only on the electrostatic potential of the macroion but also on the changes in the solvation effects.

The similarity between our results and those obtained with weak polyacids^{20,21} where site binding of hydrogen ion is known to take place must be considered as further strong evidence that the volume changes observed by us

convey the impression that site binding precludes ionic atmosphere binding. The latter must occur, to varying extents, in practically all cases of experimental interest.³⁷ A theoretical treatment relating the extents of site binding and ionic atmosphere binding is given elsewhere.⁴

Experimental

Dilatometry. Volume changes were measured at 30° in Linderstrom-Lang dilatometers immersed in a thermostat controlled within 0.001°, according to the description of Rasper and Kauzmann.²⁰ For all systems studied it was ascertained that the carefully purified kerosene which covers the aqueous solutions and reaches into the measuring capillary had no effect on the volumes of the initial and final solutions.

Polyelectrolytes. The polyphosphate and polymethacrylate samples were prepared in this laboratory, the polyacrylate sample by Miss M. Hoff of Johnson and Son, Inc. Samples of sodium polystyrenesulfonate and sodium polyvinylsulfonate were obtained from Dr. W. N. Vanderkooi of the Dow Chemical Co. and Dr. D. S. Breslow of the Hercules Powder Co., respectively.³⁸ The polyvinylphosphonate was a research sample obtained from Farbwerke Hoechst. The molecular weights of these samples were between 10⁴ and 10⁶. A cross-linked polystyrenesulfonate sample (Dowex 50-8X) was described previously.¹⁵

Effects of Concentration Changes. As has been pointed out, volume changes due to the dilution of the

(37) C. T. O'Konski, *J. Phys. Chem.*, **64**, 605 (1960).

(38) We wish to thank Miss Hoff and Drs. Vanderkooi and Breslow for their kindness in supplying us with these samples.

solutes on mixing are not always negligible.²¹ We have tried to keep such effects to a minimum by choosing our initial electrolyte concentrations so as to keep the effective ionic strength approximately constant. In the absence of sufficient literature data, we have employed the following experimental procedure to verify that we succeeded in our aim: 14 ml. of solution I being 0.19 *N* in TMAPPO₃ and 0.156 *N* in TMACl (*i.e.*, in membrane equilibrium with 0.2 *N* TMACl) was mixed with 2 ml. of solution II being 0.19 *N* in LiCl and 0.01 *N* in TMACl. Mixing produced a volume increase, ΔV , equal to 5.29 μl . Three similar experiments were now performed, each with a different modification of the first experiment. In the second experiment the polyphosphate in solution I was replaced by an equivalent amount of chloride ion. This time the volume increase, ΔV_2 , was 0.085 μl . In the third experiment the lithium ion in solution II was replaced by an equivalent amount of TMA⁺. Here ΔV_3 was 0.015 μl . The fourth time, both these changes were made at the same time. ΔV_4 was 0.02 μl . The corrected volume change, ΔV_{cor} , in which the dilution effects should cancel is given by $\Delta V_{\text{cor}} = \Delta V - \Delta V_2 - \Delta V_3 + \Delta V_4 = 5.21 \mu\text{l}$. In a similar such series of four experiments which differed from the foregoing one only in that 8 ml. each of solutions I and II was employed, ΔV was 9.23 μl . and ΔV_{cor} was 8.99 μl . In view of these findings, we did not consider it worthwhile to increase the number of our experiments by a factor of four in order to reap the slight benefit obtainable from these small corrections.

Effect of Competing Cations. With those of the polyanions which form weak acids the pH was found to decrease as a result of the mixing. Calculations showed that, because of the smallness of the indicated changes in the hydroxyl ion concentration, any conceivable volume changes which might have resulted from these well-known effects were negligible in our systems.

There exists some evidence that the TMA⁺ may also be site bound to polyanions, though to a much lesser extent than the metal ions.¹⁴ If this were so, some of the bound TMA⁺ ions would be released when the metal ions are bound, and this release might contribute to the observed volume change. The following ex-

periments were performed in order to obtain an estimate of the order of magnitude of this effect. TMAPPO₃ (0.123 *N*, 3 ml.) was mixed with 1 ml. of 4 *N* TMACl, with a volume increase of 6.98 μl . In a control experiment, where 3 ml. of 0.123 *N* TMACl was mixed with 1 ml. of 4 *N* TMACl (*i.e.*, where the polyphosphate was replaced by chloride ion), the volume increase was 6.90 μl . In two corresponding experiments in which 3-ml. portions of 0.074 *N* LiPPO₃ and of 0.074 *N* LiCl each were mixed with 1 ml. of 4 *N* LiCl, the volume decreased by 4.27 and 4.54 μl ., respectively. The volume changes in these experiments are due mainly to the dilution of the 4 *N* salt solutions.^{22,39} However, the differences between the original and the control experiments, if any, should be due mainly to an increase of the cation binding brought about by an increase of the cation concentration in the polyphosphate solution. In the case of the TMA⁺ experiments, this difference is 0.08 μl ., or 0.2 ml./monomole of PPO₃⁻; in the case of the Li⁺ experiments it is 0.27 μl ., or 1.2 ml./monomole of PPO₃⁻. With the use of the Δv values for Li⁺ in Table II, the Li⁺ result may be attributed to an increase of approximately 0.08 in the value of β . On the other hand, the TMA⁺ result is negligibly small; thus we may conclude either that the TMA⁺ ion is not site bound, or, if it is, that the resulting volume changes are insignificant.⁴⁰ Either way, the results lead to the tentative conclusion that we can ignore such volume effects.

Acknowledgment. The authors wish to thank Professor W. Kauzmann and Mrs. A. Bodanszky of Princeton University for their valuable suggestions, and Mr. Daniel Reichenberg of the National Chemical Laboratory, Teddington, England, for many stimulating discussions during his stay at Rutgers. A fellowship to Y. P. L. from the Lever Brothers Company is also gratefully acknowledged.

(39) The increase in volume occurring on dilution of the TMA⁺ systems has also been observed with other tetraalkylammonium salts: W. Y. Wen and S. Saito, *J. Phys. Chem.*, **68**, 2639 (1964). We want to thank Professor Wen for making his data available to us prior to publication.

(40) These results also show that the change in molecular dimensions which is known to be brought about by such an increase in the TMA⁺ concentration^{12,17} does not affect the solution volume. The alternate possibility that site binding of TMA⁺ and changes in molecular dimensions each independently produce volume effects which cancel each other is considered extremely remote.