

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

$$\Lambda_s - \Lambda_{s0} = \left( \frac{d\Lambda_s}{dm_s} \right) \times (m_s - m_s') \quad (3e)$$

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

$$\kappa_{s0} = \kappa_s - \frac{m_s}{1000} \times \left( \frac{d\Lambda_s}{dm_s} \right) \times (m_s - m_s') \quad (3f)$$

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

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[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 $\text{PO}_3^-$ -Groups of Polyphosphates from Electrophoresis Measurements<sup>1</sup>

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The degree of binding of alkali metal ions to long-chain polyphosphates has been determined by electrophoresis measurements at  $0^\circ$  in aqueous solutions maintained at 0.2 ionic strength with tetramethylammonium bromide. The method depends on an empirical calibration with  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$  and  $\text{Mn}^{++}$ , 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  $\text{PO}_3^-$ -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  $\text{PO}_3^-$ -groups and of the changes in the molecular dimensions. The binding constants decreased in the order of increasing crystal radii of the cations, namely,  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+ \approx (\text{CH}_3)_4\text{N}^+$ .

In the first paper of this series, the effects of lithium, sodium, potassium and tetramethylammonium ( $\text{TMA}^+$ ) ions on the electrophoretic mobility of long-chain polyphosphates were compared.<sup>2</sup> The results indicated that the alkali metal ions were more strongly bound to the polyphosphate than was the  $\text{TMA}^+$ . 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  $\text{TMA}^+$ . 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.<sup>3</sup>

(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).

Electrophoretic mobilities were determined at  $0^\circ$  in a Perkin-Elmer Model 38 Tiselius apparatus by the method previously described.<sup>4</sup> 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 pH of all solutions was maintained between 6.2 and 7.5, in which range it did not affect the mobility.<sup>2</sup> Each solution of the potassium polyphosphate in 0.2 *N*  $\text{TMA}^+$  was introduced into a Visking cellulose bag and dialyzed against several portions of this  $\text{TMA}^+$  solution to eliminate the potassium ion. Then the dialysis was continued against several portions of the alkali metal bromide- $\text{TMA}^+$  solution against which the boundaries were to be formed.<sup>5</sup> Tumbling at  $5^\circ$  was employed to ensure the attainment of equilibrium. Dialysis for electrophoresis of the divalent counterions studied ( $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$  and  $\text{Mn}^{++}$ ) was conducted by a slightly different technique. After the removal of the  $\text{K}^+$ , carried out as described above, a portion of the polyphosphate solution was pipetted into a new dialysis bag and an amount of divalent cation ( $\text{M}^{++}$ ) 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*  $\text{TMA}^+$ . Equilibrium was obtained by tumbling for 24-36 hr. at  $5^\circ$ .<sup>6</sup>

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

(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  $\text{Ca}^{++}$  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  $\text{Ca}^{++}$  was found in the inside solutions containing the polyphosphate, while no  $\text{Ca}^{++}$  could be detected in the outside solutions. These analyses, which were carried out up to  $\text{Ca}^{++}$  to polyphosphate normality ratios of 0.3 and were accurate to  $\pm 0.02$  in this quantity, lend support to the assumption of virtually complete binding of  $\text{Ca}^{++}$  in this range.

TABLE I  
 ELECTROPHORETIC MOBILITIES AND DERIVED BINDING PARAMETERS

M <sup>+</sup>	(M <sup>+</sup> ) <sup>a</sup>	$\times 10^4$	$i$	$\beta_M$	$\beta_{TMA}$	$\frac{-e\psi}{kT}$	$K_M^c$	$K_M^c$	$K_{TMA}^c$	$\frac{K_M}{K_{TMA}}$	$\frac{K_M}{(cor.)^d}$
None <sup>a</sup>	.....	2.07	0.397	...	0.603	3.04	.....	.....	0.083 ± 0.004	...	...
Li <sup>+</sup>	0.0025	1.99	.382	0.09	.53	2.92	5.1 ± 1.4	1.3 ± 0.4	.096 ± .004	13	1.1
	.005	1.91	.367	.17	.46	2.80	5.6 ± 0.9	1.6 ± .4	.110 ± .004	14	1.2
	.01	1.78	.342	.29	.37	2.61	6.2 ± .7	2.0 ± .3	.136 ± .004	15	1.2
	.03	1.62	.311	.45	.24	2.38	4.5 ± .4	1.7 ± .2	.162 ± .001	11	0.9
	.05	1.53	.294	.54	.17	2.24	3.9 ± .3	1.6 ± .2	.155 ± .003	11	.9
	.10 <sup>b</sup>	1.41	.271	...	...	2.07	.....	.....	.....	...	...
	.20	1.23	.236	.76	...	1.80	2.7 ± .2	1.4 ± .1	.....	...	...
Na <sup>+</sup>	.01	1.93	.370	.15	.48	2.83	2.4 ± .4	0.7 ± .2	.110 ± .004	5.9	0.5
	.03	1.70	.326	.37	.30	2.49	3.1 ± .3	1.1 ± .1	.160 ± .004	7.0	.6
	.05	1.55	.298	.52	.18	2.27	3.6 ± .3	1.5 ± .2	.172 ± .003	8.7	.7
	.10 <sup>b</sup>	1.42	.273	...	...	2.08	.....	.....	.....	...	...
	.20	1.14	.219	.78	...	1.67	3.4 ± .3	1.9 ± .2	.....	...	...
K <sup>+</sup>	.01	2.02	.388	.05	.56	2.96	0.7 ± .4	0.16 ± .08	.094 ± .004	1.7	0.14
	.03	1.96	.376	.12	.50	2.87	.6 ± .1	.16 ± .04	.118 ± .005	1.4	.11
	.05	1.90	.365	.18	.46	2.79	.6 ± .1	.17 ± .03	.145 ± .005	1.2	.10
	.10	1.68	.322	.39	.29	2.46	1.0 ± .1	.38 ± .04	.284 ± .006	1.3	.11
	.20	1.41	.271	.73	...	2.07	1.7 ± .1	.79 ± .08	.....	...	...
Cs <sup>+</sup>	.03	2.00	.384	.08	.54	2.93	0.37 ± .11	.09 ± .03	.111 ± .005	0.8	0.07
	.05	1.94	.372	.14	.49	2.84	.44 ± .08	.12 ± .03	.140 ± .006	.9	.07
	.10	1.79	.344	.28	.38	2.62	.59 ± .06	.19 ± .03	.258 ± .008	.7	.06
	.20	1.59	.305	.70	...	2.33	1.11 ± .08	.44 ± .05	.....	...	...

<sup>a</sup> The solutions against which the polyphosphate solutions were dialyzed contained (M<sup>+</sup>) equivalents of alkali metal ion and 0.2 -(M<sup>+</sup>) equivalents of TMA<sup>+</sup> per liter. <sup>b</sup> These results were outside the limits of the calibration method for obtaining values of  $\beta$  and  $K$ . <sup>c</sup> The precision estimates are based on an experimental uncertainty of 0.02 in the values of  $u$ . All of the  $K$ 's have units of reciprocal normality. <sup>d</sup> These values were obtained by multiplying  $K_M$  by (0.083/ $K_{TMA}$ ). See text.

Viscosities were measured in a Bingham viscometer as previously described.<sup>2</sup>

### Results and Discussion

**Electrophoretic Mobility and Degree of Ionization.**—The effect of the alkali metal ions on the electrophoretic mobility  $u$ , expressed in cm.<sup>2</sup>/volt-sec., of the polyphosphate is shown in the first three columns of Table I, where M<sup>+</sup> represents the alkali metal ion, and (M<sup>+</sup>) its normality in the solution against which the polyphosphate solution was dialyzed. The TMA<sup>+</sup> normality of each solution was 0.2 -(M<sup>+</sup>), so that the total normality was constant at 0.2. In all cases bromide was the by-ion. The mobility is seen to decrease with increasing (M<sup>+</sup>), to a different degree with each alkali metal ion. It has been established previously that at the total electrolyte normality employed here, the polyphosphate chains are free draining.<sup>3,7</sup> Under these conditions, according to several recent theoretical treatments,<sup>8,9</sup> the electrophoretic mobility is proportional to the degree of ionization  $i$  of the polyelectrolyte. By a combined study of conductivity and electrophoresis of long-chain polyphosphates at 0°, the relationship

$$u = 5.2 \times 10^{-4} i \quad (1)$$

was found to hold in 0.2 N TMABr, KBr, NaBr and LiBr solutions.<sup>7</sup> We shall therefore assume equation 1 to be valid in all of our systems. The resulting values of  $i$  are shown in the fourth column of Table I. It is seen from these results that for a given low value of (M<sup>+</sup>), e.g., 0.01 or 0.03, where

most of the cation content is TMA<sup>+</sup> and the polymer chain therefore is roughly in the same condition,  $i$  is decreased by the different cations in the order Li<sup>+</sup> > Na<sup>+</sup> > K<sup>+</sup> > Cs<sup>+</sup>. Thus, the binding of the alkali metal ions increases with diminishing sizes of the anhydrous cations, a result which indicates that the PO<sub>3</sub><sup>-</sup>-group penetrates through the hydration layer of the cations.<sup>10</sup>

**Degree of Binding of Alkali Metal Ions.**—It is clear that with increased binding of alkali metal ions the electrical potential of the polyelectrolyte is reduced, and therefore some previously bound TMA<sup>+</sup> ions are released. Consequently the observed decrease in  $i$  must be less than the degree of binding of the alkali metal ions and cannot be used as a quantitative measure of this binding. One way to obtain such a measure is by means of an empirical calibration with cations which are known to be, for all practical purposes, completely bound. The ions chosen for this purpose were Ca<sup>++</sup>, Mg<sup>++</sup> and Mn<sup>++</sup>. These ions are very strongly bound by polyphosphates<sup>11,12</sup> but have little tendency to form complexes with other species occurring in our solutions. The electrophoresis results for these ions are shown in Fig. 1, where  $u$  is plotted against the ratio of the divalent cation normality to the polyphosphate normality. It is seen that as long as this ratio is 0.5 or less, the results with the three cations fall on the same straight line, and we may therefore assume essentially complete binding.<sup>13</sup> The above ratio is then equal to  $\beta_M$ ,

(10) See footnote 28 of ref. 2.

(11) J. R. Van Wazer and D. A. Campanella, *THIS JOURNAL*, **72**, 555 (1950).

(12) R. M. Smith and R. A. Alberty, *ibid.*, **78**, 2376 (1956).

(13) Since the binding constants are known to be different for these cations,<sup>12</sup> incomplete binding would result in different curves in Fig. 1.

(7) U. P. Strauss and S. Bluestone, *THIS JOURNAL*, **81**, 5292 (1959).

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

(9) J. J. Hermans and H. Fujita, *Proc. Akad. Amsterdam*, **B58**, 182 (1955).

the fraction of phosphate groups which are neutralized by bound metallic cations.<sup>14</sup> The line in Fig. 1 can be represented by the equation

$$\beta_M = 2.08 - u \times 10^4; \beta_M \leq 0.5 \quad (2)$$

As the abscissa in Fig. 1 exceeds 0.5, the mobility values begin to diverge, which means that at least the  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  ions are not completely bound in this region. The relative position of the curves suggests the binding order  $\text{Mn}^{++} \gg \text{Mg}^{++} > \text{Ca}^{++}$ , which is in agreement with the findings of others.<sup>12</sup> One more requirement is necessary for the validity of our calibration scheme, namely, that there is also free draining in the presence of the divalent cations. The intrinsic viscosities were therefore determined at 50% binding of  $\text{Mn}^{++}$ ,  $\text{Mg}^{++}$  and  $\text{Ca}^{++}$  and found to be 3.3, 3.7 and 2.8, respectively, at 0°. Since these values are much larger than 0.507, the value determined by Hubbard<sup>15</sup> in the theta solvent 0.415 *N* NaBr<sup>16</sup> at 25°, the polymer chain is quite expanded and therefore free draining.<sup>17</sup> The values of  $\beta_M$  for the alkali metal ions are given in the fifth column of Table I. For all the solutions containing both  $\text{M}^+$  and  $\text{TMA}^+$ ,  $\beta_M$  was calculated by eq. 2.<sup>18</sup> For the 0.2 *N* alkali metal bromide solutions,  $\beta_M$  was taken to be equal to  $(1 - i)$ .<sup>7</sup>

**Binding Constants.**—Writing the equation for the binding phenomenon,  $\text{M}^+ + \text{PO}_3^- = \text{MPO}_3$ , we may define an apparent binding constant  $K_M'$ ,<sup>19</sup> by the relation

$$K_M' = \frac{(\text{MPO}_3)}{(\text{M}^+)_{\text{eff}}(\text{PO}_3^-)_f} \quad (3)$$

The quantity  $(\text{M}^+)_{\text{eff}}$  is the effective concentration of  $\text{M}^+$  near the polymer chain and may be given by the Boltzmann relation

$$(\text{M}^+)_{\text{eff}} = (\text{M}^+) \exp(-e\psi/kT) \quad (4)$$

where  $e$  is the charge on the cation,  $k$  the Boltzmann constant and  $T$  the absolute temperature. The quantity  $\psi$  is the electrostatic potential at the surface of the polymer chain and is here assumed to be equal to the zeta potential,  $\zeta$ . The validity of this assumption has been established both on theoretical<sup>8</sup> and experimental<sup>20,21</sup> grounds. The zeta potential is calculated from the electrophoretic mobility by the relation

$$|\zeta| = 6\pi\eta u/D \quad (5)$$

where  $\eta$  and  $D$  are the viscosity and dielectric constant of the solvent, respectively.<sup>8</sup> Since the polyphosphate always moved toward the anode,  $\zeta$ , and hence  $\psi$ , are negative.

(14) In defining  $\beta_M$ , it is understood that one equivalent of  $\text{PO}_3^-$  groups is bound by one equivalent of cation. If more than one equivalent of  $\text{PO}_3^-$  groups were bound, it would not be detected by our experimental method, nor would it affect any of our conclusions.

(15) R. Hubbard, unpublished results.

(16) U. P. Strauss and P. L. Wineman, *THIS JOURNAL*, **80**, 2366 (1958).

(17) The different values of the intrinsic viscosity obtained furnish support for the previously reported conclusion<sup>2</sup> that, at equal degrees of binding, different cations have different effects on the solvent affinity of the polymer chain.

(18) The values of  $\beta_M$  calculated in this manner are independent of the values of  $i$  as obtained from eq. 1.

(19) In the calculation of  $K_M'$ , the  $\text{PO}_3^-$  groups are assumed to be independent. The effect of nearest neighbor interactions is considered below.

(20) A. Katchalsky, *J. Polymer Sci.*, **12**, 159 (1954).

(21) A. Katchalsky, N. Shavit and H. Eisenberg, *ibid.*, **13**, 69 (1954).

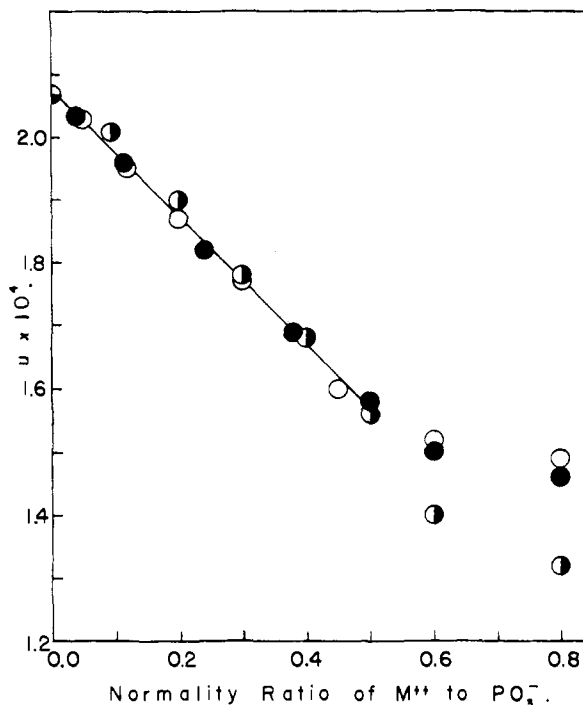


Fig. 1.—Calibration of electrophoresis method with divalent cations: O,  $\text{Ca}^{++}$ ; ●,  $\text{Mg}^{++}$ ; ◐,  $\text{Mn}^{++}$ .

The quantity  $(\text{PO}_3^-)_f$  is the normality of free phosphate groups. Its value depends on how we consider the  $\text{TMA}^+$  binding. Calculations show that if we ignore the bound  $\text{TMA}^+$  groups,  $K_M'$  and especially  $K_M$ <sup>22</sup> are not constant but change considerably with increasing  $(\text{M}^+)$ . Consequently, we shall consider the  $\text{TMA}^+$  also as site-bound. The fraction of  $\text{PO}_3^-$  groups to which  $\text{TMA}^+$  is bound,  $\beta_{\text{TMA}}$ , is given by the relation

$$\beta_{\text{TMA}} = 1 - i - \beta_M \quad (6)$$

The values of  $\beta_{\text{TMA}}$  and  $(-e\psi/kT)$  are given in the sixth and seventh columns of Table I, respectively.

Equation 3 can now be expressed in the form

$$K_M' = \frac{\beta_M}{(\text{M}^+)_i} \exp(e\psi/kT) \quad (7)$$

The values of  $K_M'$ , calculated by eq. 7, are given in the eighth column of Table I. They are seen to vary by a factor of about two to three for each cation.

More relevant values for the binding constants are obtained when the effect of nearest neighbor interactions of  $\text{PO}_3^-$  groups is taken into account.<sup>23-26</sup> A theoretical treatment based on the one-dimensional Ising lattice involving the binding of two univalent species gives the equations<sup>26</sup>

$$pK_M = \log(\text{M}^+) - 0.43e\psi/kT - \Delta pK + \log[(1 - i)/\beta_M] - 0.43 \cosh^{-1} \left( 1 + \frac{\delta}{v} \right) \quad (8)$$

$$pK_{\text{TMA}} = \log(\text{TMA}^+) - 0.43e\psi/kT - \Delta pK + \log[(1 - i)/\beta_{\text{TMA}}] - 0.43 \cosh^{-1} \left( 1 + \frac{\delta}{v} \right) \quad (9)$$

(22)  $K_M$  is defined as the binding constant for which nearest neighbor interactions of  $\text{PO}_3^-$  groups are taken into account. The details of the calculation will be given below.

(23) R. A. Marcus, *J. Phys. Chem.*, **58**, 621 (1954).

(24) F. E. Harris and S. A. Rice, *ibid.*, **58**, 725 (1954).

(25) T. L. Hill, *J. Polymer Sci.*, **23**, 549 (1957).

(26) S. Lifson, *J. Chem. Phys.*, **26**, 727 (1957).

where  $\delta = [(1 - 2i)^2/2i(1 - i)]$  and  $\Delta pK = \log v = -0.43e^2/D_E r kT$ ,  $D_E$  and  $r$  being the effective dielectric constant and the distance between neighboring  $\text{PO}_3^-$ -groups, respectively. In the ninth and tenth columns of Table I, values of  $K_M$  and  $K_{TMA}$  are given, calculated by eq. 8 and 9, respectively, with the assumptions that  $r = 3 \text{ \AA}$ . and  $D_E = 89$ . The effect of changing the assumed value of  $D_E$  is not very great. Thus, if one were to set  $D_E$  equal to 28, the values of the binding constants would be about one-half those in Table I.

It is seen that the values of  $K_M$  and  $K_{TMA}$  are reasonably constant for a given cation at low values of  $(M^+)$ . In the case of  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cs}^+$ , however, there seems to be a tendency for  $K_M$  to increase at the higher alkali metal ion concentrations. If one plots  $K_M$  against  $(M^+)$  on a double logarithmic graph, one finds that for each of these ions the curve rises smoothly to the value of  $K_M$  at  $(M^+) = 0.2$ . The effect is especially noticeable with  $K_{TMA}$  which increases with increasing  $(M^+)$  for all four alkali metal ions. We believe that this effect is caused by the contraction of the polymer coil which occurs as  $(M^+)$  increases. As the polymer coil contracts there will be more points of contact between different portions of the polymer chain. At such points of contact the binding of cations should be strengthened. One might further expect that the size of the cation should play a role. Thus, a very small cation such as  $\text{Li}^+$  might be buried sufficiently at its first binding site to make it difficult for a second potential binding site in another portion of the polymer chain to come close enough for additional complexing. This would explain the absence of the coiling effect on  $K_{Li}$  and the reversal of the normal binding order in  $0.2 N \text{ Li}^+$  and  $\text{Na}^+$  solutions.<sup>27</sup> The situation can probably be described by two binding constants for each cation. The first binding constant gives the binding to the first binding site and is probably quite well represented by  $K_M$  at low  $(M^+)$  where the polyphosphate chain is extended. This constant is seen to increase with decreasing size of the anhydrous cation. The second binding constant gives the binding of the  $M^+$  ion to an additional binding site on the polymer chain. The necessary data concerning molecular dimensions are not yet available; therefore these constants cannot be determined at this time. However, from the information available so far one can say that this second constant is smaller for  $\text{Li}^+$  than for the other alkali metal ions treated in this paper. It is

(27) This reversal is enhanced by the expected reciprocal effect; namely, that at a given degree of binding,  $\beta_M$ , of two cations the one whose  $K_M$  is affected more strongly by the coiling of the polymer chain should also be more effective in tying different parts of the chain together and thus in causing the coiling of the chain. It has been shown, for instance, that the molecular dimensions are very much smaller in  $0.2 N \text{ NaBr}$  than in  $0.2 N \text{ LiBr}$ , despite the fact that the degree of ionization is almost the same.<sup>1</sup> The phenomenon discussed here also furnishes a simple explanation for the different solvent affinities of site-bound  $\text{MPO}_3$  groups which were reported previously.<sup>1</sup> This discussion may also be applicable to the observation that carrageenin is gelled by  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  but not by  $\text{Li}^+$  and  $\text{Na}^+$  (D. B. Smith and W. H. Cook, *Arch. Biochem.*, **45**, 232 (1953)).

seen that the first and second binding constants may go in opposite directions as the size of the cation changes. This result explains to some extent the frequently observed complexity of the binding behavior of polyelectrolytes and ion-exchange resins.

If the values of  $K_{TMA}$  are affected by changing molecular dimensions in the same way as those of  $K_M$ , the ratio  $K_M/K_{TMA}$  should be constant for a given alkali metal ion. This ratio is also independent of the electrical potential, of whether the nearest neighbor interactions are considered or not, and hence of the effective dielectric constant and the distance between charged groups. Thus, it is not surprising that, on the whole, the values of  $K_M/K_{TMA}$  show less variation for each alkali metal ion than do the values of  $K_M$ .<sup>28</sup>

This result suggests a way of extrapolating the values of  $K_M$ , at constant ionic strength of 0.2, to infinite dilution of  $M^+$ . The extrapolation, which because of the scattering in the  $K_M$ -values would be difficult to perform directly, is achieved by multiplying each  $K_M$  by the quantity  $(0.083/K_{TMA})$ .<sup>29</sup> The resulting corrected values of  $K_M$  denoted by  $K_M(\text{cor.})$ , are given in the last column of Table I and are seen to be quite constant. These constants are useful for comparing the relative binding order of polyphosphates for the univalent cations, which is  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+ \approx \text{TMA}^+$ . This order has been partially observed by others for long-chain polyphosphates,<sup>11</sup> for lower phosphate polymers,<sup>30-32</sup> for phosphoproteins<sup>33</sup> and phosphonous and phosphonic ion-exchange resins.<sup>34</sup>

The results show that the association of individual  $\text{PO}_3^-$ -groups with univalent cations follows the Law of Mass Action, modified for the effects of the potential, of nearest neighbor interactions between adjacent  $\text{PO}_3^-$ -groups and of the changes in the molecular dimensions of the polymer. The reported values of  $K_M(\text{cor.})$ ,  $K_M$  and  $K_{TMA}$  also provide at present the best estimates for the hypothetical binding constants of the individual  $\text{PO}_3^-$ -groups for the various univalent cations in a constant ionic medium of  $\text{TMA}^+$ .<sup>35</sup>

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(28) In the case of  $\text{Li}^+$ , this result is somewhat misleading. It is quite clear that the values of  $K_{Li}$ , while fluctuating fairly widely, remain essentially constant while those of  $K_{TMA}$  increase consistently with increasing  $(M^+)$ . Therefore  $K_{Li}/K_{TMA}$  decreases as expected from the previous discussion. It is the fluctuations in the value of  $K_{Li}$  which obscure this decrease of  $K_{Li}/K_{TMA}$  in the table.

(29) The value 0.083 represents  $K_{TMA}$  in the absence of alkali metal ion. See Table I.

(30) R. M. Smith and R. A. Alberty, *J. Phys. Chem.*, **60**, 180 (1956).

(31) J. I. Watters, S. M. Lambert and E. D. Loughran, *This Journal*, **79**, 3651 (1957).

(32) S. M. Lambert and J. I. Watters, *ibid.*, **79**, 4262 (1957).

(33) C. W. Carr and W. P. Engelstadt, *Arch. Biochem. Biophys.*, **77**, 158 (1958).

(34) J. I. Bregman and Y. Murata, *This Journal*, **74**, 1867 (1952).

(35) It is of interest that in the case of  $\text{TMA}^+$  and  $\text{Cs}^+$  the binding constants are close to the value 0.05 obtained for the strong electrolyte  $\text{HNO}_3$  by an optical method (O. Redlich and J. Bigeleisen, *ibid.*, **65**, 1883 (1943)).