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Counterion Binding by Polyelectrolytes. IV. Membrane Equilibrium Studies of the Binding of Univalent Cations by Long-chain Polyphosphates[1]

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The binding of Li^+, Na^+, K^+ and Cs^+ by long-chain polyphosphates was determined by membrane equilibrium in aqueous solutions maintained at constant ionic strength with $(CH_3)_4NBr$. Analysis for the alkali metal concentrations after completion of the dialysis was carried out by means of flame photometry. The binding results obtained at 0.2 ionic strength for Li^+ and Na^+ agreed with those previously determined by electrophoresis, but in the case of K^+ and Cs^+, the membrane equilibrium method yielded much higher values for the degree of binding than did the electrophoresis technique. The difference between the methods was attributed to an excess of K^+ and Cs^+ in the ionic atmosphere surrounding the polyphosphate chain, caused by the fact that these cations have smaller hydrated sizes than has the $(CH_3)_4N^+$ ion. Except at very low concentrations of Li^+ and Na^+ where the extent of binding increased slightly with rising temperature, the results were identical at 5° and at 25°. However, the degree of binding increased strongly with decreasing total ionic strength. This increase was ascribed to a decrease in the shielding effect of the ionic atmosphere, causing an increasing number of neighboring PO_3^--groups to become effective in strengthening the binding of a cation by a given PO_3^--group.

In the work described in the preceding paper of this series[2] the binding of four of the alkali metal ions by polyphosphates was determined by electrophoresis measurements. In this paper, we shall present results involving the determination of such binding by membrane equilibrium experiments. The purpose of these studies was threefold, namely, (1) to show by an independent method that the alkali metal ions are, in fact, bound by polyphosphates; (2) to compare the results of the electrophoresis and membrane equilibrium methods quantitatively, and thereby test the validity of both methods; and (3) to investigate the effects of total ionic strength and of temperature on the extent of binding.

It has been shown elsewhere that, with only one counterion present, the membrane equilibrium results are not suitable for a determination of the counterion binding.[3] However, in the presence of a large excess of another counterion, which is not bound very strongly, the Donnan Effect is suppressed and the difference in the concentrations of the alkali metal ion on the two sides of the membrane becomes a measure of the number of counterions bound. The results reported in this paper were all obtained with the alkali metal bromide contained in a large excess of tetramethylammonium (TMA^+) bromide. The TMA^+ normality was such that the total ionic strength ranged from 0.02 to 0.5 with the bulk of the data at 0.2. The temperatures used were 5 and 25°.

Experimental

The potassium polyphosphate used was the same Kurrol's salt (our sample No. H-2170-W, degree of polymerization = 9,400) described in the previous paper.[2] The preparation of our conductivity water, employed throughout this work, also was described there.

The dialysis procedure for the solutions of total ionic strength 0.2 N was carried out as follows. A weighed quantity of the Kurrol's salt and a known volume of 0.2 N TMABr were introduced into a cellulose casing bag (Visking Corporation No. 18/32 or No. 24/32), a Pyrex glass bead was added to aid mixing, and the bag was sealed and placed into a large test-tube containing 200 ml. of 0.2 N TMABr. The tube was stoppered and gently tumbled in a water-bath thermostated at 25°. The 0.2 N TMABr outside the bag ("outside solution") was changed several times to obtain quick dissolution of the Kurrol's salt and removal of K^+ from the solution inside the bag ("inside solution"). Then solutions having the desired normality (0.5, 1.0, 2.5, 10 and 30 $\times 10^{-3}$ N) of the alkali metal ion (Li^+, Na^+, K^+ and Cs^+) with the total normality brought to 0.2 with TMA^+ were employed as outside solutions in subsequent exchanges. The outside solution was changed intermittently four times, with at least 36 hours allowed for the last outside solution. In the case of the lower temperature work, after the first exchange at 25°, the tubes were tumbled in a cold room maintained at 5 ± 0.5°, with subsequent changes of the outside solution being made there. At the end of the tumbling period, the inside and outside solutions were transferred to polyethylene bottles and prepared for analysis as described below.

A similar procedure was employed for the solutions of total ionic strength different from 0.2 N.

In all cases, the pH was maintained between 6.2 and 7.5 so as to render the extent of H^+ binding negligible and to minimize hydrolytic degradation of the polyphosphate.[4] Total phosphate analysis of the outside solution indicated diffusion of any phosphate species through the membrane to be negligible. Blank runs without polyelectrolyte showed no effect of the membrane on the counterion concentration or distribution.

The attainment of equilibrium by the above procedure was confirmed by means of several experiments in which equilibrium was approached from the opposite direction, *i.e.*, by beginning with an excess of alkali metal ion in the inside solution so that the alkali metal ion would diffuse, from the inside to the outside solution.

The analyses for the alkali metal ion concentrations both in the inside and in the outside solutions were carried out with a Perkin–Elmer Model 146 flame photometer, using the internal standard procedure.[5] Lithium ion was used as the comparison element for the analyses of Na^+, K^+ and Cs^+. The method was calibrated with known solutions containing Li^+ (0.010 to 0.015 N) and the alkali metal ion to be determined over the concentration range 0.0005 to 0.01 N. The total ionic strength was brought up to the desired quantity (usually 0.2 N) with TMABr, so as to be similar to the unknowns, although it was found that the presence of TMABr (between 0.02 and 0.5 N) had no effect on the alkali metal analysis. Where necessary, the samples from the dialysis experiments were brought into the desired concentration range for analysis by dilution with TMABr solution. Then an amount of the same LiBr master solution as used in the preparation of the standard solutions was added to the unknowns so as to make the Li^+ concentration of standards and unknowns identical. It was also found necessary to degrade the polyphosphate in the inside solutions with a few

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

(3) U. P. Strauss and P. Ander, *ibid.*, **80**, 6494 (1958).

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

(5) 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.

drops of concentrated HBr in order to decrease the viscosity. If this was done, there was no effect of the phosphate on the analytical results.

The analyses of Li^+ were performed in a similar manner, with Na^+ serving as the comparison element. However, in order to avoid realignment of the light-directing slit, the usual procedure was modified. The lithium spectral line was, as before, directed toward the "internal standard" phototube, and the sodium line toward the "unknown" phototube. In this way, the scale reading was calibrated to be an essentially reciprocal measure of the lithium concentration.

Constant reference was made to the standard solutions throughout the analysis, and the average of four analyses was taken as the final result.

Results and Discussion

Calculation of Binding Results.—In this discussion the following symbols are used: (M^+), (TMA^+) and (PO_3^-) are the normalities of the alkali metal ion M^+, of TMA^+ and of the polyphosphate, respectively; the subscripts o, i, b and f refer to the outside solution, to the inside solution (which contains the polyphosphate) and to the bound and free species, respectively; the simultaneous absence of both of the latter subscripts implies the total concentration of the species.

We have then

$$(M^+)_b = (M^+)_i - (M^+)_{if} \qquad (1)$$

We shall next make the assumption that the free M^+ is distributed across the membrane in the same way as the free TMA^+. This assumption is embodied in the equation

$$\frac{(M^+)_{if}}{(M^+)_o} = \frac{(TMA^+)_{if}}{(TMA^+)_o} \qquad (2)$$

Eliminating $(M^+)_{if}$ between equations 1 and 2, rearranging terms and dividing by (PO_3^-), we obtain

$$\beta_M \equiv \frac{(M^+)_b}{(PO_3^-)} = \frac{(M^+)_i - (M^+)_o}{(PO_3^-)} - \frac{(M^+)_o}{(TMA^+)_o}\left[\frac{(TMA^+)_{if} - (TMA^+)_o}{(PO_3^-)}\right] \qquad (3)$$

where β_M is the fraction of PO_3^--groups neutralized by bound M^+. The expression in brackets can be brought into a more convenient form with the help of the relation

$$\frac{(TMA^+)_{if}}{(PO_3^-)} = \frac{(TMA^+)_i}{(PO_3^-)} - \beta_{TMA} \qquad (4)$$

and two further equations expressing the conditions of electroneutrality on each side of the membrane. Equation 3 then leads to the relation

$$\beta_M = \frac{(M^+)_i - (M^+)_o}{(PO_3^-)} - \frac{(M^+)_o}{(TMA^+)_o}\left[1 - A - \beta_{TMA} - \frac{(M^+)_i - (M^+)_o}{(PO_3^-)}\right] \qquad (5)$$

where $A = [(Br^-)_o - (Br^-)_i]/(PO_3^-)$ which can be determined by analyses for Br^-. In two instances where β_{TMA} was available from electrophoresis results[2] the requisite bromide analyses were carried out and the second part on the right-hand side of eq.5 was found to be smaller than the experimental error in the first part, so that only the latter need be retained. We obtain then the working relation

$$\beta_M = \frac{(M^+)_i - (M^+)_o}{(PO_3^-)} \qquad (6)$$

which is used in this work.

The results obtained at 0.2 ionic strength and at the temperatures 5 and 25° are given in Table I. Each value of β_M represents an average of results obtained at three or more polyphosphate concentrations. There was no effect of polyphosphate concentration in the range used in these experiments (0.01–0.15 *N*). Several experiments with a potassium polyphosphate (our sample No. KPP-12) of degree of polymerization equal to 5000 yielded identical values of β_M as the main sample whose degree of polymerization was 9400.

TABLE I

BINDING OF ALKALI METAL IONS BY POLYPHOSPHATE AT 0.2 IONIC STRENGTH FROM DIALYSIS MEASUREMENTS

	t = 5°		t = 25°	
M^+	$(M^+)_o \times 10^3$	β_M	$(M^+)_o \times 10^3$	β_M
Li^+	0.47	0.038 ± 0.002	0.46	0.051 ± 0.002
	0.95	.066 ± .005	1.00	.081 ± .005
	2.42	.12 ± .01	2.40	.13 ± .01
	5.03	.20 ± .01	5.01	.23 ± .02
	9.72	.31 ± .03	9.93	.30 ± .02
	31.81	.44 ± .03	29.12	.42 ± .04
Na^+	0.52	0.018 ± 0.0006	0.51	0.021 ± 0.0005
	0.99	.034 ± .001	1.01	.039 ± .001
	3.09	.104 ± .002	3.16	.115 ± .003
	4.98	.147 ± .004	4.98	.158 ± .005
	10.18	.23 ± .01	9.86	.25 ± .01
	30.19	.43 ± .02	30.07	.43 ± .02
K^+	1.47	0.047 ± 0.003	1.54	0.052 ± 0.003
	3.11	.095 ± .003	3.04	.098 ± .003
	5.01	.141 ± .003	5.05	.139 ± .004
	10.24	.23 ± .01	10.32	.24 ± .01
	28.93	.40 ± .02	28.49	.41 ± .02
Cs^+	1.00	0.036 ± 0.0005	1.02	0.036 ± 0.0005
	2.46	.087 ± .004	2.46	.081 ± .001
	4.91	.138 ± .008	4.91	.138 ± .007
	9.86	.22 ± .02	9.85	.216 ± .007
	30.44	.40 ± .01	31.08	.40 ± .03

Comparison with Electrophoresis Results.—It is of interest to compare these results, which indicate binding of alkali metal ions by polyphosphate, with those obtained by electrophoresis. The comparison is made in Fig. 1 where, for the sake of convenience in presentation, the values of the binding constants K_M have been used. These binding constants were calculated by eq. 8 of the previous paper of this series,[2] employing the values of the potential ψ and the degree of ionization i as obtained from electrophoresis. Therefore, the calculations of the dialysis K_M and of the electrophoresis K_M differed only in the values of β_M employed.[6] Several striking conclusions can be drawn from the results in Fig. 1. In the case of both Li^+ and Na^+, the values of K_M obtained by dialysis are quite constant[7] and agree, within the limits of experimental error, remarkably well with those obtained by electrophoresis. This agreement does much toward establishing the validity of both methods for determining the degree of

(6) In view of the small or negligible temperature dependence of β_M (*cf.* Table I), the fact that the electrophoresis results were obtained at 0° and the dialysis results at 5° should not affect the validity of the comparison.

(7) The small rise at the highest Na^+ concentration has been ascribed to a contraction of the polymer coil.[2]

binding of Li^+ and Na^+. However, in the case of K^+ and Cs^+, the situation is different. The values of K_M obtained by dialysis are constant at low (M^+) and decrease at higher (M^+), and they are about three to four times as large as those obtained by electrophoresis in the (M^+)-region where both methods were used.[8] This discrepancy far exceeds the combined experimental errors. The question now arises, as to which of the two methods, if either, is valid for obtaining the desired binding parameters. Somewhat of a case can be made in favor of the dialysis method in that it gives, at low (M^+), the binding constant for Li^+, Na^+ and K^+ in the same ratio, 2:1:1, as was obtained by Smith and Alberty[9] for the complexing of these cations by the $HPO_4^=$ ion. However, with polyphosphates these authors obtained a difference between the values of K_M of Na^+ and K^+, and, moreover, there is some disagreement in the literature as to whether the binding of alkali metal ions by $HPO_4^=$ is measurable by the acid–base titration method employed by Smith and Alberty.[10]

A much better case can be made for the conclusion that for K^+ and Cs^+ the dialysis values of K_M are too high. The argument is based on the fact that the effective radii of K^+ and Cs^+ in aqueous solution are about half that of TMA^+. It can be shown by statistical mechanical reasoning that in a potential gradient, such as exists in the double layer around the polyphosphate chain, which affects two species equally—(here the TMA^+ and either the K^+ or the Cs^+)— the concentrations of the two species may not follow the Boltzmann relation, $c \propto e^{-E/kT}$, but the species with the smaller volume tends to be relatively more concentrated in the regions of high field strength where the total concentration is very large.[11] Simple calculations show that the concentration of TMA^+ in the double layer becomes high enough in our experiments for this effect to be significant. This excess of K^+ or Cs^+ in the double layer reveals itself in the values of β_M determined by membrane equilibrium but not in those determined by electrophoresis since the surface of shear is close to the polymer chain so that only the cations bound directly to the polymer chain are reflected in the electrophoresis values of β_M.

The absence of the "double-layer binding" effect in the case of Li^+ and Na^+ can be explained by the fact that the radii of these hydrated ions, which are 3.7 and 3.3 Å., respectively, are very close to that of TMA^+ which is 3.5 Å.[12]

(8) The high values of K_M at $(M^+) = 0.1$ N, which previously have been ascribed as due to a contraction of the polymer coil, are not important for the discussion to follow, since corresponding dialysis values were not determined.

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

(10) S. M. Lambert and J. I. Watters, THIS JOURNAL, **79**, 4262 (1957).

(11) The site binding of the ions would not be affected by this effect since the activities do follow the Boltzmann relation. It is the activity coefficients which increase with increasing concentration more rapidly for the larger ion than for the smaller one and thereby cause the concentration effect discussed in the text. Such activity coefficient effects in solutions of mixed electrolytes also have been found experimentally (H. S. Harned and O. E. Schupp, *ibid.*, **52**, 3892 (1930)).

(12) R. A. Robinson and R. M. Stokes, "Electrolyte Solutions," Academic Press, Inc., New York, N. Y., 1955, pp. 120, 121.

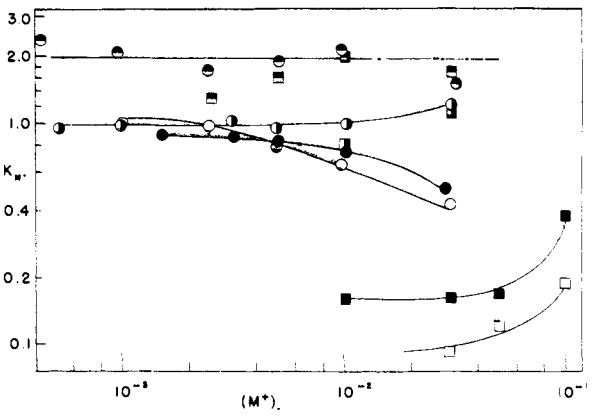

Fig. 1.—Comparison of binding constants obtained from membrane equilibrium and electrophoresis: ◓, Li^+; ◑, Na^+; ●, K^+; and ○, Cs^+, all obtained by membrane equilibrium. The corresponding points designated by squares were obtained by electrophoresis.[2]

Effect of Total Ionic Strength.—A few results obtained with Li^+ and Na^+ at different ionic strengths are given in Table II. The binding is seen to increase with decreasing (TMA^+) for both alkali metal ions. This result may be attributed to a combination of several factors: (1) the activity coefficient of the alkali metal ion in the outside solution increases with decreasing ionic strength. (2) The competitive binding of TMA^+ is reduced as its concentration is diminished, thereby freeing more PO_3^--groups for the binding of alkali metal ion. (3) As the binding of TMA^+ is reduced the potential on the polyelectrolyte increases. (4) With decreasing ionic strength the shielding effect of the ionic atmosphere decreases; thus an increasing number of neighboring PO_3^--groups becomes effective in strengthening the binding of a cation by a given PO_3^--group.

TABLE II

EFFECT OF IONIC STRENGTH ON BINDING OF Li^+ AND Na^+ BY POLYPHOSPHATE FROM DIALYSIS MEASUREMENTS

Temp., °C.	M^+	$(TMA^+)_0$	$(M^+)_0 \times 10^3$	β_M[a]	$\beta_M/(M^+)_0$
5	Li^+	0.02	0.46	0.106 ± 0.001	231
			.85	.202 ± .001	238
		.053	.54	.070 ± .003	130
			.85	.133 ± .002	156
		.5	.85	.044 ± .002	52
	Na^+	.02	.53	.082 ± .003	155
			.99	.139 ± .002	140
		.053	.48	.045 ± .003	94
			.99	.082 ± .001	83
		.5	1.01	.019 ± .001	19
25		.5	1.01	.019 ± .001	19

[a] Calculated by eq. 5.

Of these four factors, the first probably is not very significant; the second and third are also not very important because the electrophoretic mobility increases only little with decreasing TMA^+ concentration[4]; we believe, therefore, that the large effect of ionic strength is due mainly to the fourth factor.

The importance of the shielding factor is substantiated further by the observation that if the

ionic strength is brought to 0.2 N with tetraethylammonium (TEA^+) bromide, the binding of Na^+ is about twice as large as it is with TMABr at the same ionic strength.[13] Because of their larger size the TEA^+ ions cannot shield the PO_3^--groups as effectively from each other as can the TMA^+ ions.

Effect of Temperature.—If the data obtained at 5 and 25° in Table I are compared, one finds that the values of β_M are somewhat larger at 25 than at 5° at the few lowest concentrations of both Li^+ and Na^+. The effect seems to disappear at higher $(M^+)_0$ and also is not observable with K^+ and Cs^+. The results suggest that the change of enthalpy on binding is slightly positive at low (Li^+) and (Na^+) and very close to zero in the other cases. Since values of equilibrium constants were not obtained at 25°, no quantitative calculation of ΔH and ΔS can be made.

(13) P. D. Ross and U. P. Strauss, unpublished results.

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The Lactone–Acid–Salt Equilibria for D-Glucono-δ-lactone and the Hydrolysis Kinetics for this Lactone

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Polarimetric and coulometric methods have been used for the study of the hydrolysis rate for D-glucono-δ-lactone at various solution conditions. The hydrolysis reaction is first order in lactone concentration and independent of pH from pH 3 to pH 5. The rate constant k at 25° is: by optical rotation, 2.26×10^{-4} sec.$^{-1}$; by coulometry, 1.31×10^{-4} sec.$^{-1}$. The activation energy for the lactone hydrolysis reaction is 15 kcal. per mole for the temperature range from 20 to 25°. To carry out the polarimetric studies it was necessary to redetermine the specific optical rotations for D-glucono-δ-lactone, gluconic acid and sodium gluconate; the values of $[\alpha]^{25}D$ for the three species are, respectively +66.0, +5.40 and +12.0°. The constants for several of the lactone–acid–salt equilibria have been determined at 25° by pH and optical rotation measurements (L, HGH_4 and GH_4^- represent D-glucono-δ-lactone, gluconic acid and gluconate ion, respectively): $K = (H^+)\cdot(GH_4^-)/[(HGH_4) + (L)] = 1.76 \pm 0.05 \times 10^{-4}$; $K_A = (H^+)(GH_4^-)/(HGH_4) = 1.99 \pm 0.07 \times 10^{-4}$; and $K_L = (HGH_4)/(L) = 7.7$.

The existence of strong metal–gluconate complexes, which are formed by the salts of D-glucono-δ-lactone, has brought about renewed interest in the aqueous solution chemistry of this lactone.[1-3] Because the equilibrium constants for the lactone–acid–salt equilibria are frequently necessary for the calculation of the metal–gluconate stability constants, accurate evaluation of the equilibrium constants is desirable. Previous workers[4-6] have reported various values for the dissociation constant of gluconic acid, but they have not taken into account the lactone–acid equilibria and, in some cases, details of temperature and of the purity or preparation of the acid were not reported.

Although empirical data have been reported for the hydrolysis of D-glucono-δ-lactone,[7] quantitative relations were not developed and the effect of the competing equilibria was neglected. Furthermore, the specific rotations which were used for some of the hydrolysis rates do not agree with our values or those reported in the literature[8] and the rotation due to sodium gluconate was not included in the calculations of data reported. The salts of D-glucono-δ-lactone are being used widely as chelating agents and a more fundamental understanding of the hydrolysis kinetics for this lactone is of value. Also, kinetic data may be helpful in establishing the mechanism for chelation and in determining the structure of various metal–gluconate chelates.

The results of a systematic study of the lactone–acid–salt equilibria for D-glucono-δ-lactone are presented as well as a detailed study of the hydrolysis kinetics for the lactone by coulometric and polarimetric techniques. The constants for the equilibria have been evaluated by combining pH measurements with optical rotation data. The specific rotations for gluconic acid, sodium gluconate and the δ-lactone have been determined in order to evaluate the equilibrium constants and the rate constants.

Experimental

The coulometric generator and cell which were used for the kinetic studies have been described previously.[9] The generator provides a continuously variable constant current for the range from 1 to 150 milliamperes which is regulated to one-quarter of one per cent. Details for the cell system, the electrolyte solution and the procedure for making a rate constant determination are identical to those used in the previous kinetic studies of water-soluble esters.[9] Approximately 28 ml. of electrolyte solution (0.1 F K_2SO_4 and 0.03 F KBr) is introduced into the cell (the cell solution is degassed with purified nitrogen) and the pH is adjusted to the desired value (pH 3.4 to pH 4.6) coulometrically. The weighed sample is introduced as pure solid D-glucono-δ-lactone. The generation of hydroxide is started immediately and the current is adjusted until the desired pH is obtained.

All pH measurements were made with a Beckman Model GS pH meter, which was standardized with N.B.S. buffers. Unless otherwise noted all measurements were made at 25.0 ± 0.1°.

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(3) Chas. Pfizer and Co., "Gluconic Acid and Derivatives," Technical Bulletin No. 33, Brooklyn, N. Y., 1955.

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