

Ion Exchange Equilibria

II. A Study of the Association in Sodium Polymetaphosphate Solutions Containing Zinc, Copper, and Manganese

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Using a cation exchange resin, the exchange of sodium ions for bivalent ions (Zn, Cu, Mn) has been studied in polymetaphosphate solutions. The experiments indicate that not only the bivalent ions but also sodium ions are associated with the polyanion and that there is a competition between the bivalent cations and the sodium ions for places in the polymer coil. The results suggest that the association equilibrium in metaphosphate solutions can as a first approximation be calculated using the Rothmund and Kornfeld formula originally suggested to describe ion exchange equilibria between a solid exchanger and electrolyte solutions.

Sodium polymetaphosphate (Graham's salt) is known as an efficient complex forming agent, which gives complexes with various metal cations. Several methods have been used to study the properties of these complexes but the results are contradictory.

In the present paper solutions containing zinc, copper, and manganese polymetaphosphate have been studied by means of an ion exchange method. The method is in principle the same as described in an earlier paper on iron-(III)polymetaphosphate¹ (*cf.* also Ref. ²).

EXPERIMENTS

Materials. The ion exchange resin and the nitrate solutions were the same as described in Part I³. Polymetaphosphate was prepared by heating $\text{NaH}_2\text{PO}_4 \cdot 2 \text{H}_2\text{O}$ at 725°C for 2 h in a platinum dish and subsequently quenching with ice water. The metaphosphate glass was dissolved in a calculated volume of water to obtain a 0.1 N solution. The molecular weight of the metaphosphate was about 12 000 determined according to the end group method⁴. The solution was kept in a refrigerator to depress depolymerization, which occurs more rapidly at higher temperature. The solutions used in the experiments have never been more than a week old. The concentrations were checked according to the ion exchange method by passing the solution through a cation exchanger in the hydrogen form and subsequent titration against standard alkali using methyl red as

Table 1. Ion exchange equilibria Na—Mn in metaphosphate solution.

		Reagents added:	
I. 1.000 g Na ⁺ resin (= 2.17 mequiv.) 5 ml 0.0490 M Mn(NO ₃) ₂ a ml 0.098 N NaPO ₃ 40—a ml 0.100 M NaNO ₃ 5 ml dist. water	II. 1.000 g Na ⁺ resin (= 2.17 mequiv.) 15 ml 0.0500 M Mn(NO ₃) ₂ a ml 0.098 N NaPO ₃ 20— $\frac{a}{2}$ ml 0.200 M NaNO ₃ 15— $\frac{a}{2}$ ml dist. water		

	a	n _{PO₃⁻} equiv./l ml × 10 ³	X	$\frac{n_{Mn^{2+}}}{n_{Na^+}}$ × 10 ⁴	Calculations acc. to Method I			Calculations acc. to Method II		
					n _{Na⁺} equiv./l × 10 ³	n _{Mn²⁺} equiv./l × 10 ³	n _{Mn_P} equiv./l × 10 ³	n _{Na⁺} equiv./l × 10 ³	n _{Mn²⁺} equiv./l × 10 ³	n _{Mn_P} equiv./l × 10 ³
I.	10	19.6	0.0419	211	81.4	140	7.84	69.6	102	7.88
	15	29.4	0.0127	58.7	80.0	37.6	9.21	59.8	21.0	9.23
	20	39.2	0.00392	17.8	79.4	11.2	9.62	49.8	4.41	9.63
	25	49.0	0.00179	8.05	79.0	5.03	9.72	39.7	1.27	9.72
	30	58.8	0.00099	4.45	78.8	2.76	9.75	29.8	0.395	9.76
	35	68.6	0.00063	2.84	78.6	1.75	9.77	19.8	0.111	9.77
	40	78.4	0.00054	2.43	78.4	1.49	9.78	9.8	0.0233	9.78
II.	20	39.2	0.177	1140	86.9	861	21.44	69.1	544	21.76
	25	49.0	0.117	655	84.0	462	24.46	59.5	232	24.69
	30	58.8	0.0728	378	82.0	254	26.59	49.8	93.7	26.75
	35	68.6	0.0452	222	80.6	144	27.90	39.9	35.3	28.01

Table 2. Ion exchange equilibria Na—Mn in metaphosphate solution.

Reagents added: 1.000 g Na⁺ resin (= 2.17 mequiv.)
 10 ml 0.0490 M Mn(NO₃)₂
 a ml 0.098 N NaPO₃
 40—a ml 0.100 M NaNO₃
 100 ml dist. water

	a	n _{PO₃⁻} equiv./l ml × 10 ³	X	$\frac{n_{Mn^{2+}}}{n_{Na^+}}$ × 10 ⁴	Calculations acc. to Method I			Calculations acc. to Method II		
					n _{Na⁺} equiv./l × 10 ³	n _{Mn²⁺} equiv./l × 10 ³	n _{Mn_P} equiv./l × 10 ³	n _{Na⁺} equiv./l × 10 ³	n _{Mn²⁺} equiv./l × 10 ³	n _{Mn_P} equiv./l × 10 ³
	6	3.92	0.275	2200	30.6	206	2.35	29.0	185	2.37
	8	5.23	0.234	1680	30.0	151	3.00	27.8	130	3.02
	10	6.53	0.193	1250	29.3	107	3.64	26.4	87.1	3.66
	12	7.84	0.158	950	28.8	78.8	4.17	25.1	59.9	4.19
	15	9.80	0.113	620	28.1	49.0	4.84	23.2	33.4	4.86
	20	13.1	0.0594	290	27.3	21.6	5.65	19.9	11.5	5.66
	25	16.3	0.0265	122	26.7	8.70	6.14	16.5	3.32	6.15
	30	19.6	0.0128	57	26.5	4.00	6.34	13.2	0.993	6.35
	35	22.9	0.00627	27.4	26.3	1.90	6.44	9.8	0.263	6.44
	40	26.1	0.00371	16.2	26.2	1.11	6.48	6.6	0.0706	6.48

Table 3. Ion exchange equilibria Na—Mn in metaphosphate solution.

		Reagents added:	
I.	1.000 g Na ⁺ resin (= 2.17 mequiv.) 5 ml 0.0500 M Mn(NO ₃) ₂ a ml 0.098 N NaPO ₃ 40—a ml 0.100 M NaNO ₃ 105 ml dist. water	II.	1.000 g Na ⁺ resin (= 2.17 mequiv.) 15 ml 0.0500 M Mn(NO ₃) ₂ a ml 0.098 N NaPO ₃ 40—a ml 0.100 M NaNO ₃ 95 ml dist. water
		III.	1.000 g Na ⁺ resin 20 ml 0.100 M NaNO ₃ 20 ml 0.098 N NaPO ₃ a ml 0.0500 M Mn(NO ₃) ₂ 110—a ml dist. water

a	n _{PO₃⁻} equiv./l ml × 10 ³	X	$\frac{n_{Mn^{2+}}}{n_{Na^+}}$ × 10 ⁴	Calculations acc. to Method I			Calculations acc. to Method II			
				n _{Na⁺} equiv./l × 10 ³	n _{Mn²⁺} equiv./l × 10 ³	n _{Mn_P} equiv./l × 10 ³	n _{Na⁺} equiv./l × 10 ³	n _{Mn²⁺} equiv./l × 10 ³	n _{Mn_P} equiv./l × 10 ³	
I	10	6.53	0.0456	218	27.2	16.1	2.66	23.3	11.8	2.66
	15	9.80	0.0136	60.6	26.7	4.32	3.13	20.0	2.42	3.13
	20	13.1	0.00406	17.7	26.5	1.24	3.27	16.7	0.494	3.27
	25	16.3	0.00189	8.20	26.3	0.567	3.31	13.3	0.145	3.31
	30	19.6	0.00111	4.90	26.3	0.339	3.32	10.0	0.0490	3.32
	35	22.9	0.00076	3.30	26.2	0.227	3.32	6.62	0.0145	3.32
	40	26.1	0.00058	2.50	26.1	0.170	3.33	3.33	0.00277	3.33
II	15	9.80	0.283	2270	30.6	213	5.69	26.5	159	5.74
	20	13.1	0.198	1300	29.3	112	7.02	23.2	70.0	7.06
	25	16.3	0.132	750	28.3	60.1	8.03	20.0	30.0	8.06
	30	19.6	0.0829	423	27.5	32.0	8.77	16.7	11.8	8.79
	35	22.9	0.0507	243	26.9	17.6	9.25	13.3	4.30	9.26
	40	26.1	0.0288	132	26.5	9.27	9.57	10.0	1.32	9.58
III	2	13.1	0.00028	1.24	26.4	0.0864	1.33	14.6	0.0264	1.33
	4	13.1	0.00171	7.4	26.4	0.516	2.64	15.9	0.187	2.64
	6	13.1	0.00876	38.6	26.5	2.71	3.87	17.3	1.16	3.87
	8	13.1	0.0302	140	26.9	10.1	4.89	18.7	4.90	4.89
	10	13.1	0.0677	337	27.4	25.3	5.66	20.0	13.5	5.67
	12	13.1	0.114	620	28.1	49.0	6.30	21.3	28.1	6.33

indicator³. As a check the sodium ions taken up by the resin were eluted with hydrochloric acid and determined as chlorides. Good agreement was obtained for the two methods.

Procedure. The ion exchange equilibria were studied in a way similar to that used in Part I. Instead of sodium nitrate, varying proportions of sodium nitrate solution and polymetaphosphate solution were added. The flasks were shaken for 17–18 h in a shaking apparatus. Preliminary experiments had shown that equilibrium was attained within 4 h and that the equilibrium was independent of the sequence in which the reagents were added. Afterwards the resin was separated from the solution and collected quantitatively on a small glass filter. The equilibrium solution was drained off as completely as possible and subsequently the resin was washed with water. The ions taken up by the ion exchanger were displaced with 3 N hydrochloric acid, the hydrochloric acid driven off by evaporation and the bivalent ion determined in the residue.

Table 4. Ion exchange equilibria Na—Mn in metaphosphate solution.

Reagents added: 1.000 g Na⁺ resin (= 2.17 mequiv.)
 10 ml 0.0490 M Mn(NO₃)₂
 a ml 0.098 N NaPO₃
 40—a ml 0.100 M NaNO₃
 450 ml dist. water

a ml	$n_{\text{PO}_3^-}$ equiv./l $\times 10^3$	X	$\frac{n_{\text{Mn}^{2+}}}{n_{\text{Na}^+}}$ $\times 10^4$	Calculations acc. to Method I			Calculations acc. to Method II		
				n_{Na^+} equiv./l $\times 10^3$	$n_{\text{Mn}^{2+}}$ equiv./l $\times 10^6$	n_{Mn_P} equiv./l $\times 10^3$	n_{Na^+} equiv./l $\times 10^3$	$n_{\text{Mn}^{2+}}$ equiv./l $\times 10^6$	n_{Mn_P} equiv./l $\times 10^3$
6	1.18	0.288	2320	9.24	19.8	0.690	8.75	17.8	0.692
8	1.57	0.251	1860	9.06	15.3	0.855	8.35	13.0	0.857
10	1.96	0.208	1410	8.86	11.1	1.05	7.95	8.91	1.05
12	2.35	0.168	1060	8.68	7.99	1.22	7.55	6.04	1.22
15	2.94	0.122	679	8.46	4.86	1.43	6.95	3.28	1.43
20	3.92	0.0613	299	8.18	2.00	1.69	5.95	1.06	1.69
25	4.90	0.0281	128	8.02	0.823	1.84	4.96	0.315	1.84
30	5.88	0.0133	58.6	7.94	0.369	1.90	3.96	0.0919	1.90
35	6.86	0.00682	29.7	7.88	0.184	1.93	2.95	0.0258	1.93
40	7.84	0.00401	17.3	7.86	0.107	1.94	1.96	0.00665	1.94

The analytical methods were those described in Part I. In the case of manganese the equilibrium solution was also analysed in some experiments. It was observed that the colorimetric determination of manganese was not affected by the presence of metaphosphate. Good agreement was obtained between the two methods. The calculations presented in Tables 1—4 are based upon the analysis of the resin when the main part of the manganese was present in the solution and vice versa.

Calculations. From the determination of the bivalent ion (M) in the resin or in the solution the equivalent fraction X in the resin is calculated and inserted in eqn. (1) in Part I. The selectivity coefficient K_X at a given value for X is taken from the experimental data obtained for nitrate solutions (*cf.* Part I) and the ratio n_M/n_{Na^+} calculated from eqn. (1) in Part I. The results obtained with solutions containing manganese are given in the Tables 1—4.

If it is valid to assume that sodium metaphosphate is completely dissociated (and that there is no associate formation of any kind between sodium ions and metaphosphate ions) the equivalent concentration of free M-ions (n_M) can be calculated by putting n_{Na} equal to the total concentration of sodium ions in the solution. The activity coefficients can, at least at present, not be accounted for in these polyelectrolyte systems and in the present work all deviations from ideality are included in the degree of dissociation. The calculations presented under Method I were made with the assumption that sodium metaphosphate is completely dissociated.

However, as discussed below, this approach cannot explain the behaviour of the metaphosphate solutions and therefore the assumption had to be made that not only bivalent ions but also sodium ions are strongly bound to metaphosphate. This is in agreement with results recently published by Schindewolf and Bonhoeffer⁵ as well as by Wall *et al.*⁶ Sufficient data are lacking for a quantitative interpretation of the systems studied in the present work. Therefore as a first approximation we have chosen the alternative of considering every PO₃-unit, which is not bound to a bivalent cation as being bound to sodium. The results are given in the tables under Method II.

As may be seen from the tables the two methods of calculation give values for n_M which differ considerably, the differences being largest for systems which contain a considerable excess of metaphosphate in comparison with the bivalent ion. Independent

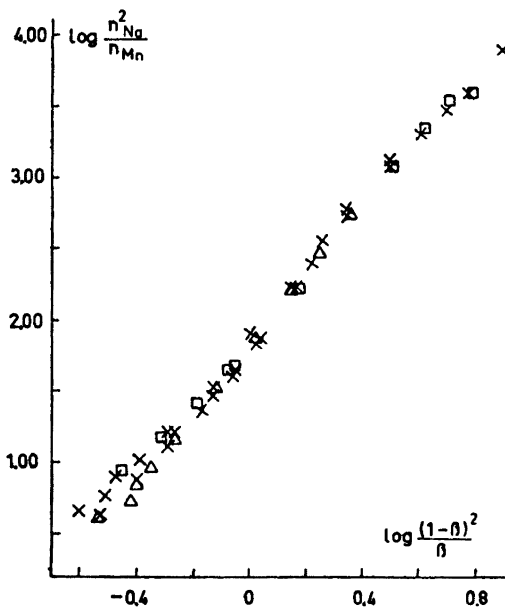


Fig. 1. $\log n^2_{\text{Na}}/n_{\text{Mn}}$ versus $\log (1-\beta)^2/\beta$. Volume of solution: \square 50 ml; \times 150 ml; \triangle 500 ml.

of the method of calculation the equivalent concentration of M-ions bound to the metaphosphate (n_{MP}) is calculated as the difference between the total concentration of M-ions in the solution and n_{M} . The data presented in the tables show that the differences in n_{MP} when calculations are made according to the two methods are rather small and in certain cases negligible. Consequently it may be of interest to find a correlation between n_{MP} and the ratio $n_{\text{M}}/n^2_{\text{Na}}$. The discussion in the subsequent part of this paper is restricted to calculations based upon Method II, but from the above it is obvious that even if Method I had been chosen the influence upon the empirical constants in the equation representing this correlation would be small. The symbol β is used for the ratio $n_{\text{MP}}/n_{\text{PO}_4}$, where n_{PO_4} is the total equivalent concentration of metaphosphate. In accordance with the assumption made in the calculations according to Method II, the concentration of sodium ions bound to the metaphosphate is $(1-\beta)n_{\text{PO}_4}$.

DISCUSSION

When a solution containing a complex salt is diluted, the complex equilibrium is changed in the direction towards a decomposition of the complex. For the metaphosphate solutions studied in the present investigation this rule does not hold true. A probable explanation is that not only the bivalent ions but also the sodium ions are associated in some way with the metaphosphate. An attempt has been made to find an empirical equation which can represent the experimental results.

Figs. 1 and 2 show a plot of $\log n^2_{\text{Na}}/n_{\text{M}}$ against $\log (1-\beta)^2/\beta$. It is observed that over a considerable range of concentration all experimental points fall upon one curve. Fig. 1 contains all experimental data with manganese from

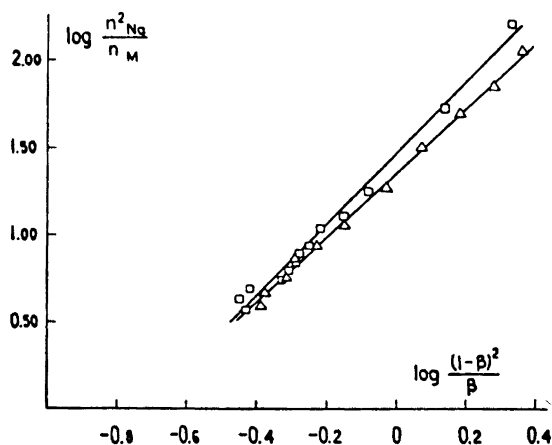


Fig. 2. $\log n^2_{\text{Na}}/n_{\text{M}}$ versus $\log (1-\beta)^2/\beta$. \square System Na—Zn; \triangle System Na—Cu.

Tables 1—4. At low values for $n^2_{\text{Na}}/n_{\text{Mn}}$, *i.e.* at high values for β , there seems to be some deviations, but as the experimental errors may have a considerable influence no attempt will be made to account for these deviations. As a first approximation the curve can be considered as a straight line represented by the following equation:

$$(1-\beta)^2/\beta = k (n^2_{\text{Na}}/n_{\text{M}})^p \quad (1)$$

The numerical values for the parameters are reproduced in Table 5.

Experiments have been performed over a large concentration interval (volume 50—500 ml) and it is obvious that β , *i.e.* the association of manganese to metaphosphate, increases when diluting the solution. This peculiar behaviour might be explained by the polyelectrolyte character of the metaphosphate. For ion exchange resins, which are cross-linked polyelectrolytes, it is known that the uptake of bivalent ions by the resin increases when a solution containing bivalent and monovalent ions is diluted. Furthermore eqn. 1 shows that there is a competition between bivalent ions and sodium ions for metaphosphate in a similar manner as in a solid cation exchanger. Formally eqn. (1) is equivalent to the Rothmund and Kornfeld equation⁷

Table 5. Parameters in equation (1).

System	k	p
Na—Zn	0.19	0.49
Na—Cu	0.18	0.54
Na—Mn	0.17	0.42

which is an empirical formula used to represent ion exchange equilibria. This equation has been used successfully to describe ion exchange equilibria in inorganic as well as in organic ion exchangers. In general this equation has proved to be the best among the numerous formulas proposed for this purpose. From the present investigations it is evident that this equation can be useful also for calculations of the association equilibrium in solutions, which besides metaphosphate contain an ordinary salt, *e.g.* nitrate, the polymer metaphosphate being formally considered as an ion exchanger, *i.e.* as a separate phase. The coincidence might be explained by the ability of linear polyelectrolytes to coil, the cations being held in the coil in a similar manner as the counter ions in an ion exchanger.

The results from experiments with metaphosphate solutions, containing zinc and copper, are reproduced in an analogous manner in Fig. 2. As may be seen from the figure, the curves can as a good approximation be considered as straight lines. The parameters are given in Table 5. From these data it is obvious that the differences in behaviour between manganese, zinc and copper are rather small. Manganese is associated more strongly with the metaphosphate than zinc and copper.

The present approach can only be considered as a first approximation, the use of which is restricted to polymetaphosphate solutions containing besides another electrolyte. It has been observed that besides associated sodium ions, a considerable amount of free sodium ions are present in a pure solution of sodium polymetaphosphate⁵, but sufficient data are not available to permit the application of a correction.

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REFERENCES

1. Samuelson, O. *Iva* **17** (1946) 9.
2. Samuelson, O. *Ion Exchangers in Analytical Chemistry*, Wiley & Sons, New York, 1953 and Almqvist & Wiksell, Stockholm 1952.
3. Djurfeldt, R. and Samuelson, O. *Acta Chem. Scand.* **11** (1957) 1209.
4. Samuelson, O. *Svensk Kem. Tidskr.* **56** (1944) 343.
5. Schindewolf, U. and Bonhoeffer, K.-F. *Z. Elektrochem.* **57** (1953) 216.
6. Wall, F. T. and Doremus, R. H. *J. Am. Chem. Soc.* **76** (1954) 868.
7. Rothmund, V. and Kornfeld, G. *Z. anorg. Chem.* **103** (1918) 129.

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