[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Electrolytic Transference Properties of Polyphosphates

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Electrolytic conductance and transference measurements have been carried out on solutions of polymeric sodium phosphates. From the results of these experiments it was found that the fraction of sodium ions bound to polyphosphate ions increases with molecular weight of the polymer. For sodium polymetaphosphate with a chain length of about 150 units, 70% of the sodium ions become associated with the polyanions. When strontium ions are substituted for some of the sodium ions, nearly all of the strontium ions become bound to the polyphosphate anions, but the charge and mobility of the polymer ion remain substantially unchanged. The bound-free cation-exchange rate, as determined by special transference experiments, was constant with time of electrolysis for the sodium polymetaphosphate solutions, indicating that the exchange rate is not dependent upon the location of the bound ion on the polymer chain. The average bound-free cation-exchange rate was of the same order of magnitude as the rate previously found for polyacrylic acid–sodium hydroxide solutions.

Introduction

Although aqueous solutions of phosphates have been the subject of numerous investigations for some time, their ionic properties have been relatively little understood in spite of their widespread industrial applications. Starting with the simple metaphosphate group, —PO_3,— polymeric materials can be built up with chain lengths varying from two units (pyrophosphate) to over one thousand units. Reviews of the chemistry of these compounds can be found in the literature.[1,2] The water-soluble glass known as Graham's salt, or sodium hexametaphosphate, is now generally believed to be a high polymer which can be represented by the formula $NaO(NaPO_3)_nNa$, or more simply by $(NaPO_3)_n$ if we disregard end groups. There is good reason to believe that each metaphosphate group is linked to only two other such groups, so that the polymer molecule can be considered a straight chain with no branching or cross linking.[3,4]

The techniques that have been used to study organic polyelectrolytes also have been helpful in investigating the polymetaphosphates.[3,4] A transference method developed in this Laboratory allows one to calculate such quantities as the polyion transference number, the fraction of cations bound to polyions, and the polyion charge fraction for aqueous solutions of polyelectrolytes.[5] Moreover, the exchange rate between free and bound cations also can be calculated by a modification of this transference experiment.[6,7] Various polyphosphates were investigated by these two methods to provide new information as to their configurations in solution, as well as to provide further tests of certain theories pertaining to polyelectrolytes.

Experimental

The sodium polyphosphate used in this investigation was made by heating reagent grade sodium monobasic orthophosphate, NaH_2PO_4, to 900° and rapidly cooling the resulting melt to form a glassy material.[8] This glass was dissolved in water and fractionated to cut down the amount of low molecular weight material. The number average degree of polymerization of the fractionated polymer was found to be about 150 by the end group titration method used by Van Wazer.[3] The rate of hydrolysis of the aqueous polyphosphate appears to be rapid immediately after preparation of the solution, but it decreases to a negligible rate after a few hours, and continues to be small for at least a week's time.[4] Since all experiments on the polyphosphates were carried out a few hours after solution preparation, but before a week had elapsed, any degradation by hydrolysis should have been at a minimum.

The other materials used were commercially available reagent grade substances, except for the tripolyphosphate, $Na_5P_2O_{10}\cdot 6H_2O$, which was supplied by Professor L. F. Audrieth of the University of Illinois.

In order to study the complexing of divalent ions by the polymetaphosphates, strontium ions were substituted for sodium ions in the polymer solution by means of a cation-exchange resin, "Dowex 50." The acid form of the resin was converted to the sodium form and packed into a glass column. A standard solution of strontium chloride to which strontium tracer had been added was then passed through the column. By determining the tracer activity of the standard solution, the concentration of strontium in any particular solution was easily found from its radioactive count. After the column was washed free of excess strontium chloride, a freshly prepared solution of sodium polymetaphosphate was passed through it, giving a solution with both sodium and strontium cations but only polymetaphosphate anions.

The sodium ion concentration was measured by means of the radioactive isotope, sodium 22, which was obtained from Washington University, St. Louis, Mo. The strontium tracer used was a mixture of radioactive strontium 89 and 90 and was obtained from the Oak Ridge National Laboratory, Oak Ridge, Tennessee. The phosphate concentrations were measured by a colorimetric method.[9]

The apparatus and experimental procedures used in the various conductance and transference experiments have been described previously.[5,7] The change in polymer concentration attending a transference experiment was found by analyzing the resultant solutions for total phosphorus. All experiments were carried out at 25° except for one sodium polymetaphosphate solution run at 0°.

Discussion of Results

Nomenclature:

c, polymer concn. in equiv./l.
Λ_p, eq. conductance of polyanions in cm.^{2}/eq.-ohm
Λ_j, eq. conductance of free cations of species j
f_j, fraction of cations of species j free in soln.
t_p, polymer ion transference no.
i, av. no. of charges on a polymer ion
s, degree of polymerization
ω_p, polyion mobility
r_j, total concn. in equiv./l. of cation species j
K, total specific conductance of a soln. in ohm^{-1} cm.$^{-1}$
N, total number of electrical equivalents
k, exchange rate constant in l./eq.-min.

The fraction of cations bound to polymer ions and the polyion equivalent conductance, transfer-

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ence number, charge fraction and mobility for a number of phosphate solutions are shown in Table I. These values were calculated from the results of conductance and transference experiments by methods described previously.[5]

As would be expected, the fraction, 1-f, of cations bound to polyions increases with polymer chain length at least for low degrees of polymerization. It is interesting to note that even for Na_2HPO_4 an appreciable fraction (5%) of the sodium is bound to the anion. (We assume that a negligible amount of hydrogen is ionized from this compound. The completely neutralized salt, Na_3PO_4, was not investigated because of its high degree of hydrolysis and alkalinity.) The fraction of sodium bound to the pyrophosphate ion varied from 15 to 30% over a tenfold range of concentrations. For the triphosphate the fraction bound was observed to vary from 20 to 30% over a comparable concentration range. The polyphosphate, on the other hand, had 70% of its cations associated with anions and as far as could be determined this percentage was relatively independent of concentration. All save one of the experiments were carried out at 25°, but the single experiment at 0° suggests that the fraction of sodium ions bound to the polyphosphate is independent of the temperature.

The transference number of the phosphate ion, whether it be of low or high degree of polymerization, is in the general neighborhood of 50%. Actually it is higher for the low molecular weight materials but the shift with degree of polymerization is not a tremendous one.

The mobility, ω_p, of the various phosphate anions decreases with increase in s, the chain length, because of the increase in ion size. The long-chain polymetaphosphates have properties quite similar to those of the polyacrylic acid–sodium hydroxide solutions.[5,6]

If more than one metallic cationic species is present in a polymer solution, the fraction of each species bound can be calculated separately as follows. If q_j is defined as the increase of equivalents of cation species j in the anode compartment of a two compartment transference cell during an electrolysis experiment, then

$$q_j = \frac{r_j N}{K(10)^3} [(1 - f_j)\Lambda_p - f_j\Lambda_j] \tag{1}$$

This equation says that the net amount of j cation which flows through a cross section of a transference cell during an electrolysis experiment is equal to the amount of the j cation bound which flows through the cross section plus the amount of free j cations which cross it. Since all of the quantities in equation 1 except f_j can be determined from the results of conductance and transference experiments,[5] f_j for each species can be calculated by using this equation. If two cationic species a and b are present, and q_a is known while q_b is not, f_b can be found from the following equation

$$f_b = \frac{K(10)^3 - r_a f_a(\Lambda_p + \Lambda_a) - C_H(\Lambda_H + \Lambda_p) - C_{OH}(\Lambda_{OH} - \Lambda_p)}{r_b(\Lambda_p + \Lambda_b)} \tag{2}$$

This equation can be derived by a method similar to that used for the one cation case.[5]

The results of experiments run on a sodium polymetaphosphate solution in which strontium ions were substituted for some of the sodium ions are also shown in Table I. The equivalent sodium and strontium concentrations were 0.0502 and 0.00507 N, respectively, meaning that 9.18% of the sodium ions had been replaced by strontium ions. The value of f for the strontium ion was calculated from equation 1; the f value for the sodium ion was then found from equation 2. Almost all of the strontium ions are bound to the polyanions for this solution; this would be expected in view of the well known ability of the polymetaphosphates for sequestering alkaline earth ions, thus accounting for their water softening properties. The charge and mobility of the polymer ion remain substantially the same as when all the cations were sodium. Thus the strontium ions merely interchange with equivalent amounts of sodium ions in the polymer coil, and do not appear to change the polyion configuration.

TABLE I

CONDUCTANCE AND TRANSFERENCE PROPERTIES OF POLYPHOSPHATES

Solution	c	$1 - f$	Λ_p	t_p	i/s	$s\omega_p \cdot (10)^{-9}$
Na_2HPO_4	0.0346	0.046	48	0.52	0.934	0.34
$Na_4P_2O_7$	.010	.149	67	.58	.847	.51
	.025	.203	62	.58	.795	.50
	.040	.210	54	.55	.790	.44
	.050	.210	51	.52	.790	.42
	.100	.315	50	.54	.684	.48
$Na_5P_3O_{10}$	.010	.191	65	.58	.807	.52
	.025	.277	61	.57	.721	.54
	.040	.285	51	.53	.714	.47
	.050	.289	51	.54	.711	.46
	.100	.366	47	.53	.634	.49
$(NaPO_3)_n$ at 0°	.041	.708	20	.44	.292	.41
$(NaPO_3)_n$ at 25°	.0425	.701	37	.44	.299	.82
	.0925	.707	37	.46	.293	.82
$(Na[^1/_2Sr]PO_3)_n$	.0554		36	.44	.285	.82
Strontium		.989				
Sodium		.686				

Values of the specific exchange rate, k, for bound to free sodium ion exchange for two polymetaphosphate solutions are given in Table II. The definition of k and its calculation from the results of special transference experiments have been described.[6,7] These values of k are reasonably constant with time of electrolysis, in contrast to the k values found for the organic polymer solutions investigated.[7] Thus the original assumption that the cation-exchange rate is independent of the loca-

TABLE II

BOUND-FREE SODIUM ION-EXCHANGE RATE CONSTANTS FOR SODIUM POLYMETAPHOSPHATE SOLUTIONS

Time of electrolysis, min.	Exchange rate constant, l./eq. min. 0.041 N at 0°	0.0425 N at 25°
130	5.50	
120	5.41	3.55
100	5.39	
80	2.54	4.29
40	3.10	3.26
Av.	4.4	3.7

tion of the bound cation on the polyion coil[6] seems to be valid for the sodium polymetaphosphate solutions. This probably is partly due to the fact that the polymetaphosphates have a lower degree of polymerization than the organic polymers which were investigated. In any event, the average polymetaphosphate *k* values are of the same order of magnitude as the *k* values found for many of the other polymers. The exchange rates at 0 and 25° are not very different, showing that the energy of activation for exchange is low.

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Electrophilic Displacement Reactions. III. Kinetics of the Reaction between Hydrogen Peroxide and Benzeneboronic Acid[1]

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A study of the kinetics of the reaction between hydrogen peroxide and benzeneboronic acid at values of *p*H between 2 and 6 has been made. Two ionic mechanisms are distinguishable; each is first order in peroxide; one is first order and the other is second order in boronic acid. The rates of both reactions increase with *p*H but are independent of buffer concentration in the case of phthalate buffers. In acetate and chloroacetate buffers the same specific rate constants are observed as in phthalate. Specific catalytic effects are exhibited by boric acid, zinc perchlorate, citrate and tartrate. The mechanisms of the reactions are discussed in the light of these experimental facts.

Among the reactions of benzeneboronic acid that with hydrogen peroxide is particularly interesting.[2] It is the only reaction involving replacement of the boronic acid function which both aromatic and aliphatic[3] boronic acids are known to undergo under comparable conditions. A second point of interest involves the relative ease of replacement of hydrogen and the boronic acid function in aromatic compounds. Both are replaced with comparable ease by halogens.[3,4] Replacement of hydrogen by hydroxyl, however, is not nearly as facile as replacement of the boronic acid group. The former requires either a strongly basic medium and the presence of hydroxyl groups in the ring[5] or catalysis by iron salts[6] in which case a free radical mechanism is clearly indicated.

$$C_6H_5B(OH)_2 + HOOH \longrightarrow C_6H_5OH + B(OH)_3$$

An investigation of the kinetics of the reaction between benzeneboronic acid and hydrogen peroxide is repeated herein. The results obtained to date suggest mechanisms which render the above observations reasonable.

Experimental

Materials.—Benzeneboronic acid was prepared as described by Bean and Johnson[7] and stored as the anhydride, m.p. 214–216°.[1] Chloroacetic acid (Matheson) was recrystallized from benzene and the sodium salt prepared by addition of the acid to sodium methoxide in anhydrous methanol. All other reagents were the purest grade available commercially and were used without further purification. Sodium perchlorate was used in adjusting ionic strengths.

Stoichiometry of the Reaction.—A solution at *p*H 5.6, 0.0500 *M* in boronic acid and 0.64 *M* in hydrogen peroxide was allowed to stand three hours. From previous rate measurements this period was known to be long enough for greater than 99% consumption of boronic acid. Titration of an aliquot showed a change of 0.0504 *M* in peroxide concentration. At this time another aliquot (5 ml.) was removed. To this were added 1 ml. of concd. hydrochloric acid, 10 ml. of water, 0.5 g. of sodium bromide and 0.5 ml. of 0.5 *M* ammonium molybdate. The bromine thus formed could brominate the phenol present. After 15 min. potassium iodide was added and the iodine titrated with thiosulfate. The difference between this last titer and the preceding one indicated a change of 0.146 *M* in bromine concentration as compared with 0.150 *M* required on the basis of boronic acid originally present.

A similar determination on a reaction in 4.12 *M* perchloric acid showed consumption by the phenol produced in the reaction of 0.0742 *M* bromine *vs.* 0.0750 *M* calculated.

This procedure for quantitative estimation of phenol is a modification of that given by Siggia.[8]

Rate Measurements.—A flask containing appropriate concentrations of boronic acid, buffer and sodium perchlorate was placed in a bath at 25.10 ± 0.02°. After at least 15 minutes an aliquot of hydrogen peroxide solution at the same temperature was added. Aliquots were removed at intervals and transferred to flasks containing 5 ml. of 4 *M* sulfuric acid, 5 ml. of 5% potassium iodide solution and 5 drops of 0.5 *M* ammonium molybdate.[9] The resulting iodine was titrated with freshly standardized sodium thiosulfate, 0.01 *N* or 0.02 *N*. When runs were made in acid solutions the sulfuric acid was omitted from the quenching solution.

In the presence of chelating agents the catalytic effect of molybdate on the iodine–peroxide reaction is negligible and therefore the iodometric analysis is unreliable. The colorimetric method involving titanium(IV)[10] was used. Measurements were made with a Bausch and Lomb photoelectric colorimeter, Model 35. At 415 mμ Beer's law is obeyed in the concentration range 1×10^{-4} to 8×10^{-4} mole per liter (13-mm. cuvettes). The optical density was not affected by any of the solutes. A slow decrease in absorption occurred with time when boronic acid and tartrate or citrate were present, but readings were always completed within two minutes so that the error introduced was never as much as 0.5% in the peroxide concentration.

Determinations of *p*H were made with a Beckman model H2 *p*H meter.

Results

Preliminary experiments showed that the reaction proceeds at a conveniently measurable rate

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