Long-chain Phosphates. II. Reactions of Crystalline Sodium Metaphosphates with Solutions of Various Metal Salts

By Shigeru OHASHI and Takashi NAKAMURA

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Four modifications of crystalline sodium metaphosphate are known. They are designated as $NaPO_3$-I, $NaPO_3$-II, $NaPO_3$-III and $NaPO_3$-IV. As $NaPO_3$-I is sodium trimetaphosphate, $(NaPO_3)_3$, it is out of the scope of this investigation. $NaPO_3$-II, $NaPO_3$-III and $NaPO_3$-IV are long-chain phosphates. $NaPO_3$-II is called sodium Maddrell salt of high temperature form, $NaPO_3$-III, sodium Maddrell salt of low temperature form, and $NaPO_3$-IV, sodium Kurrol salt.

In the previous paper[1] it was found by Ohashi and Yamagishi that the reaction of crystalline potassium Kurrol salt with a solution of nickel sulfate is a kind of cation-exchange reaction. They investigated also the cation-exchange reactions of crystalline potassium Kurrol salt with various metal ions other than the nickel ion. The present authors have investigated the cation-exchange reactions of the crystalline sodium metaphosphates having long-chain structures with aqueous solutions of various metal salts.

Experimental

Preparation of $NaPO_3$-II.—$NaPO_3$-II is usually prepared by dehydrating sodium dihydrogen orthophoshate at a relatively high temperature in a humid atmosphere[2]. In a platinum dish 100∼150 g. of sodium dihydrogen orthophosphate dihydrate was dehydrated by the use of an electric furnace. After the temperature of the furnace reached about 160°C, aqueous steam was introduced over the sample. Then the temperature of the furnace was gradually raised to 400°C. After being kept at 400°C for 3 hr., the sample was removed from the furnace and chilled by holding the lower part of the dish in water. A white powdery product was obtained. The small amount of soluble phosphate remaining in the product was removed by washing it with distilled water. An X-ray diffraction pattern of the sample was identical with that of the ASTM cards.

Preparation of $NaPO_3$-III.—It is very difficult to prepare $NaPO_3$-III in a pure state and in a high yield. The dehydration of sodium dihydrogen orthophosphate should be carried out at a relatively low temperature in a dry atmosphere[3]. When the temperature is too high, $NaPO_3$-II is also produced. When the temperature is too low, a large amount of disodium dihydrogen pyrophosphate remains and the yield of $NaPO_3$-III becomes very low. In a porcelain dish 20∼40 g. of sodium dihydrogen orthophosphate dihydrate was gradually dehydrated. The temperature of the furnace was raised from room temperature to 260°C in 5∼6 hr. and kept at 260°C for 2.5 hr. A white powdery product was obtained. The product was washed with distilled water to remove the pyrophosphate. Although the X-ray diffraction pattern of the sample was identical with that of the ASTM cards, the yield was only 0.3%. $NaPO_3$-III supplied by Dr. T. P. Kickline of the Monsanto Chemical Co. was used in the present investigation on the cation-exchange reactions. 82% of the sample was composed of $NaPO_3$-III and 18% of $NaPO_3$-II.

Preparation of $NaPO_3$-IV.—$NaPO_3$-IV was prepared by Griffith's method[4]. In a platinum dish about 150 g. of sodium dihydrogen orthophosphate dihydrate was dehydrated at a relatively low temperature and melted at 800°C for 2∼3 hr. in an electric furnace. Then the platinum dish was removed from the furnace and transferred to another furnace, which had been previously controlled at 550°C. The temperature of the second furnace was raised to 580°C by introducing the hot dish but fell back to 550°C within 15 min. Seed crystals of $NaPO_3$-IV, supplied by Dr. E. J. Griffith of the Monsanto Chemical Co., were then added to the sample. After being kept at 550°C for 2 hr., the sample was removed from the furnace and chilled by holding the lower part of the dish in water. In order to remove Graham salt and sodium trimetaphosphate, the sample was crushed and washed with distilled water. Although there is no available data on the X-ray diffraction pattern of $NaPO_3$-IV, the pattern of the sample obtained was quite different from those of $NaPO_3$-II and $NaPO_3$-III. Moreover, the appearance of the sample was asbestos-like and quite similar to that of potassium Kurrol salt. The sample was doubtless $NaPO_3$-IV.

The experimental conditions for the cation-exchange reactions and the analytical methods for the determination of phosphate and metal ions were essentially the same as those used in the previous investigation[1].

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[1] S. Ohashi and K. Yamagishi, This Bulletin, 33, 1431 (1960).

[2] J. R. Van Wazer, " Phosphorus and its Compounds ", Vol. I, Interscience Publishers, New York (1958), pp. 668—669.

[3] Private communication from Dr. T. P. Kickline of the Monsanto Chemical Co.

[4] Private communication from Dr. E. J. Griffith of the Monsanto Chemical Co.

Results and Discussion

When any one of the sodium metaphosphates was added to a solution of nickel sulfate, the white crystalline sodium metaphosphate was gradually converted into a green gummy substance. The adsorption of the nickel ion was investigated in the following manner. At the bottom of an Erlenmeyer flask of 300 ml., 1 g. of the ground sodium metaphosphate was placed flat, and then 200 ml. of a 0.1 M solution of nickel sulfate was added to it. The mixture was kept at 20°C without agitation. The variation in the amount of the nickel ion adsorbed as time went on was determined by measuring the decrease in the nickel ion concentration in the solution. As shown in Fig. 1, after about 24 hr. the reaction reached equilibrium in every case of the three sodium metaphosphates. The reaction of $NaPO_3$-IV with a solution of cobalt sulfate also reached equilibrium after about 24 hr., as is shown in Fig. 2.

The cation exchange reactions between the sodium ions in the solid sodium metaphosphates and various metal ions in their solutions were investigated as follows. In an Erlenmeyer flask of 100 ml., about 250 mg. of each crystalline sodium metaphosphate was placed, and then 50 ml. of an about 0.1 M solution of a metal salt was added to it. After being kept at 20°C for 24 hr. without agitation, an aliquot of the solution was taken and analyzed for the metal ion remaining in the solution and for the phosphate dissolved into the solution. From these data a percentage of the sample dissolved, an amount of the sample remaining as a solid phase, and a percentage

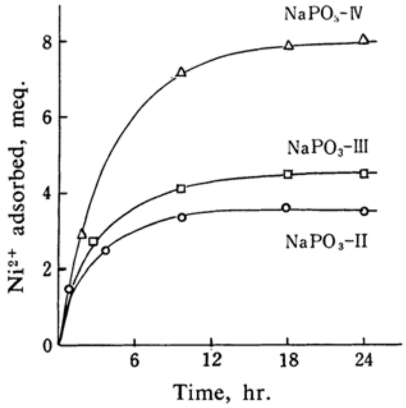

Fig. 1. The variation of the amounts of nickel ion adsorbed with time.

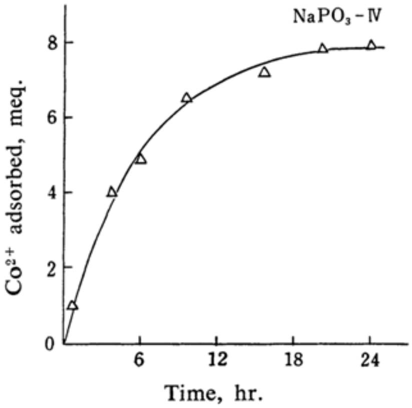

Fig. 2. The variation of the amounts of cobalt ion adsorbed with time.

TABLE I. CATION-EXCHANGE REACTIONS BETWEEN SODIUM METAPHOSPHATE AND SOLUTIONS OF VARIOUS METAL SALTS

Metal salt, initial concn. and pH	Form of $NaPO_3$	Sample added meq.	Sample dissolved %	Sample remaining meq.	Sodium exchanged %	Final pH
$CaCl_2$	II	2.48	0.4	2.46	40.7	4.85
0.0990 M	III	2.45	2.0	2.40	82.8	3.86
pH 6.15	IV	2.48	0.4	2.47	98.4	4.85
$MgCl_2$	II	2.48	0.4	2.47	23.5	4.70
0.1029 M	III	2.45	1.6	2.41	80.5	3.60
pH 5.85	IV	2.47	0.4	2.46	87.8	4.70
$FeSO_4$	II	2.46	0.8	2.44	13.9	3.56
0.1020 M	III	2.47	2.4	2.40	70.7	3.08
pH 3.60	IV	2.46	2.4	2.40	80.8	3.40
$CoCl_2$	II	2.53	0.4	2.52	23.0	4.20
0.1024 M	III	2.46	2.1	2.41	78.0	3.24
pH 4.40	IV	2.46	0.4	2.45	85.7	4.14
$NiSO_4$	II	2.46	0.9	2.44	37.7	4.70
0.1074 M	III	2.45	4.3	2.23	72.7	4.32
pH 5.60	IV	2.45	2.0	2.40	95.0	4.55
$CuSO_4$	II	2.50	39.8	1.50	5.3	3.28
0.1030 M	III	2.46	58.1	1.03	36.9	2.90
pH 4.30	IV	2.50	26.4	1.84	34.8	3.20

of the sodium ion exchanged by the metal ion at the end of the reaction were calculated. Before and after the reaction, the pH values of the solution were measured. The results are summarized in Table I.

The percentages of the cation exchange in the cases of magnesium, calcium, iron(II), cobalt(II) and nickel(II) ions were in the range of 14 to 41 for $NaPO_3$-II, 70 to 83 for $NaPO_3$-III, and 81 to 98 for $NaPO_3$-IV. The tendency of the cation exchange of the sodium metaphosphates for these metal ions decreases in the order:

$$NaPO_3\text{-IV} \gtrapprox NaPO_3\text{-III} > NaPO_3\text{-II}$$

In the case of potassium Kurrol salt, the percentages of the cation exchange for these cations were in the range of 82 to 94, as mentioned in the previous paper[1].

The following facts in regard to the dissolution of the sodium metaphophates in water were described by Van Wazer[2]. $NaPO_3$-II is dissolved in water at a very slow rate, 1.8×10^{-2} %/hr., and $NaPO_3$-III is also dissolved in water at a slow rate, 0.34%/hr. $NaPO_3$-IV appears to be dissolved more rapid; it forms a gel-like substance when it is kept in water for a long time. These facts may indicate that the tendency toward hydration of the sodium metaphosphates decreases in the following order:

$$NaPO_3\text{-IV} > NaPO_3\text{-III} > NaPO_3\text{-II}$$

which coincides with the order of the tendency of the cation exchange of the sodium metaphosphates. Therefore, in the course of the cation exchange of the sodium metaphosphates, the process of the hydration may play an important role.

The percentages of the phosphates dissolved during the cation exchange reactions were in the range of 0.4 to 4 for almost all of the bivalent metal ions tested in the present investigation. However, only in the case of copper(II) ion were large amounts of the phosphates, which ranged from 26 to 58%, dissolved in the course of the reactions. In the reaction of potassium Kurrol salt with the copper(II) ion, 32% of the phosphate was dissolved. It is a well-known fact that potassium Kurrol salt is not easily soluble in pure water, but it is soluble in dilute solutions of salts of alkali metals other than potassium; furthermore, crystalline sodium metaphosphates with long-chain structures are also not easily soluble in pure water, but they are soluble in dilute solutions of salts of alkali metals other than sodium. In regard to the reactions with the long-chain phosphates, the copper(II) ion has an intermediate property between alkali metals and bivalent metals such as magnesium, calcium and so on.

In all cases the pH of the solutions of the metal salts decreased in the course of the reactions. The decrease in pH may be due to the dissolution and the hydrolysis of the sodium metaphosphates. Actually, in the case of $NaPO_3$-III, both the percentages of the phosphate dissolved and of the decrease in pH were larger than in the case of the other metaphosphates. As indicated by Wieker and Thilo[5], the hydrolysis of the metaphosphates may be accelerated by the catalytic actions of the metal ions.

Summary

Three kinds of crystalline sodium metaphosphates with a long-chain structure, $NaPO_3$-II, $NaPO_3$-III and $NaPO_3$-IV, were prepared, and the cation exchange reactions of the solid sodium metaphosphates with aqueous solutions of bivalent metal salts, calcium, magnesium, iron(II), cobalt(II), nickel(II) and copper(II), were investigated. The tendency of the cation exchange of the sodium metaphosphates for these metal ions, except for copper(II), decreases in the order:

$$NaPO_3\text{-IV} \gtrapprox NaPO_3\text{-III} > NaPO_3\text{-II}$$

which coincides with the order of the tendency of the hydration of the sodium metaphosphates. Only in the case of copper(II) ion were large amounts of the sodium metaphosphates dissolved in the course of the reactions.

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Department of Chemistry
Faculty of Science
Kyushu University
Fukuoka

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5) W. Wieker and E. Thilo, *Z. anorg. u. allgem. Chem.*, 306, 48 (1960).