[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF IDAHO]

A Polarographic Study of Sodium Polyphosphates[1]

BY JACK ALLEN CAMPBELL

It has been shown[1a] that a polarographic measurement of the amount of barium removed by various complex phosphates furnishes some indication of the nature of these compounds. All of the sodium present in a dilute, unbuffered solution of sodium metaphosphate glass is replaceable by barium, forming a white precipitate. Crystalline sodium metaphosphate, on the other hand, does not form a precipitate with barium. Although one mole of sodium triphosphate, $Na_5P_3O_{10}$, is capable of precipitating 2.5 moles of barium, a slowly cooled melt of composition $3Na_2O \cdot 2P_2O_5$, corresponding to the sodium tetraphosphate of Fleitmann and Henneberg,[2] yields a product capable of also removing but 2.5 moles of barium. This is the result predicted by the conclusions of Partridge, Hicks and Smith[3] that this substance is an equimolecular mixture of sodium triphosphate and crystalline sodium metaphosphate. It is the purpose of the present communication to report similar measurements made on both glasses and crystalline sodium phosphates having Na_2O/P_2O_5 ratios between 1.00 and 2.00.

The substances studied had Na_2O/P_2O_5 ratios of 1.25, 1.50, 1.67 and 1.75, corresponding to the compositions $5Na_2O \cdot 4P_2O_5$, $3Na_2O \cdot 2P_2O_5$, $Na_5P_3O_{10}$ and $7Na_2O \cdot 4P_2O_5$, respectively. The technique was the same as that in the earlier work,[1a] except that hydrogen was used for degassing, and the barium diffusion currents, from which the concentrations were determined, represented average values obtained at potentials between −1.95 and −2.00 v. (saturated calomel). The instrument used was again a Fisher "Elecdropode." The temperature was 25°, and recrystallized tetramethylammonium bromide was the only supporting electrolyte.

Experimental

Tetrasodium pyrophosphate was prepared from recrystallized reagent grade disodium orthophosphate. The product was twice recrystallized, and its purity was checked by its phosphorus pentoxide content.

Crystalline sodium metaphosphate was prepared by an excellent method based upon the observations of Pascal.[4] Monosodium orthophosphate was recrystallized according to the directions of Beans and Kiehl.[5] From this, sodium metaphosphate glass was prepared by heating the orthophosphate at about 1000° in a platinum dish for several hours and quenching the resulting melt between two polished steel slabs. The crystalline modification resulted from devitrifying this glass at 500° for about fifteen hours. After being twice recrystallized from water with alcohol, its purity was checked[6] and found to be as high as the products of more elaborate methods[5,6] of preparing this compound.

The glasses were prepared by mixing the meta and pyrophosphates in the proper proportions, heating at about 1000° for three hours and quenching. The glasses corresponding to $5Na_2O \cdot 4P_2O_5$ and $3Na_2O \cdot 2P_2O_5$ were clear, while $Na_5P_3O_{10}$ and $7Na_2O \cdot 4P_2O_5$ were somewhat white and opaque.

A portion of each glass then was devitrified by the same technique used for the sodium metaphosphate. After this treatment, the $5Na_2O \cdot 4P_2O_5$ appeared still to contain a slight amount of residual glass. The other substances immediately crumbled to a fine powder upon removing from the muffle.

Experimental Results

The results obtained with the glasses are given in Table I. The equivalent weights were calculated on the basis of the number of sodium atoms in the empirical formula.

TABLE I

EFFECT OF POLYPHOSPHATE GLASSES ON BARIUM CHLORIDE SOLUTIONS

Amount of phosphate added = 2.00 milliequivs. per liter; concentrations of Ba^{++} in milliequivs. per liter.

Na_2O/P_2O_5	Initial concn. $BaCl_2$	Final concn. Ba^{++}	Milliequivs. Ba^{++} removed	Average % Na^+ replaced
1.25	5.00	3.10	1.90	92.5
	3.00	1.20	1.80	
1.50	5.00	3.16	1.84	91.0
	3.00	1.20	1.80	
1.67	5.00	3.12	1.88	95.6
	3.00	1.16	1.94	
1.75	5.00	2.96	2.04	97.0
	3.00	1.16	1.84	

It will be noticed that more than 90% of the sodium in the glasses was replacable by barium. The fact that all of the sodium is not replaced is anticipated from the work of Jones,[6] who found that there was always present in metaphosphate glass about 5–10% of inactive crystalline sodium metaphosphate. It is concluded that the glasses studied behave as though they would form a continuous series of homogeneous substances, having all sodiums replacable by barium, if complete

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[1] Presented at the Regional Meeting of the American Chemical Society, Puget Sound Section, Bagley Hall, University of Washington, Seattle, Washington, October 20, 1946.

[1a] Campbell and Schenker, THIS JOURNAL, **67**, 767 (1945).

[2] Fleitmann and Henneberg, *Ann.*, **65**, 304 (1848).

[3] Partridge, Hicks and Smith, THIS JOURNAL, **63**, 454 (1941).

[4] Pascal, *Bull. soc. chim.*, **35**, 1131 (1924).

[5] Beans and Kiehl, THIS JOURNAL, **49**, 1990 (1927).

[6] Jones, *Ind. Eng. Chem., Anal. Ed.*, **14**, 536 (1942).

conversion to the vitreous form could be realized by more rapid quenching.

Table II shows the data obtained from a similar study of the devitrified glasses.

TABLE II

EFFECT OF DEVITRIFIED POLYPHOSPHATES ON BARIUM CHLORIDE SOLUTIONS

Amount of Phosphate Added = 2.00 milliequivs. per liter
Concentrations of Ba^{++} in milliequivs. per liter.

Na_2O/P_2O_5	Initial concn. $BaCl_2$	Final concn. Ba^{++}	Milliequivs. Ba^{++} removed	Average moles Ba^{++} per mole phos.
1.25	5.00	3.96	1.04	2.7
	3.00	1.84	1.16	
1.50	5.00	3.34	1.66	2.4
	3.00	1.42	1.58	
1.67	5.00	2.96	2.04	2.5
	3.00	1.06	1.94	
1.75	5.00	3.22	1.78	6.2
	3.00	1.22	1.78	

According to the thermal studies of Partridge, Hicks and Smith,[3] the crystalline products are mixtures of sodium triphosphate and crystalline metaphosphate or pyrophosphate, depending on whether the Na_2O/P_2O_5 ratio is less than or greater than 5/3. Table III gives a comparison between the results expected from this theory and those actually found.

TABLE III

COMPARISON OF THEORETICAL AND OBSERVED VALUES OF MOLES Ba^{++} PER MOLE PHOSPHATE FOR DEVITRIFIED POLYPHOSPHATE GLASSES

	Composition of 1 mole of phosphate				
Na_2O/P_2O_5	Moles $NaPO_3$ (cryst.)	Moles $Na_5P_3O_{10}$	Moles $Na_4P_2O_7$	Moles Ba^{++} per mole phos. Calcd.	Obs.
1.25	5	1	..	2.5	2.7
1.50	1	1	..	2.5	2.4
1.67	..	1	..	2.5	2.5
1.75	..	2	1	7.0	6.2

The agreement is such as to inspire additional confidence in the Partridge, Hicks and Smith formulation of the system $NaPO_3$–$Na_4P_2O_7$.

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Summary

From a polarographic comparison of barium removal by both glasses and the devitrified products of the system $NaPO_3$–$Na_4P_2O_6$, it is concluded that:

1. Sodium phosphate glasses of Na_2O/P_2O_5 ratios between 1 and 2 would, if pure, have all sodiums replacable by barium, and thus behave as though they form a continuous series.
2. Additional support has been given to the phase studies of Partridge, Hicks and Smith on the $NaPO_3$–$Na_4P_2O_7$ system.

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The Conductances of Lead Chloride in Ethylene Glycol–Water Mixtures

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The purpose of this investigation is to present data for the conductances of lead chloride at various low concentrations in pure water, pure ethylene glycol and in four mixtures of ethylene glycol and water consisting of 20, 40, 60, 80% of glycol, and to compare these values with the Onsager equation. Previously measured activity coefficients of lead chloride in these six solvents will be compared with the Debye–Hückel limiting law. We shall be able to show qualitatively some of the reasons for the failure of these theories. The general conclusions which will be reached are that the principal cause of discrepancy between theory and experiment is that the effective dielectric constant in the Debye–Hückel equation is less than the measured macroscopic dielectric constant, and that the effective dielectric constant in the Onsager equation, which applies when an external field is present, is considerably less than the effective dielectric constant in the Debye–Hückel equation.

Experimental

Lead Chloride.—Triple distilled water at 100° was saturated with Mallinckrodt Analytical Reagent lead chloride. After filtration precipitation was brought about by cooling and by the addition of a small percentage of reagent quality concentrated hydrochloric acid. The product was dried at 110° for twenty-four hours and was stored in a desiccator until used.

Ethylene Glycol.—Eastman Kodak best grade ethylene glycol (E. K. Co. 133) was dried over anhydrous sodium sulfate and decanted. The dried glycol was distilled twice at reduced pressure. The middle third was kept each time.

Solutions.—The solvents and solutions were prepared gravimetrically and the weights were converted to vacuum weights. All the solvents and solutions were in equilibrium with air. The accuracy desired was 0.1%, and all the weight concentrations were determined to well within this accuracy.

Apparatus.—The apparatus has been described by Garrett and Vellenga.[1] The frequency of the oscillator was 2000 cycles/second. The detector was an oscilloscope arranged as suggested by Lamson.[2] The cell was cleaned by the method of Morgan and Lammert,[3] and was kept filled with hot triple distilled water for several days to remove adsorbed ions from the cell and electrode surfaces.

Data

The data are given in Table I and are shown

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[1] Garrett and Vellenga, THIS JOURNAL, **67**, 225 (1945).

[2] Lamson, *Rev. Sci. Instruments*, **9**, 273 (1938).

[3] Morgan and Lammert, THIS JOURNAL, **45**, 1692 (1923).