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Progress Report on Project AT(30-1)1018: Pola: -Nonpolar or Amphipathic Inorganic Compounds.

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By U. P. Strauss



It is the ultimate aim of this project to study inorganic amphipathic compounds. Such compounds are envisioned as molecular chains which are terminated at one or both ends by groups whose affinity for a given solution or surface is different from that of the main body of the chain.

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The linear polyphosphates ranging in molecular weight from 5,000 to 20,000 were chosen as the starting point for this research because previous reports had given some indication that these compounds possessed the desired chain-like structure. Moreover, there was some evidence in the patent literature that the suspending power of these compounds could be greatly enhanced if they were fused with the oxides of certain elements such as Mo or V. However, nothing was reported concerning the molecular structure of the resulting fusion products.

Before any work on these complex fusion products could be started, it was considered necessary to first learn something about the properties of the unmodified polyphosphates. Three such properties appeared of primary importance, namely, (1) their molecular structure, (2) their hydrolytic stability, and (3) their behavior with different cations.

The first of these properties was studied on sodium and lithium polyphosphates ranging in molecular weight from 5,000 to 1,200,000

by light-scattering and viscosity techniques. The results showed that, depending on the chemical composition, the polyphosphates are either linear or branched flexible chain molecules. Since the branch-points were shown to be easily destroyed by hydrolysis, the polyphosphate chains can be counted upon to be linear a few hours after dissolution in water. These studies also established the relation between the viscosity and the molecular weight of the polyphosphates. This relation has increased the facility and accuracy of molecular-weight determinations.

Considerable progress has also been made in the investigation of the hydrolytic stability of polyphosphates. A kinetic study of the hydrolysis at the branching points in the polymer chains has established the mechanism for this process. This result serves as a guide towards understanding the more complex kinetics of the hydrolytic degradation of the linear portions of the polyphosphate chains. These studies have shown that the rate constants are much smaller for the splitting of internal bonds than for the hydrolysis near the chain ends, where both monomer and trimeric rings are formed. While chains of all lengths split off monomer, the shortest linear polyphosphate which degrades into rings has been established to be the pentamer. The pentamer should be especially suitable for kinetic studies because all the degradation products can be determined analytically by ion-exchange chromatography. Such kinetic studies have been started.

The influence of different univalent cations on the behavior of polyphosphates was studied by electrophoresis, conductivity, membrane equilibrium and viscosity measurements. The results indicated that the alkali metal ions were specifically bound by polyphosphates. The extent of this binding was determined by several independent methods which also furnished information about the distribution of small ions in the neighborhood of the polyphosphate chain and about the electrical transport properties of polyphosphates. It was also found that complexes between the phosphate groups and the various cations have different solvent affinities which affect the molecular dimensions and interactions of the polyphosphates. Extension of these studies to divalent cations was started.

The following work continued during the contract year 1961-62.

Hydrolytic Stability

The kinetic study of the degradation of sodium pentaphosphate was continued. Several difficulties had to be overcome. One was the preparation of a reasonably pure sample from troenelite which is crystalline calcium polyphosphate. The other was the control of calcium ion, traces of which would influence both the rate and the nature of the degradation products. Both these difficulties appear to have been overcome, reproducible rates have been obtained, and initial results indicate that in the absence of calcium the formation of each trimeric

ring is accompanied by the formation of two orthophosphate rather than by one pyrophosphate molecule. (Jean Day, B.Scott, R. Prabhu).

Binding of Cations

The studies with univalent dye-cations with which spectral changes occur on binding have been continued. The binding studies with magnesium ion have been completed. The binding was measured by an ion-exchange resin method. The effect of the binding on the electrophoretic mobility, molecular dimensions and solubility of the polyphosphate was determined, and it was found that at equal degrees of binding the effects of the divalent ion fell within the range previously observed for univalent ions. A theory was developed concerning the simultaneous binding of divalent and univalent cations to a linear array of anionic groups, taking into account nearest neighbor electrostatic interactions (jointly with S. Lipson). The agreement of the experimental and theoretical results is not yet as good as hoped for, but much better than was obtainable with previous theories. The experimental work is being extended to other divalent cations in order to improve our understanding of these binding phenomena. (L. Muschiatti, B. Nelson, A. Siegel).

The following paper has been submitted for publication to the Journal of the American Chemical Society (also submitted as Technical Report NYO-9836 to A.E.C.):

U.P. Strauss and P. Ander, "Molecular Size and Interactions of Lithium Polyphosphate in Aqueous Solutions of Lithium Bromide".

Several other papers on the work done on this project are being prepared for publication.

Fourteen publications which have appeared from this research previously were listed in previous Progress Reports.

Future Work

The following lines of research are planned for the next contract year.

Hydrolytic Stability:

The kinetic studies of the degradation of sodium pentaphosphate will be continued with the aim of determining the mechanism. The main parameters whose effects we want to study are pH, temperature, and type and concentration of added cations.

Binding of Cations:

The binding studies with multivalent cations will be continued. By studying a number of different cations it is hoped to separate specific from general effects. In addition to the binding isotherms, the effects of binding on various properties of the polyphosphates will also be studied. It is planned to extend the theory of the simultaneous binding of divalent and univalent ions with a polyelectrolyte chain to include effects at the chain

ends. In this way it is hoped to lay both experimental and theoretical foundations for understanding the effects of the more complex vanadium, molybdenum and still larger cations on the polyphosphate chains. It is also planned to continue the binding studies with univalent cationic dyes which exhibit spectral changes on binding.

Scientific Personnel

The current and projected distribution of scientific personnel working on the project is as follows:

For 1961-62:

Day, Jean; Research Assistant on project (hydrolytic)

Muschiatti, Lawrence: Research Assistant on project
(binding of dye cations)

Prabhu, Rayapa: Research Assistant on project for seven months
(hydrolysis)

Scott, Bruce: Research Assistant on project for three months
(technical assistant)

Nelson, Burnet: Graduate student doing research on project,
but not supported by project
(binding of divalent cations)

For 1962-63:

Jean Day, Lawrence Muschiatti, Burnet Nelson, half-time,
research assistants on project; one full-time technical
research assistant to be employed.

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