

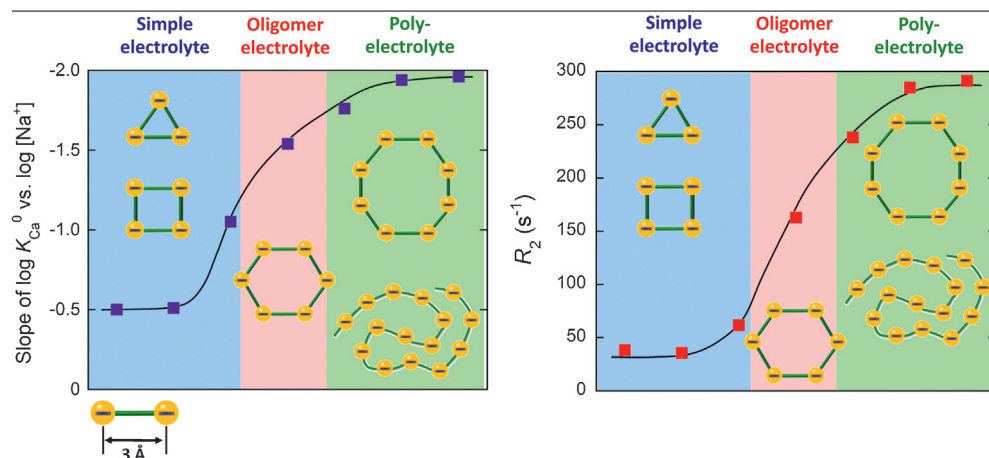
Transitions from simple electrolyte to polyelectrolyte in a series of polyphosphates



Hideshi Maki*, Kie Ibaragi, Yoshiaki Fujimoto, Hiroyuki Nariai, Minoru Mizuhata

Department of Chemical Science and Engineering, Graduate School of Engineering, Kobe University, 1-1 Rokkodai-cho, Nada-ku, Kobe 657-8501, Japan

GRAPHICAL ABSTRACT



HIGHLIGHTS

- Dependence of polyelectrolyte effects on the number of ionic groups was revealed.
- Polyelectrolyte effects increased non-monotonically with phosphate groups number.
- These behaviors were observed not only electrochemical titration but also ²³Na NMR.

ARTICLE INFO

Article history:

Received 22 May 2015

Received in revised form 28 July 2015

Accepted 31 July 2015

Available online 3 August 2015

Keywords:

Donnan model

²³Na NMR

Polyion

Charge density

Two variable theory

Polymerization degree

ABSTRACT

The dependence of polyelectrolyte characteristics on the number of phosphate groups in a series of polyphosphates was clarified by potentiometric titration and ²³Na nuclear magnetic resonance using the Donnan model. Ca²⁺ ion binding to various polyphosphates was consistently inhibited as supporting electrolyte concentration increased. The electrostatic interactions between polyions and counterions, which is peculiar to polyelectrolytes, was enhanced by an increase in the number of phosphate groups. The polyelectrolyte characteristics increased non-monotonically with the number of phosphate groups that constituted the molecules, that is, (1) gradual emergence with three or four phosphate groups, (2) marked strengthening from four to eight phosphate groups, and (3) saturation with eight or more phosphate groups. The characteristics of polyelectrolyte molecules comprising eight or more phosphate groups were independent of the degree of polymerization. These interesting behaviors were observed to be closely similar using two quite different experimental techniques, electrochemical titration and nuclear magnetic resonance.

© 2015 Elsevier B.V. All rights reserved.

* Corresponding author. Fax: +81 788036168.

E-mail address: maki@kobe-u.ac.jp (H. Maki).

1. Introduction

Many phosphate compounds are currently used daily in an extremely wide range of applications such as fertilizers, water treatment agents, food additives, paints, ceramics, catalysts, and active materials for secondary batteries. These various phosphate compounds form a variety of condensed phosphates by hydrolysis and dehydration condensation reactions through heating (i.e., chain-, *cyclo*-, and ultraphosphates). The chemical properties of these various condensed phosphates differ widely because of their degree of polymerization, molecular shape, and molecular skeleton structure, such as crosslinked atoms and ionic groups. Clarification of the essential causes of these differences would be extremely useful for the development of new phosphate materials and their novel applications.

Many studies have been carried out to date on the complex formation behaviors of long-chain and cyclic polyphosphates [1–6]. However, many of those studies assumed the polyphosphates act as simple electrolytes and thus determined the complex formation constants in accordance with the simple mass action law. It must be noted, however, that various polyphosphate anions, from low to high molecular weight, possess some of the features of polyelectrolyte, as follows [7,8];

- (1) Many negative charges are attached to the molecular skeletons of the polyphosphate anions.
- (2) A negative electric field of high charge density exists in the vicinity of the polyphosphate anions because the phosphate groups themselves form molecular skeletons.

In simple electrolyte solutions, the electrolyte molecules are almost uniformly dispersed because of their stable solvation by solvent molecules. The distance between individual electric charges depends only on the electrolyte concentration. However, in polyelectrolyte solutions, the distribution of electric charges in solution is quite different from simple electrolyte solutions. The individual ionic groups are mutually and rigidly bound by strong covalent bonds that cannot be cleaved by the solvation energy, thus the polymer skeletons containing fixed individual ionic groups disperse into solution. As a result, several tens to several thousands of static charges are overcrowded in space in several-ten to several-hundred nanometer order. The polyelectrolyte phase is therefore formed in the vicinity of the polymer skeleton, whereas the static charge density decreases remarkably in the bulk solution phase. Clearly, using acid dissociation theory to describe the complexation equilibria of solutions with very different electrostatic distributions is not a valid approach.

Polyelectrolytes form a strong electrostatic field in the vicinity of their polymer skeletons and the counterions condense in the same vicinity. Accordingly, electrostatic interactions become the main cause of acid dissociation and counterion binding reactions. Consequently, it is difficult to accurately express the complexation equilibria of polyelectrolytes on the basis of a simple electrolyte, that is, using the mass action law [9]. Therefore, we contend that acid dissociation and complex formation constants determined by the mass action law do not accurately express the various chemical equilibria of polyelectrolyte solutions. In the case of polyphosphate in particular, accurate description of polyelectrolyte complexation equilibria using parameters obtained through treating them as simple electrolytes is practically impossible.

To quantitatively express the complicated counterion binding equilibria that occurs in polyelectrolytes, use of the Donnan model, in which a polyelectrolyte phase with constant electrostatic potential is assumed in the vicinity of the polymer skeletons, has been advocated [10–12]. In the Donnan model, the equilibrium system of polyelectrolyte solutions is divided for convenience into two

phases (i.e., a polyelectrolyte phase with high charge density and a bulk solution phase), and it is assumed that simple ion exchange equilibrium is established between the phases. The Donnan model has been identified as a model that enables the complex formation equilibria of polyelectrolytes to be expressed accurately [13–20]. In this work, the Donnan model was used to identify the polyelectrolyte characteristics affecting the complexation equilibria of various cyclic and long-chain polyphosphate anions having different degrees of polymerization, using calcium ions as model alkaline earth cations. Furthermore, the influences of the degree of polymerization in long-chain polyphosphate anions, the number of phosphate groups constituting cyclic polyphosphate anions, and differences in polymer skeletons on polyelectrolyte characteristics are discussed.

2. Experimental

2.1. Chemicals

2.1.1. Chemicals used

All chemicals used in this work were of analytical grade. 85% orthophosphoric acid, H_3PO_4 , hexachlorocyclotriphosphazene (phosphonitrilic chloride trimer), $\text{P}_3\text{N}_3\text{Cl}_6$, and trisodium *cyclo*-triphosphate hexahydrate (trisodium $\text{P}_{3\text{m}}$), $\text{Na}_3\text{CP}_3\text{O}_9 \cdot 6\text{H}_2\text{O}$, were purchased from Nacalai Tesque Inc. (Kyoto, Japan), Otsuka Chemical Co., Ltd. (Osaka, Japan), and Taihei Chemical Industrial Co., Ltd. (Osaka, Japan), respectively. $\text{Na}_3\text{CP}_3\text{O}_9 \cdot 6\text{H}_2\text{O}$ was purified by recrystallization of three times from an aqueous solution. Tetrasodium *cyclo*-tetraphosphate tetrahydrate (tetrasodium $\text{P}_{4\text{m}}$), $\text{Na}_4\text{CP}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$, was prepared as our previously reported method [21]. All other chemicals were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Representative structures of various polyphosphates applied in this work are shown in Scheme 1.

2.1.2. Synthesis of hexasodium *cyclo*-hexaphosphate hexahydrate, $\text{Na}_6\text{CP}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$

Hexasodium *cyclo*-hexaphosphate hexahydrate (hexasodium $\text{P}_{6\text{m}}$), $\text{Na}_6\text{CP}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$, was prepared by an improvement of the previously reported method [22]. Hundred and twelve gram of lithium carbonate, Li_2CO_3 , and 250 g of H_3PO_4 were thoroughly kneaded in a porcelain dish, and after standing overnight in atmosphere, the mixture was reacted in an electric furnace at 100 °C for 1 h, at 200 °C for 1 h, and at 270 °C for 15 h. Hexalithium *cyclo*-hexaphosphate, $\text{Li}_6\text{CP}_6\text{O}_{18}$, as the intermediate of $\text{Na}_6\text{CP}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$ was synthesized by slow cooling of this reaction product under atmosphere. $\text{Li}_6\text{CP}_6\text{O}_{18}$ was dissolved in 300 mL of water, and then filtered by suction. Lithium ions in the filtrate was completely exchanged for sodium ions by the passing through a Na-form strongly acidic cation exchange resin column (i.e. 5 cm in diameter and 20 cm in height of DOWEX 50W × 8 (100–200 mesh)). Then 400 mL of ethanol was put into the effluent. After filtration of the solution, a white precipitate was dissolved in 250 mL of water, and 300 mL of ethanol was put into the solution. $\text{Na}_6\text{CP}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$ as a white precipitate was collected by suction filtration and washed with 50 vol% aqueous ethanol and then 100 vol% acetone, and dried in air. The total yield was 44%.

2.1.3. Synthesis of octasodium *cyclo*-octaphosphate hexahydrate, $\text{Na}_8\text{CP}_8\text{O}_{24} \cdot 6\text{H}_2\text{O}$

Octasodium *cyclo*-octaphosphate hexahydrate (octasodium $\text{P}_{8\text{m}}$), $\text{Na}_8\text{CP}_8\text{O}_{24} \cdot 6\text{H}_2\text{O}$, was prepared by an improvement of the previously reported method [23]. Ninety six gram of $\text{Na}_4\text{CP}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$ was dissolved in 500 mL of water with stirring at a speed of 800 rpm, and then 400 mL of 1.0 mol/L $\text{Pb}(\text{NO}_3)_2$ aqueous solution was added gradually. After 30 min, the reaction product was collected by suction filtration and washed with

Download English Version:

<https://daneshyari.com/en/article/6978654>

Download Persian Version:

<https://daneshyari.com/article/6978654>

[Daneshyari.com](https://daneshyari.com)