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ORIGINAL CONTRIBUTION

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Interaction of a cationic surfactant to sodium polyphosphates with different degrees of polymerization

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Abstract The binding behavior of dodecylpyridinium chloride to sodium polyphosphate of various degrees of polymerization (DP) was studied by means of a potentiometric titration method using a surfactant-selective electrode in the presence of 10 mM NaCl at 30 °C. Binding isotherms were analyzed by direct calculation of a matrix expressing the partition function. It is found that binding affinity depends prominently on the polymer chainlength when the DP value is less than ca. 35, but becomes nearly independent on DP thereafter. No binding was observed for linear triphosphate or cyclic trimetaphosphate anions. The picture that arises for the binding is that the polymer's end-effect reduces the apparent cooperativity, while the hydrophobic interaction with neighboring surfactant remains constant because of the short-range nature of the interaction. The so-called end-effect is associated with a superimposition of electrostatic potentials around the polymer rods. Both the matrix method and the Satake–Yang equation were carried out for simulations, and the matrix one shows a better fitting with the experimental data for the short-chain polyelectrolyte.

Key words Polyphosphate – degree of polymerization – electrostatic potential – surfactant – binding isotherm

Introduction

Inorganic polyphosphates are composed of phosphate tetrahedral units linked by P–O–P bonds, with degree of polymerization varying from two to several thousands. Up to now, both linear and cyclic polyphosphates with various degrees of polymerization have been utilized for diverse industrial purposes, and many theoretical and practical studies have been carried out to evaluate the complex-ion ability of polyphosphate anions. Phosphate molecules play an important role in many biological processes as well, and binding studies have also been carried out from this aspect. Among these inorganic polyphosphates, a long-chain polyphosphate attracts special attention, because its sodium salt is easily dissociated in aqueous solution to form a well-defined linear polyanion. This polyanion is one of the most hydrophilic polyanions without any hydrophobic moieties on its backbone. In relation to counterion binding studies of "fat" phosphate polymers [1, 2], such as DNA, systematic studies on the "thin" polyanions have so far been carried out [3–5]. However, in spite of much information accumulated on the nature and extent of the metal-ion binding of these polyphosphate anions, quite little has been reported on the interaction between amiphiphiles and polyphosphate.

Surfactant–polymer interaction has been studied intensively during the last two decades and is still of recent concern [6–11]. It is well known that the binding of ionic surfactant to a polyelectrolyte with opposite charge is strong and highly cooperative and its features can be well expressed by binding isotherms. The majority of experimental data have been analyzed by the Satake–Yang equation [12], which is derived on the assumption that cooperative interactions are due to the nearest-neighboring surfactants and the polymer chain is infinite. Therefore, in the case of a polyelectrolyte with smaller degree of polymerization, i.e., a smaller number of binding sites, this model may not be appropriate since the end effect is not correctly counted for. It is of interest to investigate the effect of polymer chain length on the binding, although very few works have been published. Shirahama et al. measured binding isotherms for sodium dextran sulfate (DxS)–dodecylpyridinium bromide systems, where the total binding affinity is found to decrease with decreasing the binding site number of DxS [13]. In our previous paper [14], it was found that in the interaction between poly(aspartate) and alkylpyridinium (C_{12} and C_{14}) chloride, the binding affinity is quickly lost when the number of binding sites is smaller than a critical value. Here we describe the interaction of a cationic surfactant to sodium polyphosphates (NaPP) with various degrees of polymerization. Dodecylpyridinium chloride (DoP) was used as an example of a cationic surfactant, for which an excellent selective electrode is available. Binding isotherms obtained by the potentiometric titration method are analyzed by direct calculation of a matrix expressing the partition function.

Experimental

Materials

Dodecylpyridinium chloride (DoP) purchased from Tokyo Kasei Kogyo Ltd. was decolored by activated charcoal in methanol solution first and recrystallized three times from acetone. The critical micelle concentrations (cmc) of DoP determined by electric conductivity method in aqueous solution is 17.4 mM at 30 °C. Pentasodium triphosphate hexahydrate ($Na_5P_3O_{16} \cdot 6H_2O$) was recrystallized from a water–ethanol mixture solvent. Trisodium trimetaphosphate was a gift from Rasa Kogyo Co. Ltd. (Japan) and was purified by repeated recrystallization from methanol. The above recrystallized phosphate samples were checked to be higher than 99.9% by HPLC with anion-exchanger column TSK SAX (Toyosoda Kogyo, Japan) combined with an AutoAnalyzer (Technicon) detector for phosphate determination [15]. Graham's salt (sodium phosphate glass) was fractionated to obtain a sample mixture of NaPP whose average degree of polymerization is about one hundred and the ratio of weight-averaged molecular weight to number-averaged molecular weight is 1.1 ($M_w/M_n = 1.1$) [16, 17]. The phosphate glass was then fractionated according to a solubility fractionation with acetone or gel chromatographic fractionation with Sephadex G-100 column [17] to prepare different NaPP samples, whose chain-length distributions are much narrower than that of the original phosphate glass [17]. All the fractions were freeze-dried and were stored below 0 °C. End-group titration method was employed to determine DP value and the chain-length distribution was calculated by a chromatographic fractionation technique [17]. The corresponding degrees of polymerization of NaPP, being equal to the numbers of binding sites, are 150, 101, 50, 15 and 7. For abbreviation, they are referred to as PP150, PP101, PP50, PP15 and PP7, respectively. Kurrol's salt, $(KPO_3)_n$, was synthesized according to the literature [18] and its DP value is estimated to be several ten thousands. The concentrations of each phosphate stock solutions were determined colorimetrically with a molybdenum (V)–molybdenum (VI) reagent [19], where special care was taken to completely hydrolyze the P–O bonds of the NaPP with large DP.

Potentiometric titration

Free DoP concentrations were determined by means of a surfactant-selective membrane electrode. The membrane was made from poly(vinyl chloride) and a carrier complex. The carrier complex was formed by reacting DoP with highly purified sodium dodecyl sulfate, followed by extensive recrystallization from acetone. A schematic diagram of the electrode cell assembly for the measurement was described in detail previously [20]. The electromotive force (emf) was measured by a Keithley 616 digital electrometer interfaced to a microcomputer. All the experiments were carried out at 30.0 ± 0.1 °C in the presence of 10 mM NaCl. The pH of the solutions were neutral (5–6) except for the triphosphate system (9–10).

Results and Discussion

There was no binding between DoP and linear triphosphate or cyclic trimetaphosphate anions, while the binding occurred when the degree of polymerization increased. The typical emf responses is shown in Fig. 1, where emf is plotted against the logarithm of the total DoP concentration (C_s) in the absence and presence of PP150. The calibration curves obtained in a polymer-free solution were

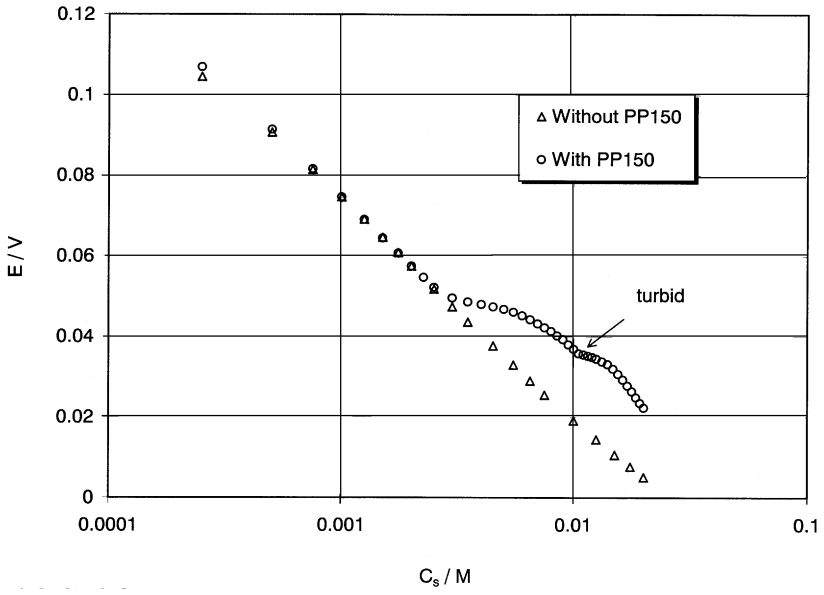

Fig. 1 EMF vs. DoP concentration (C_s) in 10 mM NaCl with and without PP150

linear from the cmc of DoP (ca. 15.9 mM in 10 mM NaCl at 30 °C) down to ca. 10^{-5} M and the slopes were 59.8 ± 0.2 mV/decade, very close to the theoretical Nernstian value of 60.2 mV/decade at 30 °C. In the presence of polymer, the solution sometimes turned turbid in the course of the titration, and became clear again on further addition of surfactant. This phase separation suggests a second-step binding exists during the process of titration, where the aggregation of NaPP–DoP complex may be formed. The hydrophobic precipitate is re-dispersed on further binding surfactants with their polar groups exposed to the bulk water phase, but their alkyl-chains in contact with the hydrophobic complex. Our discussion is mainly limited within the first-step binding. Binding isotherms can be constructed by plotting the binding degree β vs. free-surfactant concentration (C_f) as shown in Fig. 2, where

$$\beta = (C_s - C_f)/C_p \quad (1)$$

and C_p is the phosphate residual concentration. Two observations are noted in the experiment: (1) critical aggregation concentration (cac) where binding suddenly starts decreasing with increasing DP value; (2) slope of the binding isotherm becomes steeper with increasing DP, which implies an apparent increase on cooperativity in the longer-chain polymers. The reduced charge density ξ of NaPP [21], as determined by the O–P–O bond length, is about 2.9, nearly the same as that of dextran sulfate (DxS). However, the cac value for NaPP with large DP, e.g. DoP–Kurrol's salt system, is about ten times higher than that of DoP–DxS system under the same experimental conditions [22], which indicates a considerably lower binding affinity for the former. This is mainly ascribed to

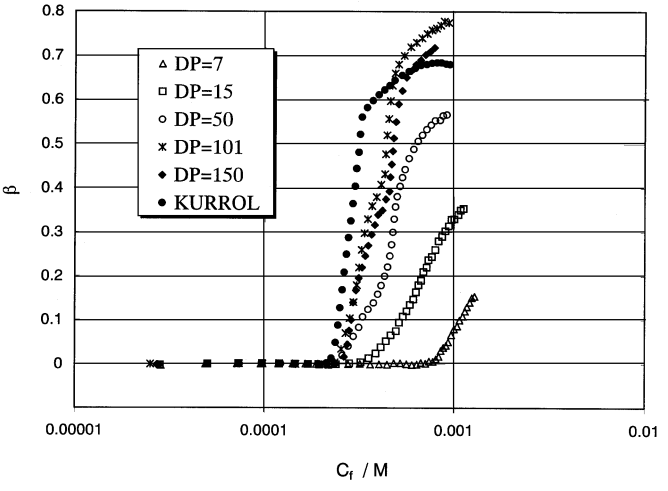

Fig. 2 Binding isotherms of DoP to NaPP with various degrees of polymerization (DP) in 10 mM NaCl at 30 °C

the lack of hydrophobic region in NaPP chains, which makes the interaction of surfactant's hydrophobic parts to the NaPP backbone considerably unfavorable. Also, the chains of NaPP are less flexible than other organic polymers and may make the conformation of globule polymer–surfactant complex with more difficulty. It is considered that NaPP is one of the weakest surfactant binders.

Binding of surfactant to polyelectrolyte can be expressed by the partition function for one-dimensional Ising model [23]

$$Z = (1, 1)\begin{pmatrix} 1 & 1 \\ s/u & s \end{pmatrix}^m \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad (2)$$

with $s = KuC_f$, where m stands for the number of binding sites on a polymer, K is the intrinsic binding constant and u a cooperativity parameter. The binding degree of surfactant by using this partition function is given as

$$\beta = (\mathrm{d}\ln Z/\mathrm{d}\ln C_f)/m \ . \tag{3}$$

Therefore, if the number of binding sites is available, which is equal to the DP value for NaPP in this work, binding degree can be readily obtained by direct matrix calculation processed by Microsoft Excel.

As for an infinite-chain polymer ($m \to \infty$), Eq. (3) together with Eq. (2) takes an explicit form after a long matrix manipulation

$$\beta = \tfrac{1}{2}\{1 - (1-s)/\sqrt{(1-s)^2 + 4s/u}\} \ . \tag{4}$$

Equation (4) is well known as the Satake–Yang equation now. Satake and Yang derived it by some other method corresponding to the regular solution theory on the assumption that the lattice is of one dimension and sufficiently long, and applied it to binding of alkyl sulfates to poly(aminoacid), the first application of the Ising model to the polymer–surfactant system [12].

We carried out curve fitting with Kurrol's salt first by using the Satake–Yang equation, since the polymer's DP is so large ($\geq 10^4$) that the polymer chain can be viewed as sufficiently long. Because the hydrophobic interaction between the surfactant neighbors bound to the polymer, which is represented by parameter u, is of short-range and therefore may not depend on the size of macroion, we determined the u and K values by choosing the parameters to fit the lower-half binding isotherm of Kurrol's salt, and then employed the same u value to analyze other NaPP systems using direct calculation of the matrix expression, where only K is the adjustable parameter. The parameters derived in this way are summarized in Table 1. The K value of the interaction, which is considered to be a function of the electrostatic potential around the polyelectrolyte, decreases as the size of the polyelectrolyte becomes smaller. Satake and Yang expressed the parameter K by

$$K = K_0 \exp\left(\frac{-Ze\psi}{k_B T}\right), \tag{5}$$

where ψ is the electrostatic potential at the polymer surface, although they did not derive any explicit expression for it [12]. In Eq. (5), K_0 is an intrinsic constant containing unknown factors representing some other contributions from the nature of the polyion–surfactant interaction besides ψ. For ease of the discussion, K_∞ is introduced as the K value for infinite-chain polymer, which can be derived from the intercept of a $\ln K$–$1/m$ plot. Thus, K_0 can be eliminated in Eq. (6)

$$\ln K/K_\infty = \frac{Ze}{k_B T}(\psi_\infty - \psi) \ . \tag{6}$$

The relationship between $\ln K/K_\infty$, which actually represents the electrostatic potential difference between a certain-length polymer and the infinite one, and the degree of polymerization DP can be seen clearly in Fig. 3. It is found that after the polymer reaches a certain minimum length, the electrostatic potential ψ is a little different from the one of infinite chain (ψ_∞), but the plot sharply falls down when DP < 30–40. We attribute this behavior to a decreased superimposition of electrostatic potential on reducing the size of the polyelectrolyte. At a point around a polyelectrolyte molecule, the electrostatic potential is a sort of sum over the potential exerted from the electric charges all over the polyion. Such superimposition effect makes the electrostatic potential valley on an infinite polymer chain much deeper than that of the corresponding monomer ion or short-length chain and results in a stronger intrinsic binding at lower concentration for the infinite one. Inversely speaking, this superimposition effect is getting smaller as the number of electric charges nearby, or the polyion size is reduced. Since the electrostatic interaction

Table 1 Binding parameters

	u	uK	K/M^{-1}
PP7	300	1270	4.2
PP15	300	2100	7.0
PP50	300	3000	10.0
PP101	300	3300	11.0
PP150	300	3300	11.0
KURROL	300	3800	12.7

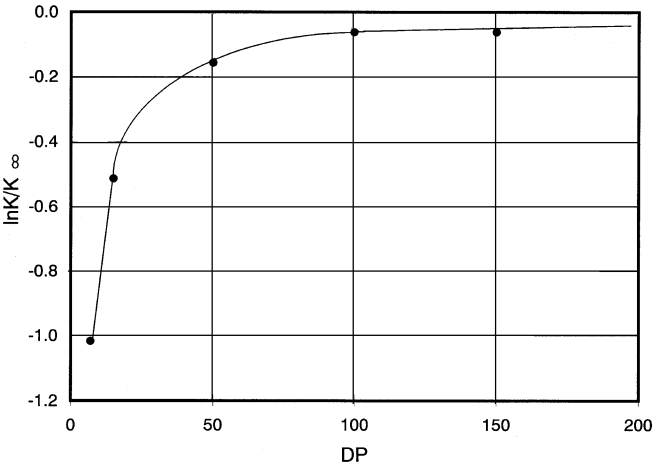

Fig. 3 Dependence of $\ln K/K_\infty$ on the size of NaPP

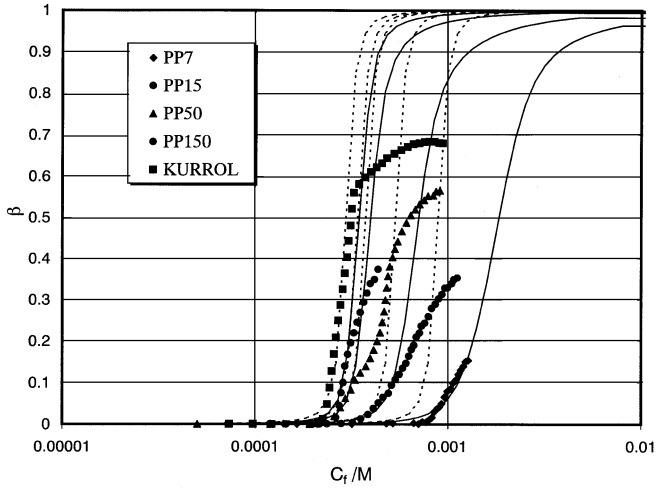

Fig. 4 Calculated and experimental binding isotherms of DoP to NaCl in 10 mM NaCl at 30 °C. Solid line: fitting curve by the matrix method; dashed line: by the infinite-chain model

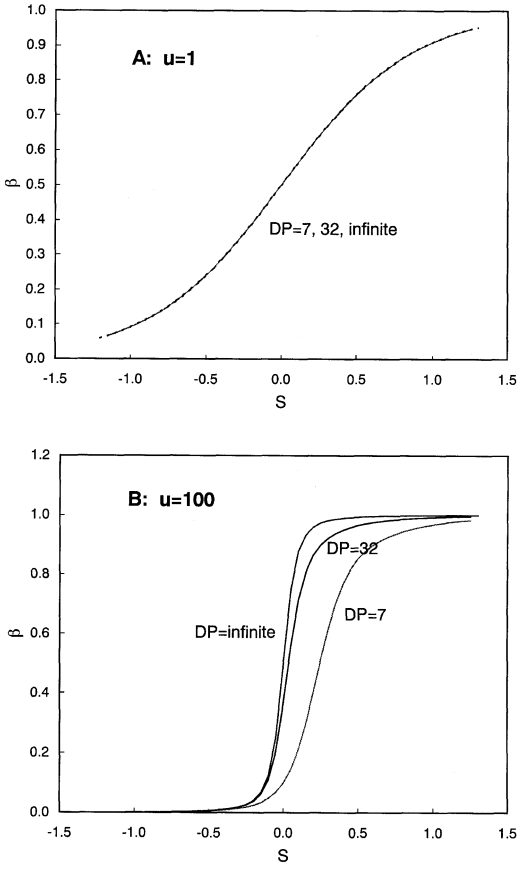

Fig. 5 Model simulation by Satake–Yang equation (DP = infinite) and matrix method (DP = 7, 32) with $u = 1$ (A) and $u = 100$ (B)

between the ionic surfactant head groups and the charged binding sites on polyions is one of the main factors determining the intrinsic binding constant, the decreased superimposition of electrostatic potential therefore mainly reduces binding affinity on decreasing the polyion size. In addition, because the superimposition is less effective at the ends, a few charged sites at both ends of the polymer chain actually cannot provide any binding sites. That gives the reason why there is no binding at all for the linear triphosphate or trimetaphosphate anions and also explains that binding for NaPP apparently saturates earlier than otherwise expected. As reflected in Fig. 3, the superimposed potential on the polymer chain is quickly lost and the electrostatic potential is too weak to attract surfactant ions when DP is below the critical value around 35. In connection with the less superimposed potential, it is interesting to note the Monte-Carlo simulation by Brender and Danino [24] for short chains (8–64 beads), with each bead carrying electric charges. The effective screening effect sharply falls when the number of beads is decreased below 32. This is closely related with a marked decrease of electrostatic potential of the short-chain polyelectrolytes, since the screening is a result of strong electrostatic attraction of counterions by the charged beads.

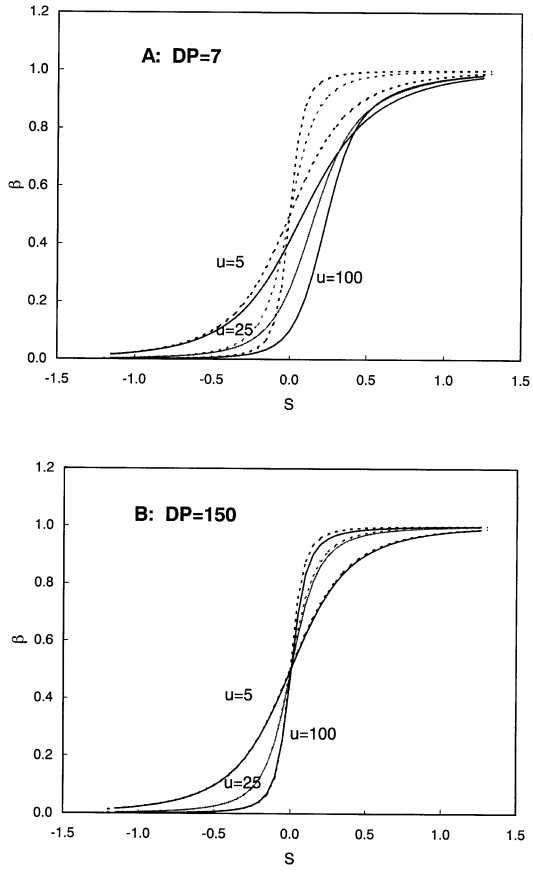

Fig. 6 Model simulation by Satake–Yang equation (dashed line) and matrix method (solid line) with various u values for DP = 7 (A) and DP = 150 (B)

The fitted curves by the matrix method with the parameters in Table 1 are given in Fig. 4, where the curves simulated by the Satake–Yang equation are also included for comparison. As for the large DP polymer, there is actually little difference between the results of these two methods; however, for short-chain polymers, such as PP50, 15 and PP7, the curves calculated from the matrix method provides a much better fitting to the experimental data than the Satake–Yang equation does. We noticed an earlier deviation occurred from the calculated isotherm to the experimental binding isotherm for the short-chain NaPP. This could also be associated with the superimposition of electrostatic potential on the polymer. The comparatively weaker electrostatic potential of the short-chain polymer, or oligomer, is even more easily reduced as surfactants are bound, and the break down of the ion-condensation effect results in a negative cooperativity on further binding.

To compare the matrix method and infinite-chain model, further model simulations were carried out by setting different parameters, as shown in Figs. 5 and 6. When $u = 1$, which is for a noncoopertive interaction, the binding isotherms for DP = 7, 150 and infinitely long-chain merge into a single plot since all of their binding sites are independent. In a cooperative binding ($u > 1$), e.g., $u = 100$, we find that the binding isotherms separate according to different degrees of polymerization. The less steep slope and early saturation of the binding isotherms for oligomers calculated by matrix method reflect the less binding affinity for the short-chain polymer as well as the weaker superimposed potential around its polymer chain, even when the u parameter remains constant. On the other hand, it is seen in Fig. 6 that the matrix method and the infinite-chain model make no difference when DP is large enough, say DP = 150, but for the case of oligomer as DP = 7 obvious variations appear between these two models, while the matrix method may provide a better simulation for the experiment data as proved by our work.

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