Cooperative Binding of Surfactant Ions by Small Oligomers of Opposite Charge†

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The binding of cationic surfactant, dodecylpyridinium ion (DP^+) by anionic oligomers, i.e., citrate (with three negative charges), triphosphate (five negative charges), and tetraphosphate (six negative charges) has been investigated in the presence of NaCl by using potentiometric techniques based on a surfactant-ion-selective solid-state membrane electrode. The binding isotherms by triphosphate and tetraphosphate both exhibit the typical feature of sigmoidal shape, indicating the occurrence of cooperative binding in these two cases. On the contrary, the obvious cooperative behavior is not observed for the case of citrate, although a nonspecific or gradual binding process is recognizable. The critical binding concentration (cbc) for citrate gives a different added-salt concentration dependency from two other oligomers. For triphosphate and tetraphosphate, cbc increases with an increase of added salt concentration, whereas for citrate it decreases as the critical micelle concentration (CMC) does. In summary, our results show that the cooperative binding of surfactant ions by oppositely charged polyion takes place when the polyion has at least five charged binding sites.

Introduction

The binding of surfactant ions by a polyion of opposite charge is characterized by its site-specific and highly cooperative nature.[1−8] The primary factor in the strong and site-specific binding (one-to-one interaction) is the electrostatic interaction between surfactant ions and charged groups on the polyions. The cooperative behavior of the binding is most often ascribed to the hydrophobic interaction between alkyl chains of neighboring bound surfactant ions. Such a system has been described successfully by applying a linear lattice model.[2,9,10] In this model, a nearest-neighboring interaction between ligands bound on the adjoining binding sites is defined as the cause to generate the cooperative binding. This means the cooperativity would take place, in principle, when at least three consecutive binding sites exist.

Our interests in this study are to know (1) whether the cooperative binding of surfactant ions takes place by ionic oligomers with only a few charged groups as binding sites and (2) whether the smallest number of binding sites required for the cooperative binding is really three, and if not, what is the smallest number by which the cooperative binding is actually observed. Such an interesting problem has not yet been clearly revealed so far. To clarify this, we have investigated the binding of dodecylpyridinium cations by anionic oligomers, i.e., citric acid, triphosphate, and tetraphosphate, which have three, five, and six negatively charged groups, respectively.

Materials and Methods

Sodium citrate, sodium triphosphate, and sodium tetraphosphate purchased from Sigma Chemical Co. were used without further purification. Dodecylpyridinium chloride (DPCl) (Tokyo Kasei Kogyo Co., Ltd.) was purified by repeated recrystallization from acetone followed by further treatment with active charcoal. Analytical grade sodium chloride, sodium hydroxide, poly(vinyl chloride) (Katayama Chem. Co.), and dioctyl phthalate (GR, Tokyo Kasei Kogyo) were used without further purification.

All aqueous solutions were prepared by weight from each salt, surfactant, and NaCl stock solution in distilled and deionized water. Concentration units for all solutions are defined as mol/kg of H_2O.

The equilibrium concentration of surfactant ion was determined potentiometrically by means of a surfactant-selective solid membrane (PVC gel) electrode. The electrodes were prepared by following the method described in detail previously.[4] A titration method was used to determine calibration curves of emf vs total surfactant ion concentration, and surfactant ion binding curves in oligomer solutions, described earlier.[4] A motorized piston buret (645 Multi-Dosimat, Metrohm) was used to add titrant solution of surfactant and NaCl. The anionic oligomer conentration of the test solution decreases by 20−40% upon adding surfactant and NaCl solution. Binding isotherms are independent of oligomer conentration for the concentration range used in this study, except in the salt-free case where a rather slight dependence was observed. The initial oligomer concentrations of the test solutions are 1.03×10^{-3}, 1.02×10^{-3}, and 1.04×10^{-3} monoequiv/kg of water for citrate, triphosphate, and tetraphosphate, respectively. The observed slopes of the calibration curves were very close to the Nernst value (60.2 ± 0.3 mV) per concentration decade for 30.0 °C. Potentials were measured with a TP-1000 ion meter (Toko, ±0.1 mV), interfaced to a microcomputer that checks for constancy of emf, actuates the piston buret, and accumulates the emf data. All the measurements were performed at 30.0 °C. The solutions were stirred continuously during the emf measurements. The emf readings reached equilibrium values within 2 or 3 min after each addition of the titrant solutions. The initial anionic oligomer concentrations of the test solutions are 1.04×10^{-3} monoequivalent of charged groups/kg of H_2O. Although the oligomer concentration of the test solution decreased by 20−40% upon adding surfactant and NaCl solution, binding isotherms were independent of oligomer concentration for the concentration range used in this work.

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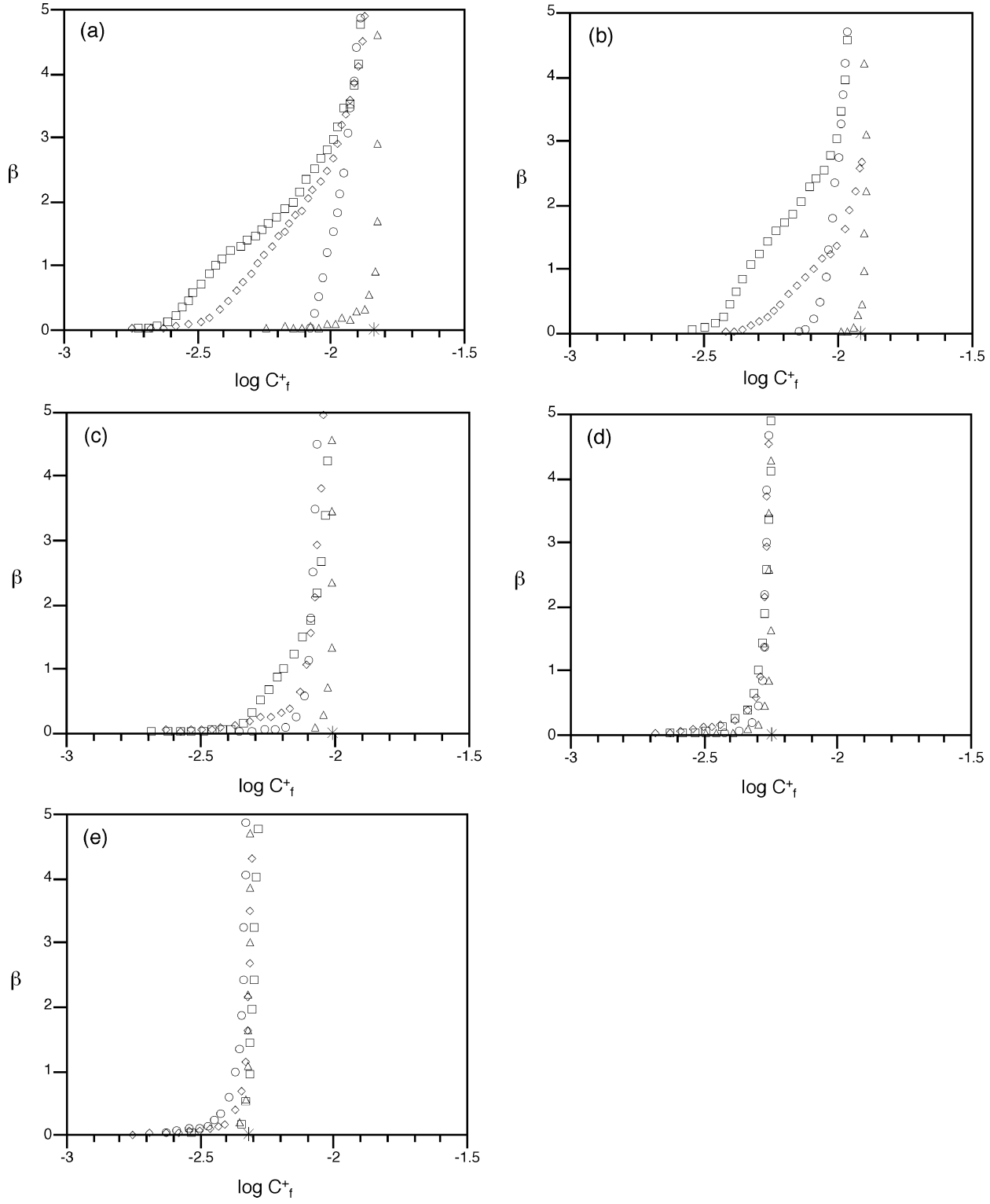

Figure 1. Binding isotherms of DP^+ ions by citrate (circle), triphosphate (diamond), and tetraphosphate (square) at 30.0 °C. A "binding isotherm" for oligomer-free DPCl solution is also plotted (triangle). Added NaCl concentration: (a) 0 mM, (b) 10 mM, (c) 30 mM, (d) 60 mM, and (e) 100 mM. The asterisk on the abscissa indicates the CMC obtained by the extrapolation method.

Results and Discussion

The binding of ionic surfactants by oppositely charged polyions is normally described by a binding isotherm, where the fraction of bound surfactant ions is plotted as a function of the equilibrium concentration of free surfactant ions.

In Figure 1a−e, binding isotherms of DP^+ ion by anionic oligomers, i.e., citrate (CA^{3-}), triphosphate (PA^{5-}), and tetraphosphate (PA^{6-}), and also in oligomer-free solutions are shown for several concentrations of added NaCl, i.e., 0, 10, 30, 60, and 100 mM, respectively. Here, the binding is treated in terms of the "degree of binding", β:

$$\beta = \frac{C_t^+ - C_f^+}{C^-} \tag{1}$$

where C_t^+, C_f^+, and C^- are the total concentration of DP^+ ion,

TABLE 1: Added NaCl Concentration Dependence of Critical Micelle Concentration (CMC) of DPCl and Critical Binding Concentration (cbc) of DPCl for Citrate, Triphosphate, and Tetraphosphate at 30.0 °C

	DPCl only		citrate (CA^{-3})			triphosphate (PA^{-5})			tetraphosphate (PA^{-6})		
added NaCl concn, C_s (mM)	CMC (mM)	counterion concn[a] (mN)	cbc (mM)	C^{-} [c] (mN)	counterion concn[b] (mM)	cbc (mM)	C^{-} [c] (mN)	counterion concn[b] (mM)	cbc (mM)	C^{-} [c] (mN)	counterion concn[b] (mM)
0	15.1	15.1	8.93	0.80	9.73	4.24	0.93	5.17	3.09	0.96	4.05
10	12.1	22.1	8.65	0.81	19.46	6.68	0.86	17.54	4.29	0.93	15.22
30	9.8	39.8	7.55	0.84	38.39	7.62	0.84	38.46	5.66	0.89	36.55
60	5.6	65.6	*d*			*d*			*d*		
100	4.8	104.8	*d*			*d*			*d*		

[a] CMC + C_s. [b] cbc + C_s + C^{-}. [c] Initial oligomer concentration is 1.04 mN/*l*. [d] Not obtained.

the concentration of free DP^+ ion and the concentration of the anionic oligomers, respectively. For the oligomer-free DPCl solution, the "binding isotherm" is calculated and plotted in the figures, assuming C^- is 1 mequiv (mN) (for convenience), although the anionic oligomers are actually not contained in the solution. In this case, the added DPCl concentration itself was used as C_f^+.

As seen in Figure 1a−c, the isotherms for triphosphate and tetraphosphate exhibit an initial steep increase across a relatively small C_f^+ range in low C_f^+ regions, followed by a region of leveling-off at a value of β somewhat higher than unity: the shape of them is distinctively sigmoidal. After passing through the region of gradual increase, they show a marked rise above a certain concentration.

The initial sharp increase with a sigmoidal shape is attributed to specific cooperative binding of DP^+ ion onto anionic binding sites, and the presence of cooperativity indicates the existence of the short range interaction, i.e., hydrophobic interaction among bound surfactant ions, as in the well-known systems of polyion−oppositely charged surfactant ion.[2−5,7,8] The critical binding concentration (cbc) at which the onset of surfactant binding occurs is sometimes used as a convenient and practical measure to characterize the binding.[6] The free surfactant concentration at $\beta = 0.5$ is usually used as the cbc instead of the onset concentration itself.[6] There is actually no practical problem in substituting the middle point for the cbc, because both values are very close to each other for the case of highly cooperative binding.

The leveling-out of the binding may be due to a saturation of the anionic binding sites with surfactant ion. The level of the plateau region corresponds to about one DP^+ ion bound to one anionic binding site. This indicates that a phosphate group could be identified as the anionic binding site and the one-to-one association between surfactant ion and phosphate group as an anionic binding site is occurring by mainly electrostaic interaction.

With a further increase of DP^+ concentration after the plateau regions, the isotherms show a gradual increase, indicating further nonspecific binding is taking place. This seems to be due to a self-association of the nonpolar tails of the surfactans through hydrophobic interaction. After this region, with a further increase of DP^+ concentration, β begins to increase rapidly at higher DP^+ concentration, which seems to correspond to the micelle formation of the surfactant. It takes place at the same concentration region where the "binding isotherm" for anionic oligomer-free DPCl solution starts to rise. This indicates the marked increase of β corresponds to the micelle formation of the surfactant.

It has been reported that the critical micelle concentration (CMC) can be determined by the electrode method as accurately as by other methods.[11] The critical micelle concentration (CMC)

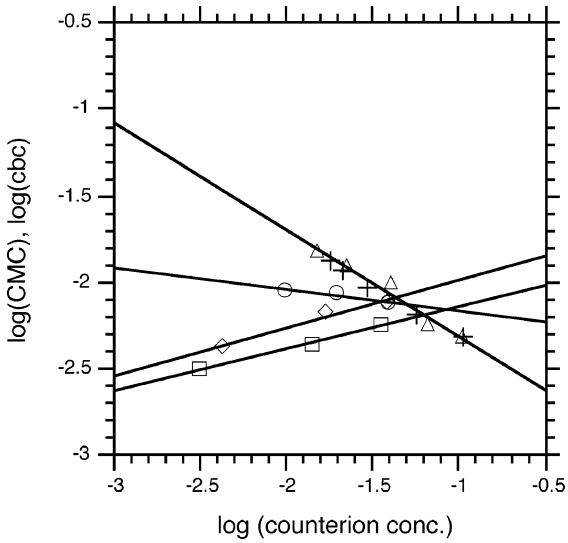

Figure 2. Relationships of cbc and CMC vs free counterion concentration in a logarithmic scale: citrate (circle); triphosphate (diamond); tetraphosphate (square). The literature values are also plotted in the figure (plus) (see in text).

of the surfactant is obtained from the isotherm by the extrapolation method; it is shown with asterisks on the abscissa in the figures.

For the case of citric acid too, it is clearly seen that DP^+ ions start to bind to anionic sites at concentrations significantly below the CMCs, although it is not necessarily the cooperative binding. This should be ascribed to a premicelle formation of surfactant ions, which is promoted by the exsistence of small oligomer ions of opposite charge. This explanation is confirmed also from the observation that the cbc for citrate shows a C_s dependence similar to that for the CMC (Table 1 and Figure 2).

The dependence of the isotherms on added salt concentration is worth describing a little more precisely here. As shown in Figure 1b, at 10 mM of added NaCl all the isotherms behave similarly to the salt-free case, except that the binding regions shift to a higher DP^+ concentration region and CMC shifts to a lower concentration. At 30 mM NaCl, the cooperative feature of the binding is still clearly observed at least in the tetraphosphate isotherm, and in the triphosphate one as well, however, only slightly (Figure 1c). With the citrate isotherm, however the binding behavior is hardly appreciated. It is important to point out that for all the solutions the micelle formation occurs at the same free DP^+ ion concentration region within experimental error, independent of whether the anionic oligomers are present or not (Figure 1c). With further increase of added NaCl concentration, at 60 and 100 mM NaCl, the micelle formation prevails over the binding and the binding disappears completely behind the micelle formation, and all the isotherms are over-

lapped with the micelle formation curve, as shown in Figure 1d,e.

The dependences of CMC of individual surfactants on added NaCl concentration in solution are summarized in Table 1 and Figure 2, together with the total counterion concentration dependence of the cbc's for the cases of triphosphate and tetraphosphate. Obtained CMC values in this work are in reasonable agreement with the literature values:[12] 1.33×10^{-2}, 1.16×10^{-2}, 9.3×10^{-3}, 6.5×10^{-3}, and 4.9×10^{-3} M at 0.005, 0.01, 0.02, 0.05, and 0.1 M NaCl, respectively, all at 50 °C. In Figure 2, the CMC and the cbc's are plotted against the total counterion concentration in a logarithmic scale. The slopes in the log(CMC) vs log(total counterion concentration) for our result and the literature value are −0.62 and −0.54, respectively, with remarkable agreement. This confirms again that the micelle formation is not influenced from the presence of the anionic oligomer molecules. From this observation, it is concluded that the CMC of DPCl is not influenced from the presence of anionic oligomer molecules such as triphosphate, tetraphosphate, and citrate.

In summary, the binding of surfactant ions by an oligomer ion of opposite charge is definitely cooperative, when the oligomers have at least five binding sites of opposite charge, such as triphosphate used in this study. However, the binding by citrate with three charged sites is rather nonspecific than cooperative, which seems to be a promotion of premicelle formation by the electrostatic attractive interaction between surfactant ions and oligomer ion.

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