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The Cooperative Binding of Surfactant Ion to Polyelectrolyte in Mixed Solvents

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(Received Sep. 12, 1994)

Abstract

The potentiometric study was made of the binding isotherm of dodecyltrimethylammonium chloride to poly (potassium vinyl sulfate) in solutions of dioxane and 1-alkanols with varying chain length. The binding cooperativity persists even in the presence of these additives. In solutions of dioxane and ethanol, the equilibrium surfactant ion concentration at half binding (C_0) increases monotonously with increasing additive concentration (C_a), while the reverse change occurs in water-butanol system. In the presence of propanol, however, a broad minimum in C_0 appears around $C_a=1$ M. These characteristic behaviors can be interpreted in terms of the regular solution treatment including an empirical expression for the electrical part of the chemical potential of the ionic site on the polyion.

Introduction

It is well known that surfactant ions bind cooperatively to polyions of opposite sign by virtue of strong electrostatic and hydrophobic interactions to give rise to the micelle-like clusters on the polymer chain (1-4). The cooperative clustering of the surfactant ions usually occurs in a narrow surfactant concentration range which depends regularly not only on the added salt concentration (5-9) but on the hydrocarbon chain length of the surfactant ion (5, 6, 10-12). In addition, the resulting clusters can solubilize the hydrophobic molecules such as dyes (13-16). The charge density (10, 17) and the local structure of the polyion (10, 18) are also found to play important roles in the cooperative interaction between polyion and surfactant ion.

In view of a striking resemblance of the surfactant ion-polyion interaction to the micellization process, the addition of 1-alkanols is anticipated to affect significantly the binding characteristics of the surfactant ion to polyion. The present paper concerns with the

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potentiometric study of the effects of the added dioxane and 1-alkanols of varying chain length on the binding isotherms of dodecyltrimethylammonium chloride to poly (potassium vinyl sulfate).

Experimental

Materials. The stock solution of dodecyltrimethylammonium chloride (DTAC) was prepared by passing the aqueous solution of DTABr (Tokyo Kasei Kogyo Co., Ltd., guaranteed grade) through an anion-exchange column (Bio-Rad Laboratories, FCX01) in the Cl^- state. The concentration of the stock solution was determined potentiometrically by using Cl^- ion selective electrode (Toko Chemical Laboratories Co., Ltd., CI-5102). Poly (potassium vinyl sulfate) (PVSK, Wako Pure Chemical Industries Co., Ltd.), 1-Pyrenecarboxaldehyde (PyCHO, Aldrich, 99%), poly (vinyl chloride) (PVC, Wako Pure Chemical Industries Co., Ltd., DP=1100), and other chemicals of guaranteed grade were used without further purifications.

Method. The binding isotherms of DTA^+ were determined potentiometrically by using the following cell.

Cl^- ion selective electrode | Sample solution (1-Alkanol, C_a : PVSK, C_p : 20mM KCl: DTAC, C) | PVC membrane | Reference solution (1 mM DTAC, 20 mM KCl) | 1 M NH_4NO_3 agar bridge | Reference electrode (Ag-AgCl)

Here, C_p refers to the concentration of PVSK in molarity of ionic groups. We used PVC membrane consisting of 10% PVC and 90% plasticizer (Elvaloy 742, Mitsui-Du Pont Polychemicals). The electromotive force (E) of the cell was measured with a Toko digital pH meter TP-1000 to a precision of 0.1 mV. In aqueous solution of DTAC containing 20 mM KCl, the semilogarithmic plot of E vs. DTAC concentration (C) gives a straight line with a slope of 57.2 mV down to 1×10^{-5} M. In the presence of propanol, butanol, and dioxane, the observed slopes tend to decrease slightly with increasing concentrations of additives. However, these calibration curves still permit the estimation of the equilibrium surfactant ion concentrations in mixed solvents, since the observed slopes are reproducible on replicate measurements. All measurements were conducted at 25°C under the conditions of constant concentrations of PVSK ($C_p=0.20$ mM) and KCl (20 mM).

The dielectric constants (ϵ) of the mixed solvents were estimated spectroscopically at 25°C by measuring the wave length (λ_{max}) of the fluorescence maximum of PyCHO excited at 356 nm, since the value of λ_{max} is known to depend linearly on ϵ (19). The observed λ_{max} of PyCHO in water-dioxane mixed solvent of known dielectric constants was well reproduced by $\lambda_{\text{max}}=0.402\epsilon+444.7$.

The critical micelle concentrations (cmc) of DTAC solutions were determined conductometrically at 25°C by using a TOA Electronics conductivity meter, model CM-50AT.

Results and Discussion

In Figs. 1–4 are plotted the binding isotherms of DTA^+ to PVS at varying additive concentrations (C_a). In all cases studied, the binding degree (β) of DTA^+ to PVS is seen to rise steeply in quite narrow range of the equilibrium surfactant ion concentration (C_f) as low as 10^{-4} M. These behaviors imply that the binding of DTA^+ ion to PVS is highly cooperative even in the presence of dioxane and 1-alkanols. In fact, the cooperativity parameter, u , estimated from the following expression based on one-dimensional lattice model for two component system (20) is 550 in the absence of additives.

$$2\beta - 1 = (y - 1) / [(1 - y)^2 + 4yu^{-1}]^{1/2} \quad (1)$$

Here, y refers to $C_f/C_f(\beta=0.5)$. Unfortunately, Eq. (1) can not be applied to the systems with additives, since the surfactant ion clusters on the polymer chain are expected to solubilize the additive molecules in their hydrocarbon moiety. It should be noted, however, that the values of u estimated tentatively at lower concentrations of 1-alkanols are of the order of 500–600. This in turn suggests that the solubilized 1-alkanols do not affect appreciably the binding cooperativity of the surfactant ion to the polyion.

An interesting feature of Figs. 1–4 is the remarkable shift of the binding isotherm arising from an increase in C_a . Figure 5 shows the change in the equilibrium surfactant ion concentration (C_0) at $\beta=0.5$ with C_a . In water-dioxane system, the value of C_0 increases monotonously with increasing C_a , while the reverse trend is observed for water-butanol system. In solutions of ethanol and propanol, however, $\ln C_0$ vs. C_a curves are concave upward and a broad minimum appears around $C_a=1$ M for propanol.

For the sake of comparison, the change in the cmc of DTAC with C_a is given in Fig. 6. Similar results have been obtained for a variety of ionic surfactant systems, e.g., for tetradecyltrimethylammonium bromide in solutions of 1-alkanols with varying chain length (21). It should be noted that the $\ln C_0$ vs. C_a curves in Fig. 5 are considerably different in their C_a dependences from the corresponding cmc vs. C_a curves in Fig. 6 with the exception of water-butanol system. In this connection, it is worth noting that an addition of 1-alkanol to micellar solution is always accompanied by the decrease in the charge density of the micellar surface because of the solubilization phenomenon. In polyion-surfactant systems, however, the local line charge density of the vacant ionic site clusters remains constant even if added 1-alkanol molecules are solubilized into surfactant ion clusters on the polymer chain. This electrostatic effect is considered to play an important role in determining the difference between the C_a dependences of C_0 and cmc in solutions of 1-alkanol with shorter chain length. In water-butanol system, an entropy effect arising from an increase in the amount of solubilized butanol molecules is supposed to overcome the electrostatic effect described above. The observed constancy of the cmc of DTAC in water-dioxane system suggests that the solubilization of dioxane molecules can virtually be ignored.

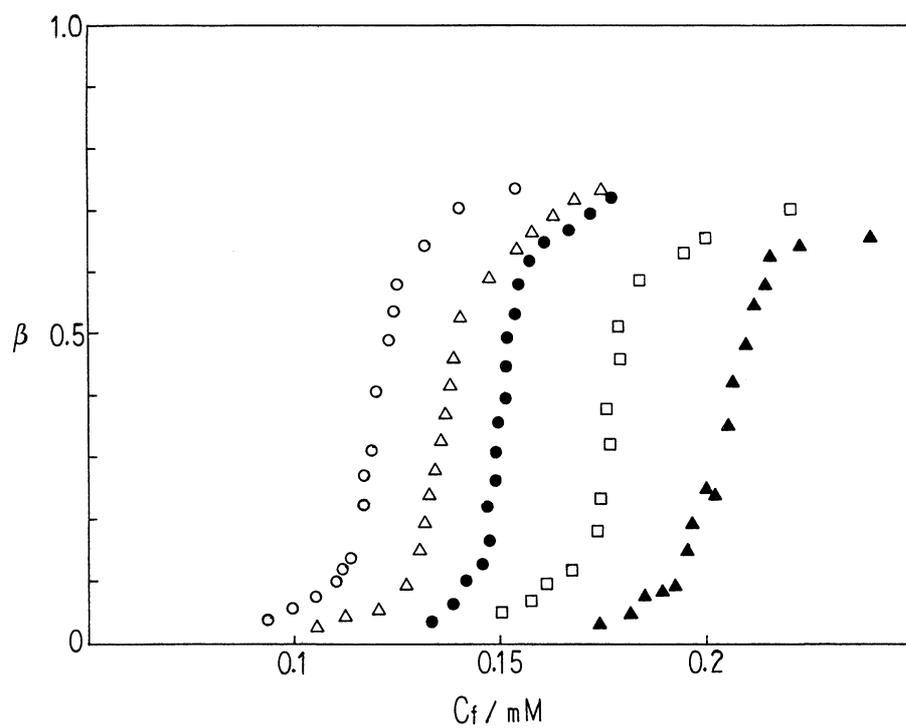


Fig. 1. The binding isotherms of DTA^+ to PVS in water-dioxane system. $C_a/M=0(\circ)$, $0.25(\triangle)$, $0.5(\bullet)$, $0.75(\square)$, and $1(\blacktriangle)$.

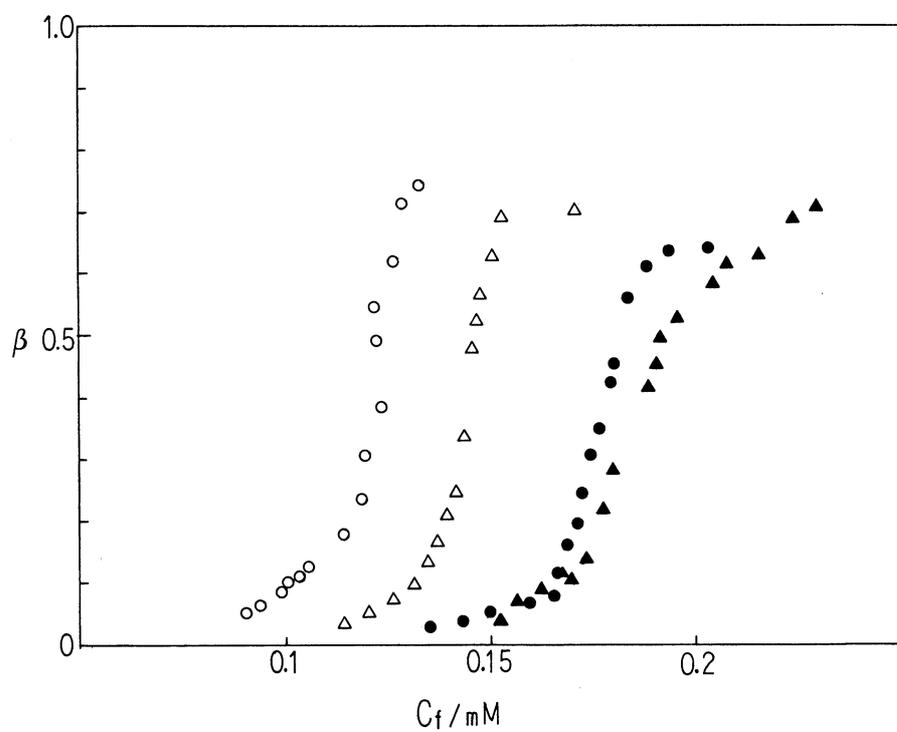


Fig. 2. The binding isotherms of DTA^+ to PVS in water-ethanol system. $C_a/M=1(\circ)$, $2(\triangle)$, $3(\bullet)$, and $3.5(\blacktriangle)$.

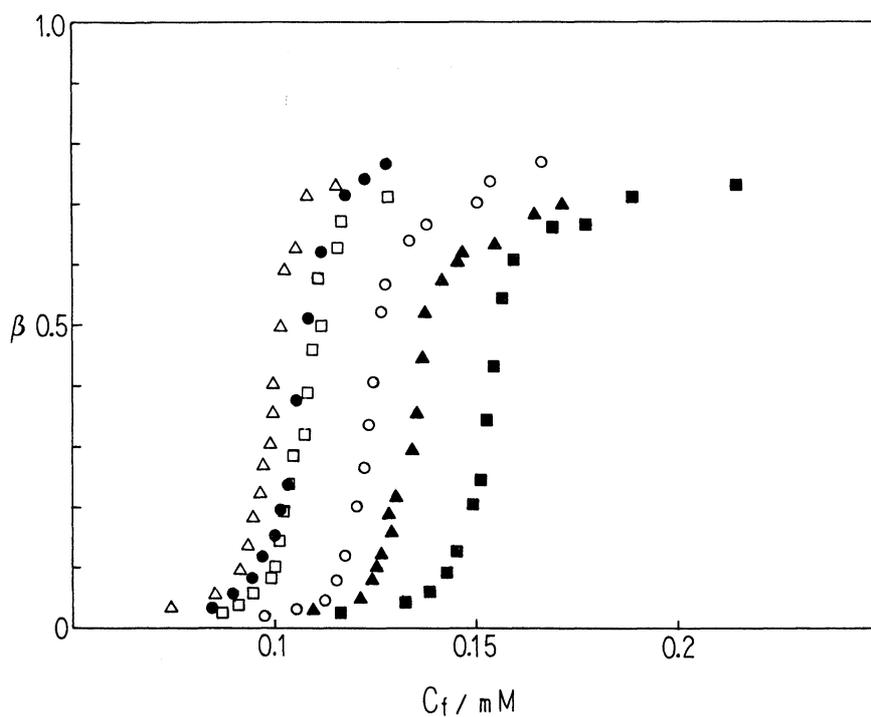


Fig. 3. The binding isotherms of DTA⁺ to PVS in water-propanol system. $C_a/M=0.5(\bullet)$, $1(\triangle)$, $1.5(\square)$, $1.75(\circ)$, $1.85(\blacktriangle)$, and $2(\blacksquare)$.

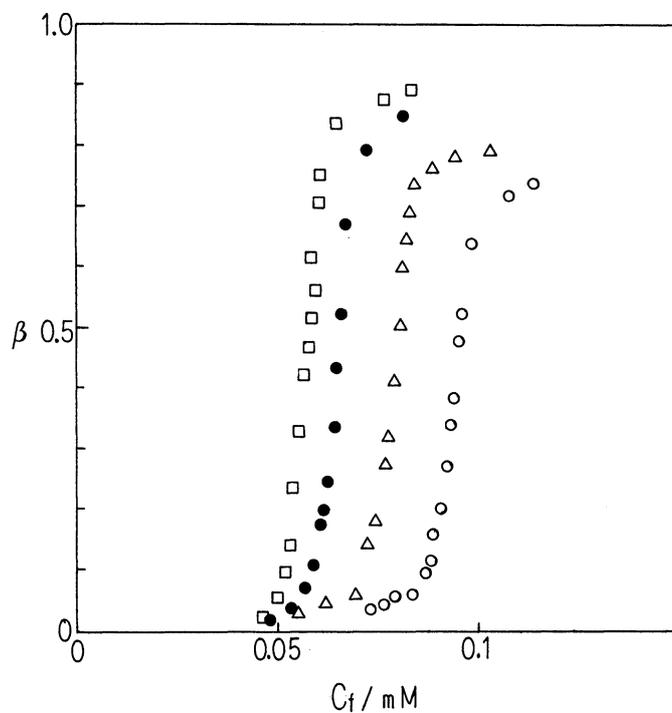


Fig. 4. The binding isotherms of DTA⁺ to PVS in water-butanol system. $C_a/M=0.13(\circ)$, $0.26(\triangle)$, $0.4(\bullet)$, and $0.5(\square)$.

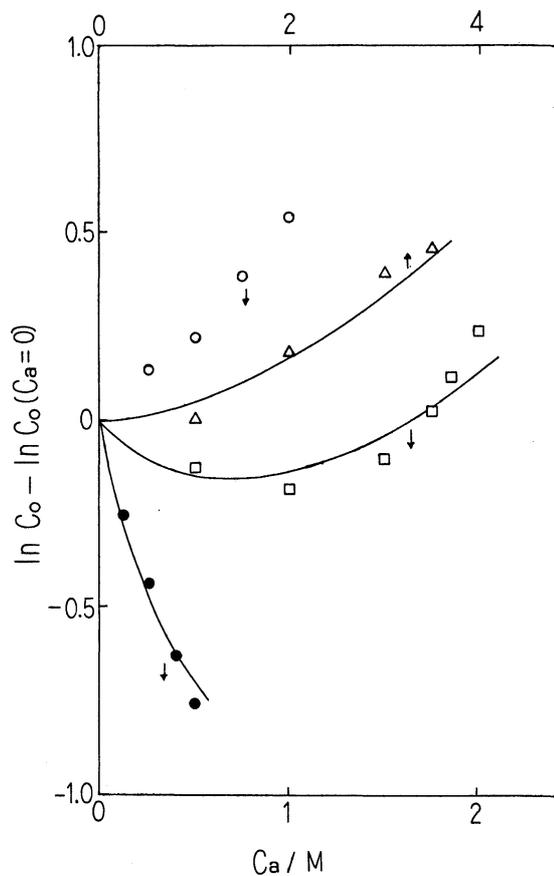


Fig. 5.

Plots of $\ln C_0 - \ln C_0 (C_a=0)$ against C_a . Arrows indicate the abscissa to be applied. Solid lines: calculated curves from Eqs. (4)~(6)

(○), water-dioxane system;
 (△), water-ethanol system;
 (□), water-propanol system;
 (●), water-butanol system.

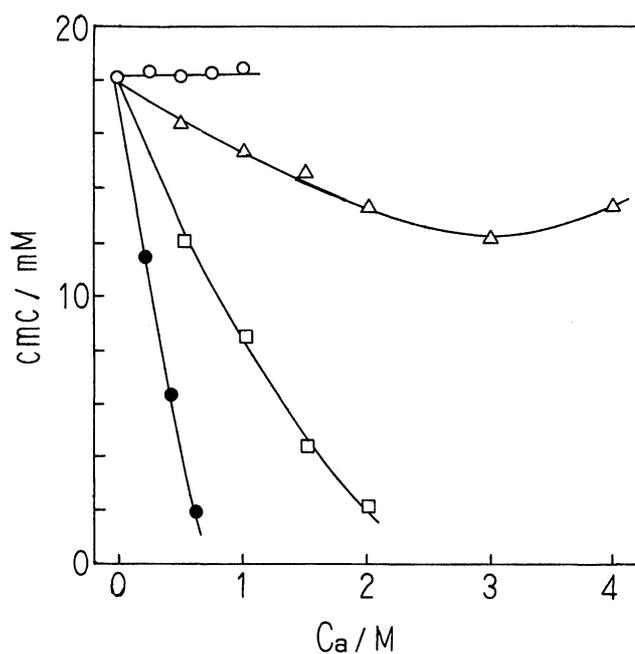


Fig. 6.

The C_a dependences of the cmc of DTAC in mixed solvents.

(○), water-dioxane system;
 (△), water-ethanol system;
 (□), water-propanol system;
 (●), water-butanol system.

It has been well known that the mixed micelle formation of two component surfactant system can be interpreted well in terms of the regular solution theory (22). It is thus reasonable to assume the regular mixing for surfactant ion cluster phase. Moreover, the bulk phase will be regarded as the ideal dilute solution, since the mole fractions of the additives are smaller than 0.07 under our experimental conditions. With these simplifications, the binding equilibrium of the surfactant ion (R) to ionic site (S) in the presence of additives at $\beta=0.5$ can be written as

$$\mu_S^0 + \mu_S^e + \mu_R^b + kT \ln X_R = \mu_{SR}^0 + kT \ln (1 - f_A) + \omega f_A^2, \quad (2)$$

where, μ_S^0 refers to the chemical potential of ionic site at $\beta=0.5$ and μ_{SR}^0 to that of bound site at $\beta=0.5$ in a hypothetical state of $f_A=0$, respectively. μ_S^e refers to the electrical part of the chemical potential of ionic site at $\beta=0.5$, μ_R^b to the standard chemical potential of the surfactant ion in bulk phase, X_R to the mole fraction of the surfactant ion in bulk phase, f_A to the mole fraction of the solubilized 1-alkanol molecule in the cluster phase, and ω to the interchange energy defined by $(2w_{AR} - w_{RR} - w_{AA})$ in terms of the interaction energy, w_{ij} , in the cluster phase, respectively. By taking into account the fact that $\mu_S^0 + \mu_R^b - \mu_{SR}^0$ is equivalent to the free energy of transfer ($\Delta\mu_R^t$) of surfactant ion from cluster phase to bulk phase, Eq. (2) can be rewritten as

$$\Delta\mu_R^t + \mu_S^e + kT \ln X_R = kT \ln (1 - f_A) + \omega f_A^2. \quad (3)$$

It is well known that the free energy of transfer of hydrocarbon from hydrocarbon phase to water is comparable to that from 1-alkanol to water. The difference between them is of the order of 60 cal per mole of methylene group (23). Under our experimental conditions ($X_A < 0.07$), therefore, the C_a dependence of $\Delta\mu_R^t$ in Eq. (3) can safely be ignored without introducing serious errors. On this simplification, we immediately have

$$\ln C_0 - \ln C_0(C_a=0) = \ln (1 - f_A) + \omega f_A^2 / kT + \{\mu_S^e(C_a=0) - \mu_S^e\} / kT, \quad (4)$$

where, C_0 is the equilibrium surfactant ion concentration at $\beta=0.5$. The value of f_A in Eq. (4) can be estimated from the following expression based on the solubilization equilibrium of 1-alkanol molecules between surfactant ion cluster and bulk phases.

$$\ln f_A + \omega (1 - f_A)^2 / kT = \ln X_A + \Delta\mu_A^t / kT \quad (5)$$

Here, $\Delta\mu_A^t$ represents the free energy of transfer of 1-alkanol molecule from pure state to water. The use of Eqs. (4) and (5) still requires a knowledge of the C_a dependence of the electrical part of the chemical potential of the ionic site in Eq. (4). Because of the lack of the theoretical expression for the electrical potential around the polyelectrolyte chain of limited length, we applied an empirical expression derived tentatively from the observed $\ln C_0 - \ln C_0$

($C_a=0$) vs. C_a plots for water-dioxane system in Fig. 5, together with an additional relation between C_a and ϵ for this system. In analogy with the micellization process of DTAC, the solubilization of the dioxane molecules into surfactant ion clusters on the polymer chain will also be ignored in this system, i.e., f_A in Eq. (4) equals zero. The variation of $\ln C_0 - \ln C_0(C_a=0)$ with ϵ in water-dioxane system can be described by the second-order polynomial. Thus, we have

$$\{\mu_s^e(C_a=0) - \mu_s^e\}/kT = 5.38 \times 10^{-2}(\epsilon_0 - \epsilon) + 2.05 \times 10^{-3}(\epsilon_0 - \epsilon)^2, \quad (6)$$

where ϵ_0 refers to the dielectric constant of water.

The solid lines in Fig. 5 show the calculated curves from Eqs. (4)~(6). The values of ω/kT and $\Delta\mu_A^1/kT$ determined by curve-fitting method are -1.6 and 0.6 for water-ethanol system, -2.1 and 2 for water-propanol system, and -2.4 and 3.2 for water-butanol system, respectively. Although slight deviations from the experimental data are unavoidable, the calculated curves reproduce well the characteristic dependences of C_0 on C_a for water-1-alkanol systems. This result seems to support the validity of underlying assumptions of the present treatment. In accordance with an increase in the hydrophobic interaction, the value of ω/kT becomes more negative as the chain length of 1-alkanol increases. As would be expected, the value of $\Delta\mu_A^1/kT$ increases regularly with increasing chain length of 1-alkanol, though it is slightly smaller than the extrapolated value from the solubility data for 1-alkanol with longer chain length than butanol (1.3 for ethanol, 2.7 for propanol, and 4.1 for butanol) (24).

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