The Binding Characteristics of Conventional and α,ω-Type Ionic Surfactant Mixtures to Polyion

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The binding isotherms of decyltrimethylammonium bromide (DeTAB) to poly(potassium vinyl sulfate) were determined potentiometrically in mixed solutions with *N,N,N,N′,N′,N′*-hexamethyl-1,20-icosanediammonium dibromide (ETMAB) and 1,1′-1,20-icosanediylbispyridinium dibromide (EPB). In both systems, an addition of the α,ω-type surfactant causes a remarkable decrease in the slope of the binding isotherm of $DeTA^+$. In addition, the binding isotherm tended to shift regularly to a low concentration range with increasing concentration of the α,ω-type surfactant. A regular solution treatment of the mixed clusters on the polyion chain suggests that substantially all of the added α,ω-type ions bind to the polyion under our experimental conditions. The observed binding isotherms can well be reproduced with interchange energies of -0.6 kT for $DeTA^+$–$ETMA^{2+}$ and -1.6 kT for $DeTA^+$–EP^{2+} pairs in the mixed clusters, respectively.

It is well known that surfactant ions bind cooperatively to polyions of opposite sign and form the micelle-like clusters on polyion chains in a remarkably low concentration range.[1—4] This concentration range as well as the binding cooperativity has been found to depend regularly on a variety of factors, such as the carbon chain length of the surfactant ion,[5—9] added salt concentration,[5,6,10—12] and charge density of the polyion.[7,13] The structure of the ionic group of the polyion also appreciably affects the surfactant ion-polyion interaction.[7,14] In analogy with the conventional surfactant micelles, the resulting surfactant ion clusters on the polyion chain not only solubilize the hydrophobic dyes, but serve as a medium for the photophysical reactions.[15—21] However, most of the studies so far reported have concerned only single surfactant ion–polyion systems.

In connection with competitive binding of the binary surfactants to the polyion, Liu et al.[22] measured the binding isotherms of 1-tetradecylpyridinium chloride (TPC) to poly(sodium L-glutamate) in mixed solutions with decylammonium chloride. In this system, an addition of the decylammonium chloride was found to cause an unusual bending of the binding isotherm together with a lowering of the concentration range where the cooperative binding of TP^+ occurs. They interpreted these characteristic behaviors in terms of an ideal mixing model for bound clusters on the polypeptide chain.

In view of the strong electrostatic interaction between the polyion and the divalent counterion, we performed a potentiometric study of the binding isotherms of decyltrimethylammonium bromide to poly(potassium vinylsulfate) in the presence of α,ω-type surfactants which have separated charges at both ends of a long carbon chain.

Experimental

Materials. α,ω-Type surfactants, i. e., *N,N,N,N′,N′,N′*-hexamethyl-1,20-icosanediammonium dibromide (ETMAB) and 1,1′-1,20-icosanediylbispyridinium dibromide (EPB) were synthesized from 11-bromoundecanoic acid (Tokyo Kasei Kogyo Co., Ltd.). The preparation and purification procedures are described elsewhere.[23] Decyltrimethylammonium bromide (DeTAB) (purity > 99%, Tokyo Kasei Kogyo Co., Ltd.) and poly(potassium vinylsulfate) (PVSK) (standard reagent for colloid titration, Wako Pure Chemical Industries Ltd.) were used without further purifications.

Measurements. The binding isotherms of DeTAB to PVSK with and without α,ω-type surfactants were determined potentiometrically by using the following poly(vinyl chloride) (PVC) membrane electrode.[24]

Ag–AgCl | 1 mol dm^{-3} KCl agar bridge | Reference solution (1 mmol dm^{-3} DeTAB) | PVC membrane | Sample solution (PVS, C_p : KCl, C_s : ETMAB or EPB, C_α : DeTAB, C) | 1 mol dm^{-3} KCl agar bridge | Ag–AgCl

Here, C_p refers to the polyion concentration in molarity of ionic group. The PVC membrane consists of 20% PVC and 80% bis(2-ethylhexyl) phthalate by weight. The electromotive force (E) of the cell was measured with a TOA Electronics Ltd. pH meter HM-60S to a precision of 0.1 mV. The measurements were conducted at 25 °C under the conditions of a constant C_p of 0.5 mmol dm^{-3}, a C_s of 20 mmol dm^{-3}, and molar ratio r ($= C_\alpha/C_p$), respectively.

Results and Discussion

Curve a in Fig. 1 shows a semilogarithmic plot of E vs. log C for DeTAB solutions in the presence of 0.1 mmol dm^{-3} EPB. A linear relation with a slope of 58.2 mV was found to hold down to 1×10^{-5} mol dm^{-3}. The observed slope agrees well with that of 58.8 mV in the absence of EPB. This fact suggests that the interference of the EP^{2+} ion to the electrode response for the $DeTA^+$ ion can safely be ignored under our experimental conditions. This is also the case for the DeTAB–ETMAB system. This calibration curve permits an estimation of the equilibrium $DeTA^+$ concentration (C_f), which leads immediately to the binding degree (β) of $DeTA^+$,

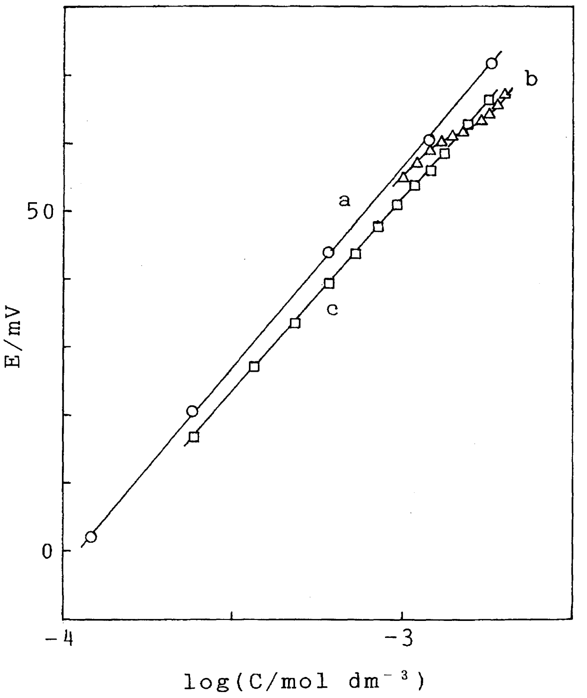

Fig. 1. Typical plots of E vs. $\log C$ for DeTAB solutions. a; C_α (EPB) = 0.1 mmol dm^{-3}, b; C_p = 0.5 mmol dm^{-3}, r = 0, c; C_p = 0.5 mmol dm^{-3}, r = 0.23 (ETMAB).

defined by $\beta = (C - C_f)/C_p$.

Curves b and c in Fig. 1 show typical E vs. $\log C$ plots for PVSK–DeTAB mixed solutions in the absence (r = 0) and presence of ETMAB (r = 0.23), respectively. An abrupt deviation of curve b from the calibration curve at around 1 mmol dm^{-3} reflects that a highly cooperative binding of DeTA$^+$ to polyion occurs in this concentration range at r = 0. However, this is not the case for r = 0.23. A comparison of curve c with the calibration curve suggests that the addition of small amounts of ETMAB causes a drastic change in the binding behavior of DeTA$^+$ to the polyion, presumably the expansion of the binding isotherm over a wide concentration range. Similar characteristic behavior is also observed for the DeTAB–EPB system.

Figure 2 shows the binding isotherms of DeTA$^+$ to PVS with and without ETMAB. In analogy with a variety of single surfactant ion–polyion systems,[1—4] the binding isotherm in the absence of ETMAB (r = 0) rises steeply over a quite narrow range of C_f. The solid line shows the calculated isotherm from the following equation based on an one-dimensional lattice model:[25]

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

Here, u represents a cooperativity parameter, defined by

$$u = \exp[(2E_{01} - E_{11} - E_{00})/kT]. \qquad (2)$$

In Eqs. 1 and 2, y refers to $C_f/(C_f)_{\beta=0.5}$, 0 to the unbound ionic site, 1 to the bound site, and E_{ij} to the interaction energy of the nearest neighbor i–j pair, respectively. As shown in Fig. 2, the calculated isotherm from Eq. 1 with $u = 250$ reproduces well the experimental data. This, in turn, reflects the strong cooperativity in the binding process due to the hydrophobic interaction among bound surfactant ions. The u value of 250 is comparable to that of 240 for the poly(L-ornithine)–sodium 1-decanesulfonate system.[9]

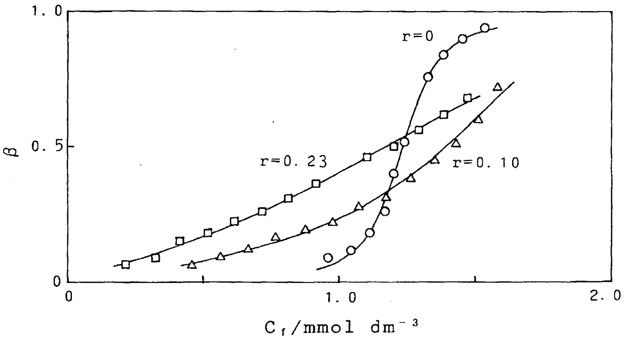

Fig. 2. The binding isotherms of DeTAB to PVSK with and without ETMAB. The solid lines show the calculated isotherms from Eq. 1 for r = 0 and Eq. 10 for r = 0.1 and 0.23, respectively. r = 0; u = 250, r = 0.10; β_0 = 0.3, A = −0.084, B = 0.40, ω/kT = −0.69, r = 0.23; β_0 = 0.3, A = −0.13, B = 0.77, ω/kT = −0.49.

As would be expected from Fig. 1, the presence of ETMAB as low as r = 0.10 results in a drastic decrease in the slope of the binding isotherm. It should also be noted that the binding isotherm shifts succesively to a low concentration range with increaseing ETMAB concentration. As is shown in Fig. 3, similar behaviors are also observed for the DeTAB–EPB system, though EPB is more effective than ETMAB in lowering the concentration range of the binding isotherm.

These characteristic behaviors are supposed to arise from the mixed-cluster formation of bound DeTA$^+$ and α,ω-type ions on the polyion chain. However, a mechanistic consideration of the observed binding isotherms requires information about the conformation of the bound α,ω-type surfactant ion, since its hydrocarbon part can assume a variety of conformations on the polyion chain from a fully extended form to a folded compact form, in which two ionic groups are

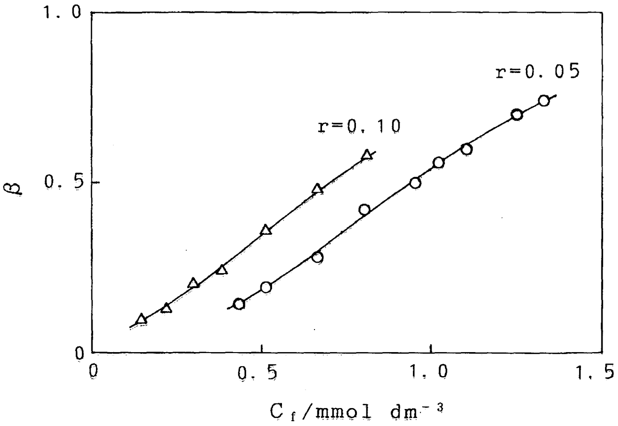

Fig. 3. The binding isotherms of DeTAB to PVSK in the presence of EPB. The solid lines show the calculated isotherms from Eq. 10. r = 0.05; β_0 = 0.3, A = −0.35, B = 1.30, ω/kT = −1.65, r = 0.10; β_0 = 0.3, A = −0.33, B = 1.47, ω/kT = −1.62.

anchored on the neighboring ionic sites of the polyion. From the standpoint of intra- and intermolecular hydrophobic interactions, the latter conformation seems to be of greater advantage than the other conformations.

In a previous study of the critical micelle concentrations (cmc) of α,ω-alkanediaminium bis(decyl sulfate) mixtures with different alkane chain lengths, we reported that the cmc vs. composition curves can be well interpreted by an ideal mixing model.[26)] On the basis of this observation, we pressumed that the α,ω-type counterions behave in the mixed micelle as if they are simple molecules with little conformational freedom, in such a way that the separated ionic head groups locate side by side, or at least close to each other at the micellar surface.

With these reservation in mind, we assume that the bound $ETMA^{2+}$ or EP^{2+} ions adopt a similar folded compact conformation on the polyion chain. Based on this simplification, together with an additional assumtion of regular mixing[27)] in the bound clusters, the binding equilibria of $DeTA^+$ and α,ω-type ion can be written as follows:

$$\mu_s + \mu_1^0 + kT\ln x_1 = \mu_{1c}^* + kT\ln y_1 + \omega y_2^2, \tag{3}$$

$$2\mu_s + \mu_2^0 + kT\ln x_2 = \mu_{2c}^* + kT\ln y_2 + \omega y_1^2, \tag{4}$$

where suffix s, 1, 2, and c refer to the ionic site of the polyion, $DeTA^+$, α,ω-type ion, and cluster, respectively. In addition, μ_{1c}^* and μ_{2c}^* represent the chemical potentials of the $DeTA^+$–s complex at $y_1 = 1$ and α,ω-type ion–s complex at $y_2 = 1$, respectively. As usual, ω refers to the interchange energy of a 1–2 pair. If we denote the fraction of α,ω-type ion bound to the polyion by δ, the mole fraction of the i-th ion in the bulk phase (x_i) and that in clusters (y_i) are given by

$$x_1 = C_f/55.5, \qquad x_2 = rC_p(1-\delta)/55.5 \tag{5}$$

$$y_1 = \beta/(\beta + r\delta), \qquad y_2 = 1 - y_1. \tag{6}$$

It follows immediately from Eqs. 3, 4, 5, and 6 that

$$kT\ln[55.5rC_p(1-\delta)y_1^2/y_2C_f^2] + \omega(2y_2^2 - y_1^2) = -\Delta G^0. \tag{7}$$

Here, $\Delta G^0 = 2(\mu_{1c}^* - \mu_1^0) - (\mu_{2c}^* - \mu_2^0)$ corresponds to the difference in the transfer free energies of the α,ω-type ion and a pair of $DeTA^+$ from aqueous to cluster phases. In the present systems, the carbon chain length of the α,ω-type ions is twice as long as $DeTA^+$. Therefore, the magnitude of ΔG^0 is expected to be fairly small, especially for the $DeTA^+$–$ETMA^{2+}$ system, in which two components have the same ionic groups. For the given values of ΔG^0 and ω, substitution of the observed β vs. C_f relationship into Eqs. 5, 6, and 7 permits an estimation of δ as a function of β. In both systems, the values of δ thus calculated are always larger than 0.99 within the experimental range of $0.1 \leqq \beta \leqq 0.8$, provided that $\Delta G^0/kT \geqq -4$ and $\omega/kT \leqq 1$. This, in turn, suggests that all of the α,ω-type ions virtually bind to the polyion, regardless of the value of β under our experimental conditions. This characteristic behavior essentially resembles the counterion condensation phenomenon of a simple counterion.[28,29)] Thus, the present systems are quite different from the conventional monovalent surfactant ion mixture–polyion system in which preferential binding of neither component occurs.[22)]

We can thus safely replace δ in Eqs. 5 and 6 with 1. Taking into account that μ_{1c}^* and μ_s in Eq. 3 are a functions of β, and r and β, respectively, Eq. 3 can be rewritten as

$$\Delta\mu_1(r,\beta) + \mu_1^0 + kT\ln x_1 = kT\ln y_1 + \omega y_2^2, \tag{8}$$

where $\Delta\mu_1(r, \beta)$ refers to $\mu_s - \mu_{1c}^*$. At constant r, which is the present experimental condition, $\Delta\mu_1(r, \beta)$ in Eq. 8 can be approximated as

$$\Delta\mu_1(r,\beta) = \Delta\mu_1(r,\beta_0) + \Delta\mu_{1\beta}(r,\beta_0)(\beta - \beta_0). \tag{9}$$

Here, β_0 is an arbitrary selected reference value of β and $\Delta\mu_{1\beta}$ is a differential coefficient of $\Delta\mu_1$ with respect to β. It follows immediately from Eqs. 8 and 9 that

$$C_f/C_{f0} = (y_1/y_{10})\exp[A + B\beta + (\omega/kT)\{r/(r+\beta)\}^2], \tag{10}$$

where, C_{f0} and y_{10} are the values of C_f and y_1 at β_0, respectively. A and B are constants defined by the following equations:

$$A = (\beta_0/kT)\Delta\mu_{1\beta}(r,\beta_0) - (\omega/kT)(1 - y_{10})^2, \tag{11}$$

$$B = -\Delta\mu_{1\beta}(r,\beta_0)/kT. \tag{12}$$

We can thus estimate the values of ω from non-linear least squares fits of Eq. 10 to the observed data shown in Figs. 2 and 3. The solid lines in Figs. 2 and 3 show the calculated binding isotherms from Eq. 10 with the most reliable parameters for $\beta_0 = 0.3$. In all cases, the aggreement between the calculated and observed isotherms is satisfactory. For a given value of r, these parameters are virtually independent of β_0. The observed constancy of B implies that $\mu_s - \mu_{1c}^*$ decreases almost linearly with increasing β. The average values of the thus-estimated ω/kT are -0.59 for the DeTAB–ETMAB system and -1.64 for the DeTAB–EPB system, respectively. The fact that the values of ω/kT are negative in both systems supports the validity of the underlying approximation of $\delta = 1$ derived from Eqs. 5, 6, and 7. In addition, the mixing of $DeTA^+$ and folded α,ω-type ions in bound clusters is considered to be more favorable than the ideal mixing proposed for the conventional surfactant mixtures, such as the 1-tetradecylpyridinium chloride–decylammonium chloride system.[22)] It should be noted, however, that a slight structural change in the ionic groups of the α,ω-type ion is accompanied by an appreciable change in the interchange energy of the order of kT. In this connection, it is interesting to note that the cmc of $ETMA^{2+}SO_4{}^{2-}$ is 1.43-times higher than that of $EP^{2+}SO_4{}^{2-}$.[23)] This is in marked contrast to the cmc's of conventional surfactants having the corresponding ionic groups. For example, with dodecyltrimethylammonium and 1-dodecylpyridinium bromides, their cmc's are virtually identical with each other.[30)] Apart from a mechanistic consideration, these facts suggest that the α,ω-type ion has a tendency to amplify the difference in the micellar parameters arising from a structural change of the ionic groups.

This characteristic effect of the α,ω-type ion is presumably responsible for the observed difference in the values of ω for the DeTAB–ETMAB and DeTAB–EPB systems.

References

1) I. D. Robb, "Anionic Surfactants: Physical Chemistry of Surfactant Action," ed by E. H. Lucassen-Reynders, Marcel Dekker, New York (1981), pp. 126—142.

2) E. D. Goddard, *Colloids Surf.*, **19**, 301 (1986).

3) K. Hayakawa and J. C. T. Kwak, "Cationic Surfactants: Physical Chemistry," ed by D. N. Rubingh and P. M. Holland, Marcel Dekker, New York (1991), pp. 189—248.

4) "Interactions of Surfactants with Polymers and Proteins," ed by E. D. Goddard and K. P. Ananthapadmanabhan, CRC Press, Boca Raton (1993), Chap. 3.

5) K. Hayakawa, J. P. Santerre, and J. C. T. Kwak, *Biophys. Chem.*, **17**, 175 (1983).

6) A. Malovikova, K. Hayakawa, and J. C. T. Kwak, *J. Phys. Chem.*, **88**, 1930 (1984).

7) A. Malovikova, K. Hayakawa, and J. C. T. Kwak, *ACS Symp. Ser. No. 253*, **1984**, 225.

8) I. Satake, K. Hayakawa, M. Komaki, and T. Maeda, *Bull. Chem. Soc. Jpn.*, **57**, 2995 (1984).

9) K. Hayakawa, H. Murata, and I. Satake, *Colloid Polym. Sci.*, **268**, 1044 (1990).

10) K. Hayakawa and J. C. T. Kwak, *J. Phys. Chem.*, **86**, 3866 (1982).

11) K. Hayakawa and J. C. T. Kwak, *J. Phys. Chem.*, **87**, 506 (1983).

12) K. Shirahama, H. Yuasa, and S. Sugimoto, *Bull. Chem. Soc. Jpn.*, **54**, 375 (1981).

13) I. Satake, T. Takahashi, K. Hayakawa, and M. Aoyagi, *Bull. Chem. Soc. Jpn.*, **63**, 926 (1990).

14) K. Hayakawa, J. P. Santerre, and J. C. T. Kwak, *Macromolecules*, **16**, 1642 (1983).

15) K. Hayakawa, T. Ohta, T. Maeda, I. Satake, and J. C. T. Kwak, *Langmuir*, **3**, 377 (1987).

16) K. Hayakawa, T. Ohyama, T. Maeda, I. Satake, M. Sata, and J. C. T. Kwak, *Langmuir*, **4**, 481 (1988).

17) K. Hayakawa, T. Fukutome, and I. Satake, *Langmuir*, **6**, 1495 (1990).

18) K. Hayakawa, I. Satake, J. C. T. Kwak, and Z. Gao, *Colloids Surf.*, **50**, 309 (1990).

19) K. Hayakawa, I. Satake, and J. C. T. Kwak, *Colloid Polym. Sci.*, **272**, 876 (1994).

20) K. Hayakawa, S. Shinohara, S. Sasawaki, I. Satake, and J. C. T. Kwak, *Bull. Chem. Soc. Jpn.*, **68**, 2179 (1995).

21) K. Hayakawa, T. Nakano, I. Satake, and J. C. T. Kwak, *Langmuir*, **12**, 269 (1996).

22) J. Liu, N. Takisawa, and K. Shirahama, *J. Phys. Chem. B*, **102**, 6696 (1998).

23) I. Satake, T. Morita, T. Maeda, and K. Hayakawa, *Bull. Chem. Soc. Jpn.*, **70**, 761 (1997).

24) T. Maeda, M. Ikeda, M. Shibahara, T. Haruta, and I. Satake, *Bull. Chem. Soc. Jpn.*, **54**, 94 (1981).

25) I. Satake and J. T. Yang, *Biopolymers*, **15**, 2263 (1976).

26) I. Satake, J. Kamikado, Y. Yasuda, T. Maeda, and K. Hayakawa, *Bull. Chem. Soc. Jpn.*, **71**, 91 (1998).

27) See for example: Y. Moroi, "Micelles," Plenum Press, New York (1992), p. 28.

28) G. Manning, *Acc. Chem. Res.*, **12**, 443 (1979).

29) G. Manning, *J. Phys. Chem.*, **88**, 6654 (1984).

30) K. Shinoda, T. Nakagawa, B. Tamamushi, and T. Isemura, "Colloidal Surfactants," Academic Press, New York (1963), Chap. 1.