ELSEVIER

Colloids and Surfaces
A: Physicochemical and Engineering Aspects 94 (1995) 115–123

COLLOIDS AND SURFACES A

The binding of cationic surfactants by various poly(carboxylic acid)s

Toshio Shimizu

Department of Information Science, Faculty of Science, Hirosaki University, Hirosaki-shi 036, Japan

Received 7 September 1993; accepted 29 June 1994

Abstract

The binding isotherms of the dodecylpyridinium ion (DP^+) by four polycarboxylates, poly(fumaric acid) (PFA), poly(maleic acid) (PMA), poly(acrylic acid) (PAA), and an alternating copolymer of maleic acid and ethylene (MAE) were determined at degrees of neutralization (α) of 0.5 and 1.0, using a potentiometric technique based on surfactant-ion-selective, solid state membrane electrodes. Surfactant binding by PFA and PMA show only single-step isotherms. In contrast, PAA and MAE show two-step binding isotherms, although the second binding step is weak. The binding isotherms of PFA and PMA with $\alpha = 1.0$, where the charge separation on the polymer backbone is half the value of PAA and MAE, level off at a degree of binding close to 0.5, possibly due to the effect of steric hindrance of the DP^+ ions at neighboring binding sites. Upon comparison of the binding isotherms in detail, we identified four types of binding site and assigned them to different chemical units contained in the chemical structures of the four polyions: $CH(COO^-)$, $CH(COO^-)CH_2$, $CH(COO^-)CH(COOH)$ (or $CH(COO^-)$ $CH_2CH(COOH)$) and $(CH)COO^- \cdots HOOC(CH)$ (hydrogen bonded). We found the standard Gibbs energies of binding for the four binding sites to be -20, -21, -22 and -23 kJ mol^{-1} respectively.

Keywords: Cooperative binding; Dodecylpyridinium chloride; Hydrophobic interactions; Poly(acrylic acid); Poly(carboxylic acid); Polyelectrolytes; Poly(fumaric acid); Poly(maleic acid); Poly(maleic acid-co-ethylene); Surfactants

1. Introduction

The interaction between ionic surfactants and oppositely charged polyions is characterized by its site-specific and highly cooperative nature [1–11]. The primary factor in the strong and site-specific binding 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. The electrostatic interaction between charged groups on the polyions and charged surfactant head groups is one of the main factors determining the intrinsic binding constant.

In previous studies, we have investigated the influence of hydrophobic side groups in the polyion chain on surfactant ion–polyion interaction, using various hydrophobic polyions such as copolymers of maleic acid with styrene, indene, ethyl vinyl ether etc. [6,10,11]. It has been found that surfactant ion binding by these polyions exhibits two-step binding isotherms. The first binding step (the stronger binding mode) in the isotherms is due to the interaction of the surfactant ion with a combined binding site containing a charged carboxyl group and its adjacent hydrophobic side group(s)

SSDI 0927-7757(94)02986-5

in the monomeric unit. The hydrophobic interaction between the bound surfactant ion and the side group(s) enhances the binding process. Unoccupied charged groups remaining isolated from the hydrophobic side groups also contribute independently to surfactant binding, and are the sites involved in the second-step binding process (the weaker binding mode). In contrast, the binding isotherms for polyions without hydrophobic side groups, such as the copolymer of maleic acid and ethylene, and poly(acrylic acid), have been regarded mostly as single-step curves. However, even in these systems, close inspection of accurately determined binding isotherms reveals a weak second binding step. This important fact has been overlooked in earlier work.

In the present paper, we extend our interests to some polycarboxylates, i.e. poly(fumaric acid) (PFA), poly(maleic acid) (PMA), poly(acrylic acid) (PAA) and an alternating copolymer of maleic acid and ethylene (MAE), and compare the binding behavior of dodecylpyridinium cations (DP^+) by these polyanions in detail. This will allow us to investigate the influences of the differences in local charge density and polyion structure on the detailed features of surfactant ion binding.

The chemical structures of the polycarboxylates used in this study are illustrated in Fig. 1. PFA and PMA are stereoisomeric polyacids, while PAA and MAE are structural isomers. PFA and PMA have a carboxyl group on every carbon atom along the main chain, and thus have charge densities twice as high as PAA and MAE. Comparing PFA and PMA, the arrangement of carboxyl groups of PMA is more compact than that of PFA as a whole. The different dissociation behavior of carboxyl groups has been reported for the two polymers [12–14]. PMA exhibits a clear two-step dissociation, while PFA dissociates in two steps similarly to PMA, but much less clearly and behaves as a whole in a manner intermede between that of PMA and PAA which do not show the two-step dissociation behavior. This difference in potentiometric pH titration behavior between PMA and PFA is related to a difference in ionization energetics, and possibly to differing behavior of the charged carboxyl groups and polymer con-

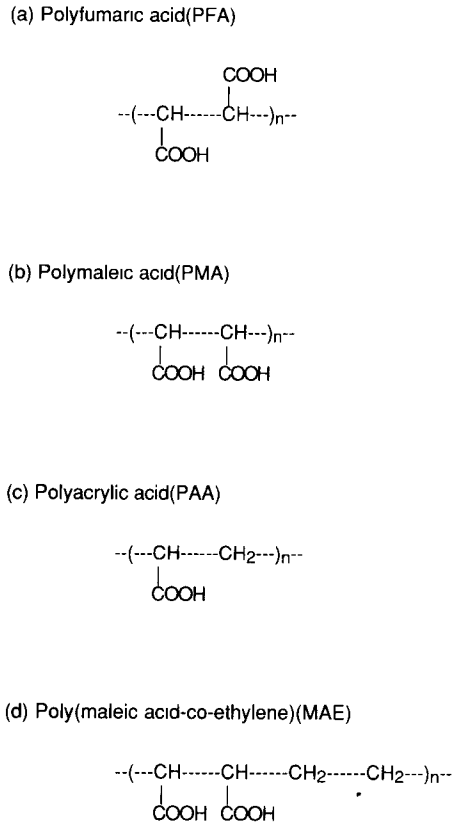

Fig. 1. Chemical structures of polyelectrolytes used in this study: (a) poly(fumaric acid) (PFA); (b) poly(maleic acid) (PMA); (c) poly(acrylic acid) (PAA); (d) poly(maleic acid-co-ethylene) (MAE).

formation. A similar two-step dissociation is observed for the maleic acid copolymers such as MAE, in which the local cis configuration of the carboxyl group pair in the monomeric unit remains during the neutralization [14]. It has been reported that ionic intramolecular hydrogen bonds are formed between all the adjacent pairs of the ionized and unionized carboxyl groups in the monomer unit of maleic acid copolymers and PMA at the half neutralization point (at $\alpha = 0.5$) [15,16]. In contrast, PAA does not form hydrogen bonds between pairs of carboxyl groups. PFA is reported possibly to form hydrogen bonds between pairs of ionized and unionized carboxyl groups not necessarily in the monomeric unit. However, the proportion of carboxyl groups forming hydrogen bonds is not as high as in PMA and MAE [16].

The cationic surfactant used is the dodecylpyridinium ion (DP^+), in the form of dodecylpyridinium chloride (DPCl).

2. Experimental

2.1. Materials

PFA and PMA were kindly donated by Dr. T. Kitano (Toyohashi University of Technology) Japan. The number-average molecular weights of PFA and PMA are reported to be 6.6×10^3 and 1.7×10^4 respectively [12]. PAA was purchased from Toagosei Chemical Industries Co. (Aron A-20, nominal molecular weight 40000). The alternating copolymer MAE was supplied by the Mitsubishi-Monsanto Chem. Co. (grade 21, average molecular weight given as 15000–20000).

Stock solutions of the polyacids were prepared as described previously [17,18]. Molal concentrations, m_p(mol kg^{-1} H_2O), of the polyelectrolytes were determined by potentiometric titration with NaOH in the presence of 1 m NaCl. The degree of neutralization α equals the number of moles of NaOH added per mole of carboxyl group. Thus, α is defined to be 1.0 at the full neutralization point where all the carboxyl groups on the polyelectrolytes are ionized. Solutions of desired values of α were obtained by adding calculated amounts of NaOH solution to the stock solutions.

DPCl (Tokyo Kasei Kogyo Co.) was purified by repeated recrystalization from acetone followed by further treatment with active charcoal.

All aqueous solutions were prepared by weight from polyelectrolyte, surfactant, and NaCl stock solutions in distilled and deionized water. Concentration units for all solutions are defined as mol kg^{-1} of H_2O.

2.2. Potentiometry

Free surfactant ion concentration was determined potentiometrically by means of a surfactant-selective solid membrane (PVC gel) electrode. The electrodes were prepared following the method described in detail previously [6,10]. A titration method was used to determine calibration curves of e.m.f. vs. total surfactant ion concentration, and surfactant ion binding curves in polyion solutions, described earlier [6,10]. A motorized piston burette (645 Multi-Dosimat, Metrohm) was used to add titrant solution of surfactant and NaCl. The polymer concentration of the test solution decreased by 20–40% upon adding surfactant and NaCl solution. Binding isotherms are independent of polymer concentration in the presence of 0.01 m NaCl for the polymer concentration range used in this work. The initial polymer concentrations of the test solutions are 0.49×10^{-3}, 0.90×10^{-3}, 0.92×10^{-3} and 1.08×10^{-3} monomol of carboxyl groups per kg of H_2O for PFA, PMA, PAA and MAE respectively. Electrode performance is independent of pH over a wide range of values encountered (i.e. from pH 3 to 9) and reliable even at ionic strengths as high as 1 m of NaCl. The observed slopes of the calibration curves were very close to the Nernst values, i.e. 60.2 ± 0.3 mV per concentration decade for 30.0°C. Potentials were measured with a TP-1000 ionmeter (Toko, ± 0.1 mV), interfaced to a microcomputer (NEC 9801F2) which checks for constancy of e.m.f., actuates the piston burette and accumulates the e.m.f. data. All the measurements were performed at 30.0°C. The solutions were stirred continuously during the e.m.f. measurements. Solution pH values were also monitored simultaneously during the titration. The e.m.f. readings reached equilibrium values within 2 or 3 min after each addition of the titrant solutions. All binding isotherms were determined at a fixed concentration of NaCl (0.01 m).

The binding isotherms and α values for each polyion were obtained by repeated e.m.f. titrations. In each case, the reported isotherm was determined at least three times, with the three independent determinations yielding binding curves identical in both shape and position, i.e., the e.m.f. measurements were repeated before the three perfectly overlapping isotherm curves were obtained. The repetition was ten times at most in each case. It should be noted here that all the binding isotherms, including ones not adopted in this paper, overlap each other within an error of 0.03 in the scale of logarithm of the free surfactant ion concentration.

3. Results and discussion

3.1. Degree of binding, binding isotherms and binding parameters

All our data will be presented as binding isotherms, where the degree of binding, β is plotted against the logarithm of the free surfactant ion concentration. In previous publications [6,10], we have described the procedure used to obtain the degree of binding in detail. The degree of binding β is defined as follows:

$$\beta = (m_D - m_D^f)/\alpha m_p \quad (1)$$

where m_D and m_D^f are the total surfactant ion concentration and the concentration of free surfactant ion respectively, m_p is the polyion concentration defined to be the total carboxyl concentration, and α is the degree of neutralization. Thus, the degree of binding β is defined as moles of surfactant ion bound per ionized carboxyl group.

In Figs. 2 and 3 binding isotherms, i.e. relationships between β and $\log m_D^f$, for PFA, PMA, PAA and MAE at a fixed 0.01 m NaCl concentration, are plotted for $\alpha = 1.0$ and 0.5. The small arrows

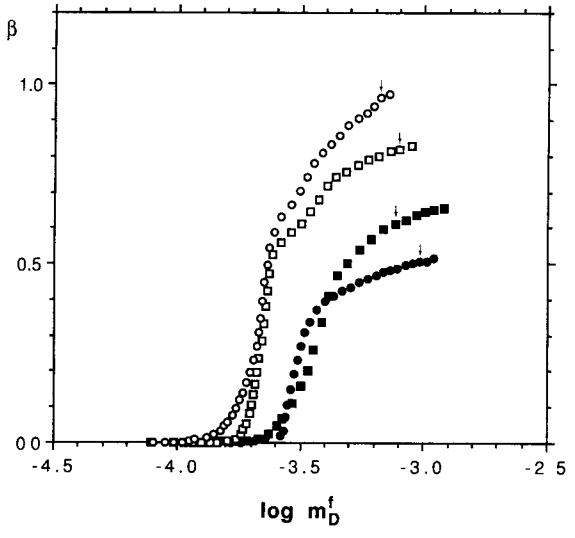

Fig. 2. Binding isotherms of DP^+ with PFA (■), PMA (●), PAA (□), and MAE (○) at $\alpha = 1.0$. $T = 30°C$, $m_{NaCl} = 0.01$ m. The m_p values for PFA, PMA, PAA and MAE are 0.49, 0.90, 0.915 and 1.08 mN respectively. Arrows indicate the points where solutions show first phase separation.

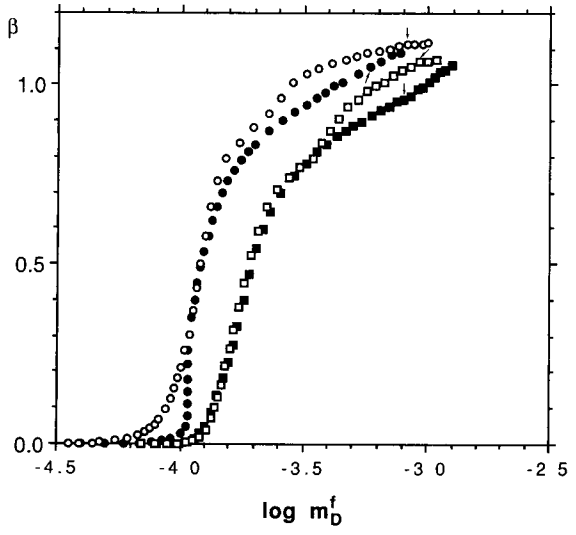

Fig. 3. Binding isotherms of DP^+ with PFA (■), PMA (●), PAA (□) and MAE (○) at $\alpha = 0.5$. $T = 30°C$, $m_{NaCl} = 0.01$m. m_p values for PFA, PMA, PAA and MAE are 0.49, 0.90, 0.915, and 1.08 mN respectively. Arrows indicate the points where solutions show first phase separation.

are drawn in the figures to indicate the points where phase separation is first observed, usually as a slight clouding of the solutions. It should be noted that data points after the phase separation takes place are less reliable.

The linear site lattice model theory was applied to analyze the binding isotherms obtained [2,8,19,20]. In this method, the binding behavior is described by two parameters: K, the intrinsic binding constant between a surfactant ion and an isolated polyion binding site, and u, the cooperative factor which is determined by the hydrophobic interaction between alkyl chains of adjoining bound surfactant ions. Values of the two parameters K and u are calculated from the experimental binding isotherms using the two equations

$$-\log(m_D^f)_{0.5} = \log Ku \quad (2)$$

$$(d\beta/d \ln(m_D^f))_{0.5} = u^{0.5}/4 \quad (3)$$

where $(m_D^f)_{0.5}$ and $(d\beta/d \ln(m_D^f))^{0.5}$ are the equilibrium surfactant ion concentration and the slope of the binding isotherm at the half-bound point ($\beta = 0.5$) respectively. In this study, the values of Ku and u were determined from the half point of each binding isotherm, which is not necessarily

identical to the half-bound point (i.e. $\beta = 0.5$). The standard Gibbs energy of binding, ΔG_b° can be estimated from the apparent binding constant Ku:

$$\Delta G_b^\circ = -RT \ln Ku \quad (4)$$

where R is the gas constant and T is the temperature [2,21].

The different binding modes in the two-step binding isotherms were separated into two single-step binding isotherm curves as follows. Binding isotherm curves were extrapolated manually from the lower to higher surfactant concentration regions to obtain smooth single-step sigmoidal curves which are regarded as first-mode binding isotherms. Then these curves were extracted from the original double-step binding isotherm curves, and the remaining parts (after the manupilation) were considered to be the second-mode binding isotherms. Fig. 4 illustrates the single-step binding isotherm curves obtained from this procedure for the case of PAA with $\alpha = 0.5$. The obtained values of Ku, K, u and ΔG_b°, calculated by applying the procedure described above and Eqs. (2)–(4) to the

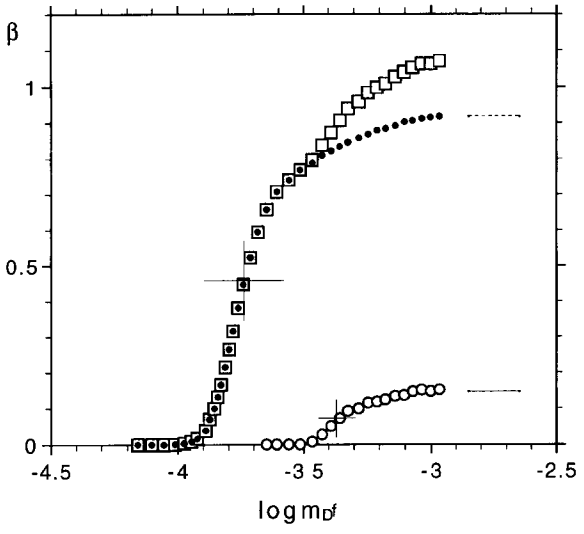

Fig. 4. Separating the double-step binding isotherm for PAA with $\alpha = 0.5$ (□) into two single-step binding isotherms, the first-step binding isotherm (●) and the second-step binding isotherm (○). Short horizontal lines drawn in the graph represent the saturation levels of the separated binding isotherms: solid line, the first-step binding isotherm; broken line, the second-step binding isotherm. The half points of the separated binding isotherms are indicated (+).

binding isotherms shown in Figs. 2 and 3 are listed in Table 1.

Attention should be paid to the following observations. As seen in Fig. 2, the binding isotherms of PFA and PMA with $\alpha = 1.0$ level off at around $\beta = 0.6$. This early saturation may be related to the effect of steric hindrance of bound DP^+ ions at neighboring binding sites (ionized carboxyl groups), as discussed in the next section. We should note here that the values of K and u obtained separately by applying Eqs. (2) and (3) to such extremely compressed binding isotherms are less reliable, because the theoretical curve extends to $\beta = 1.0$, not 0.6, and effects due to steric hindrance of bound ligands at neighboring sites are not included in the simple linear site lattice model theory. A modified linear site lattice model theory, taking account of the exclusion effect should be applied to analyze these systems. Such an extension of the theory is in preparation [22].

3.2. Description of different binding sites

Type I binding site

In the case of $\alpha = 1.0$, as shown in Fig. 2, the binding isotherms for PFA and PMA are typical single-step curves and their positions coincide within experimental error. This observation shows that PFA and PMA have the same single type of binding site. The chemical structures of PFA and PMA at $\alpha = 1.0$ are simple repetitions of the chemical unit, $CH(COO^-)$, although the stereochemical sequence of the chain carbon atoms may be different for the two polymers. Clearly, the $CH(COO^-)$ group is the only possible binding site in this case, which will be denoted as a "Type I binding site":

$CH(COO^-)$ (Type I binding site)

This conclusion is also consistent with our previous finding that each discrete binding site in polyion–surfactant ion systems contains one ionized group [6,10]. Although hydrophobic interactions with the polymer backbone also may contribute to the binding mode, this effect is probably minimal for PMA and PFA with $\alpha = 1.0$.

As seen in Fig. 2, the binding isotherms for PFA and PMA with $\alpha = 1.0$ level off at around $\beta = 0.6$

Table 1
Apparent binding constants, standard Gibbs energies and types of binding site, for the binding of dodecylpyridinium cations by PFA, PMA, PAA and MAE for $\alpha = 1.0$ and 0.5, at 30.0°C (added NaCl concentration is 0.01 mol kg^{-1} H_2O)

α	Polyion	$Ku \times 10^{-3}$ (kg mol^{-1})	K (kg mol^{-1})	u	$-\Delta G_b^\circ$ (kJ mol^{-1})	Type of binding site
1.0	PFA	2.7	49	55	20	I
	PMA	3.1	21	150	20	I
	PAA[b]	2.8			20	I
	PAA[a]	4.5	10	430	21	II
	MAE[b]	3.0			20	I
	MAE[a]	4.5	8	570	21	II
0.5	PFA	5.4	41	130	22	III
	PMA	7.9	54	150	23	IV
	PAA[b]	2.5			20	I
	PAA[a]	5.5	43	130	22	III
	MAE[b]	4.2			21	II
	MAE[a]	8.1	32	260	23	IV

[a] The first binding step.
[b] The second binding step; K and u were not estimated separately.

and 0.5 respectively, far below the binding level of other binding isotherms, where β approaches 1.0. This is most probably due to steric crowding of bound surfactants on the polyions. From a detailed analysis of potentiometric pH titration experiments [14], the average interchange separation of fully neutralized PFA or PMA has been estimated to be 0.125 nm, about half the value for PAA and MAE. The slightly lower binding level at saturation for PMA compared to PFA might be attributed to the fact that carboxyl groups in PMA are arranged more compactly [14].

Type II binding site

For the cases of PAA and MAE (Fig. 2), we recognize the characteristic two-step binding isotherms, different from the cases of PFA and PMA, although the extent of the second-step binding mode is small. The two-step binding isotherm indicates the existence of two different types of binding sites which are independent in binding behavior [6,9,10]. By separating the binding isotherms of the first (dominant) modes from the complete binding isotherms, we can extract the binding isotherms of the second (minor) modes following the procedures described in the previous section. The positions of the resulting second mode binding isotherms are found to coincide exactly with the binding isotherms of PFA and PMA. From this observation we conclude that the binding sites of the second binding modes for PAA and MAE at $\alpha = 1.0$ are identical and are also identical to the sites for PFA and PMA, i.e. the Type I binding sites.

The binding isotherms of the first-step binding modes, i.e. the stronger binding modes, of both the PAA and MAE polyions almost overlap each other, particularly with respect to the position of the two binding isotherms in the middle region of the binding process. This suggests that the binding sites in this mode are identical. There are only two chemical units, which are common to both the polyions and contain an ionized carboxyl group: $CH(COO^-)$ and $CH(COO^-)CH_2$. Excluding the $CH(COO^-)$ unit, which is already assigned to the Type I binding site, the latter chemical unit is the only possible binding site of this mode.

$CH(COO^-)CH_2$ (Type II binding site)

This Type II binding site combines the $CH(COO^-)$ binding site of Type I with a proximal methylene group, CH_2. The enhanced binding in this mode then is most likely due to the additional contribution of the hydrophobic interaction between bound

surfactants and the methylene groups on the polymer backbone. The difference in the standard Gibbs energy of binding, ΔG_b°, between the binding sites of Type I and Type II is estimated to be about -1 kJ mol^{-1}, which is thought to represent the contribution of the methylene group to the hydrophobic binding effect, if we assume that the hydrophobic interaction between bound surfactants is common for both the binding sites. This value should be compared with the standard Gibbs energy of transfer of a methylene group from water to a hydrocarbon or micelle environment, reported to be from -2.8 to -3.3 kJ mol^{-1} (from water to micelle) [23,24] or -3.7 kJ mol^{-1} (from water to hydrocarbon) [25]. The hydrophobic contribution of the methylene group to surfactant binding found above is about one third of this value. This smaller contribution is not unreasonable if we consider the more irregular nature of the contact between the bound surfactant and the polyion methylene group, and compare this to the case of the complete removal of a hydrocarbon or surfactant methylene group from an aqueous to a hydrocarbon environment.

We should mention here that the presence of only one inflection point in the binding isotherm does not necessarily mean there is only one binding mode. If there are two or more binding modes with the same or very similar free energy, they may be indistinguishable and might be considered identical from an energetic point of view.

Type IV binding site

In the case of $\alpha = 0.5$ (see Fig. 3), all the binding isotherms are located in the lower m_D^f region compared to the binding isotherms for $\alpha = 1.0$. As in the case of $\alpha = 1.0$, the binding isotherms for PFA and PMA are simple single-step curves, while the isotherms for PAA and MAE are characterized by double-step curves. The binding isotherms for PMA and MAE coincide with each other except for differences at the lower and higher extremes of the m_D^f regions. At the low concentration end, the PMA isotherm rises more abruptly than MAE and at the high concentration end the MAE isotherm shows a second binding step. The position of the second mode binding isotherm is identical to the first mode binding isotherms of PAA and MAE for $\alpha = 1.0$ (Fig. 2), indicating that the binding site of this mode is the Type II binding site.

The observation of the identical position of the first mode binding isotherms for PMA and MAE at $\alpha = 0.5$ suggests that the binding site of this mode must be common to both the polymers. As mentioned in Section 1, it has been reported that for $\alpha = 0.5$ almost all the ionized carboxyl groups of PMA and MAE form hydrogen bonds with the unionized carboxyl groups in the same maleic acid units. The repetitive chemical unit in the chemical structure of PMA at $\alpha = 0.5$ is therefore the pair of hydrogen-bonded carboxyl groups, with a single negative charge. The only chemical unit common to PMA and MAE is this hydrogen-bonded carboxyl group pair, which might be available as the binding site of this mode, i.e:

$$(CH)COO^- \cdots HOOC(CH)$$ (Type IV binding site)

The estimated value of the standard Gibbs energy of binding, ΔG_b°, for this binding site is -23 kJ mol^{-1}, which deviates from the Type I binding site by about -3 kJ mol^{-1}. This difference corresponds to about three times the contribution of this methylene group to ΔG_b°, as estimated above. The hydrogen-bonding pair of carboxyl groups in this binding site form a six-membered ring [26]. This structure may interact favorably with the pyridine ring of DP^+, leading to a more favorable standard Gibbs energy of binding.

Although binding by a Type I site might be possible for MAE at this α value as well, the existence of this binding mode is not observed in the binding isotherm. This leads to the conclusion that all the remaining free ionized carboxyl groups which are not hydrogen bonded are involved in the binding as sites of Type II. It must be noted that the single-step binding isotherm for PMA at $\alpha = 0.5$ also demonstrates that all the ionized carboxyl groups are hydrogen bonded completely with unionized carboxyl groups in the same maleic acid units.

Type III binding site

The binding isotherms of PFA and PAA for $\alpha = 0.5$ overlap almost perfectly except in the higher m_D^f region where PAA exhibits the second binding step (see Fig. 3). The binding isotherm of the

second mode for PAA is located at the same position as the binding isotherms of PFA and PMA with $\alpha = 1.0$, which indicates that the binding site of this mode is Type I.

The repetitive chemical unit in the chemical structure of PFA with $\alpha = 0.5$ is $CH(COO^-)CH(COOH)$. As mentioned in Section 1, the carboxyl group pair in this unit is considered to be hydrogen bonded to a lesser extent than the comparable units in PMA and MAE, because of differences in polymer structure. Applying the same approach as used to assign the binding sites of Types I, II and IV above, the possible chemical unit capable of behaving as the binding site of the first mode for PFA with $\alpha = 0.5$ must be the non-hydrogen-bonded pair of ionized and unionized carboxyl groups, i.e.

$CH(COO^-)CH(COOH)$ (Type IIIa binding site)

The value of ΔG_b° of this mode is estimated to be -22 kJ/mol, which represents a difference from the Type I binding site of -2 kJ/mol, and a difference of $+1$ kJ/mol from the hydrogen-bonded pair of the binding site of Type IV. The more favorable value for the Type IIIa site relative to the Type I site indicates a contribution of the polymer backbone group to hydrophobic interactions equivalent to the contribution of about two CH units.

PAA with $\alpha = 0.5$ has three chemical units having an ionized carboxyl group which may be involved in the binding: $CH(COO^-)$, $CH(COO^-)CH_2$ and $CH(COO^-)CH_2CH(COOH)$. The former two units have been characterized already as the Type I and Type II binding sites respectively. If we exclude these units as candidates for the binding site of this mode, it would follow that the last chemical unit is the binding site of this mode for PAA with $\alpha = 0.5$, i.e.

$CH(COO^-)CH_2CH(COOH)$

(Type IIIb binding site)

This is apparently a different chemical unit from the one identified as binding site Type IIIa for PFA above. Since the PFA binding isotherm and the major part of PAA binding isotherm are coincident, the binding site of this mode should be an identical chemical unit for the two polymers. Alternatively, it is possible that the binding curves do indeed represent different binding units which coincide in binding constant.

Acknowledgment

The author is grateful to Dr. T. Kitano (Toyohashi University of Technology) for donation of the PFA and PMA samples, to Dr. J.C.T. Kwak for useful comments. This research was supported by a Grant-in-Aid for Encouragement of Young Scientist (59780277) of the Ministry of Education, Science and Culture of Japan.

References

[1] E.D. Goddard and R.B. Hannan, J. Colloid Interface Sci., 55 (1976) 73.
[2] I. Satake and J.T. Yang, Biopolymers, 15 (1976) 2263.
[3] K. Hayakawa and J.C.T. Kwak, J. Phys. Chem., 86 (1982) 3866.
[4] A. Malovikova, K. Hayakawa and J.C T. Kwak, J. Phys. Chem., 88 (1984) 1930.
[5] K. Shirahama and M. Tashiro, Bull. Chem. Soc. Jpn., 54 (1984) 375.
[6] T. Shimizu, M. Seki and J.C.T. Kwak, Colloids Surfaces, 20 (1986) 289.
[7] J. Skerjanc, K. Kogej and G. Vesnaver, J. Phys. Chem., 92 (1988) 6382.
[8] K Hayakawa and J.C.T. Kwak, in D.N. Rubingh and P.M. Holland (Eds.), Cationic Surfactants: Physical Chemistry, Surfactant Sci. Series, Vol. 37, Marcel Dekker, New York, 1991, Chapter 5.
[9] B. Lindman and K. Thalberg, in E.D. Goddard and K.P. Ananthapadmanabhan (Eds.), Interactions of Surfactants with Polymers and Proteins, CRC Press, New York, 1993, Chapter 5.
[10] T. Shimizu and J.C.T. Kwak, Colloids Surfaces A: Physiochem. Eng. Aspects 82 (1994) 163.
[11] T. Shimizu, Colloids Surfaces A: Physiochem. Eng. Aspects 84 (1994) 239.
[12] T. Kitano, A. Ishigaki, G. Uematsu and S. Kawaguchi, J. Polym. Sci., Polym. Chem. Ed., 25 (1987) 979.
[13] S. Kawaguchi, T. Kitano, K. Ito and A. Minakata, Macromolecules, 23 (1990) 731.
[14] T. Kitano, S. Kawaguchi, K Ito and A. Minakata, Macromolecules, 20 (1987) 1598.
[15] S. Kawaguchi, T. Kitano and K. Ito, Macromolecules, 24 (1991) 6030.

[16] S. Kawaguchi, T. Kitano and K. Ito, Macromolecules, 25 (1992) 1294.
[17] T. Shimizu, T. Tomiyama and A. Minakata, Polymer, 21 (1980) 1427.
[18] T. Shimizu, A. Minakata and N. Imai, Biophys. Chem., 14 (1981) 333.
[19] B.H. Zimm and J.K. Bragg, J. Chem. Phys., 31 (1959) 526.
[20] G. Schwarz, Eur. J. Biochem., 12 (1970) 442.
[21] J.P. Santerre, K. Hayakawa and J.C.T. Kwak, Colloids Surfaces, 13 (1985) 35.
[22] T. Shimizu and J.C.T. Kwak, to be published.
[23] K. Hayakawa, J.P. Santerre and J.C.T. Kwak, Macromolecules, 16 (1983) 1642.
[24] K. Shirahama and N. Ide, J. Colloid Interface Sci., 54 (1976) 450.
[25] C. Tanford, The Hydrophobic Effect: Formation of Micelles and Biological Membranes, 2nd edn., Wiley, New York, 1980, Chapter 3.
[26] P.L. Dubin and U P. Strauss, J. Phys. Chem., 74 (1970) 2842.