

The aggregation of nonionic surfactants in the presence of poly(methacrylic acid)

D. F. Anghel · S. Saito · A. Băran · A. Iovescu ·
M. Cornițescu

Received: 16 June 2006 / Accepted: 2 November 2006 / Published online: 14 February 2007
© Springer-Verlag 2007

Abstract The solution properties of homogeneous hexaethylene and octaethylene glycol mono(*n*-dodecyl) ethers, $C_{12}E_6$ and $C_{12}E_8$, respectively, and octaethylene glycol mono(*n*-decyl) ether, $C_{10}E_8$, with poly(methacrylic acid) (PMA) were investigated by dye solubilization, surface tension, fluorescence, viscosity, and pH measurements. The data were discussed regarding non-cooperative and cooperative binding of surfactant to polymer. Whereas in the interaction with poly(acrylic acid) (PAA), the critical aggregation concentrations (cac or T_1) of these surfactants were lower than the respective critical micelle concentration (cmc), in that with the more hydrophobic PMA, T_1 's of $C_{12}E_6$ and $C_{12}E_8$ were higher than the respective cmc, but that of $C_{10}E_8$ was lower than its cmc. These may be ascribed to the hydrophobic microdomains (HMD) of the PMA coil in water, probably in its inside. It is considered that some surfactants are bound first to the HMD non-cooperatively and then they are abruptly bound cooperatively at T_1 . This raises T_1 higher than cmc when the cmc is low, and the amount bound by the HMD is relatively large and vice versa. T_1 of $C_{12}E_6$ or $C_{12}E_8$ is the former case, and that of $C_{10}E_8$ is the latter. Thus, different from PAA, T_1 for PMA + nonionic surfactant system consists of the amount of non-cooperative binding and the cac of the cooperative binding in equilibrium. Therefore, this T_1 has a different

meaning from that for PAA and should be called apparent T_1 . As the binding to the HMD is dependent on PMA concentration and cac is not, which is like in the PAA system, separation of apparent T_1 from the HMD binding was achieved by extrapolating T_1 's to zero PMA concentration (denoted intrinsic T_1). This value for $C_{12}E_8$ was found to be lower than the respective cmc and also lower than the respective T_1 for PAA. With increase in surfactant concentration, the pH of PMA solution rose and demonstrated a peak. This pH rise and fall may be induced by loosening of the HMD coil due to binding increase and by rearrangement of PMA + surfactant complex in high surfactant concentrations region. By raising the initial pH, the HMD were loosened; consequently, T_1 rose a little, and at higher pH, no surfactant binding took place.

Keywords Poly(methacrylic acid) · Nonionic surfactant · Critical aggregation concentration (cac or T_1) · Polymer–surfactant interaction

Introduction

In polymer and surfactant interaction in aqueous solution [1, 2], the combination of polymeric acids and polyethoxylated nonionic surfactants represents a special case of mixture of two interactive polymers, in which the attachment of an alkyl chain at the end of poly(ethylene oxide) (PEO) makes the phenomenon quite unique [3–11]. The interaction involves multiple hydrogen bondings between the carboxyls and the glycol oxygens enforced by strong hydrophobic attraction between both species. The particular character of this interaction arises from cooperative, micellar binding of the surfactants to the polymer chain, and several reviews have already dealt with it [12–14].

D. F. Anghel · S. Saito · A. Băran (✉) · A. Iovescu
Department of Colloids,
“Ilie Murgulescu” Institute of Physical Chemistry,
Spl. Independenței 202,
060021 Bucharest, Romania
e-mail: abaran@icf.ro

M. Cornițescu
“St. S. Nicolau” Virology Institute,
Mihai Bravu Blvd. 285,
030304 Bucharest, Romania

The interaction, or complex formation, between poly (acrylic acid) (PAA) and the nonionic surfactants takes place when the surfactant concentration goes beyond a certain critical value [critical aggregation concentration (cac) or T_1] that is lower than the critical micelle concentration (cmc). In a series of commercial PEO nonionic surfactants [12–15], T_1 was dependent on the hydrophobic moiety but almost independent of PEO chain length and temperature. There is also a report that T_1 was increased with PEO chain length [16]. Although the complex was insoluble at low pH, below T_1 , no precipitation occurred: T_1 was the limit of precipitation [5, 15, 17]. From phase behavior of PAA + nonionic surfactant system at 25 °C, it was found that two isotropic solution phases (L_1 and L_2) and one hexagonal liquid crystalline phase exist [18]. Self-diffusion measurements in the isotropic solution region showed that the surfactant diffused slowly when PAA was added, suggesting that PAA stabilizes the surfactant aggregates. The melting point of the hexagonal liquid crystal was increased by the presence of PAA [18].

Similar results regarding T_1 were confirmed in the series of homogeneous octaethylene glycol mono(*n*-alkyl) ether (C_nE_8) surfactants with different *n*-alkyl (C_n) moieties [19–21]: T_1 was independent of pH between 2.75 and 4.5 and of PAA concentration. The PAA carboxyls triggered the abrupt cooperative binding of the surfactants at the same concentration T_1 below the cmc, irrespective of the PEO chain length and of temperature [21]. The numbers of hexaethylene glycol mono(*n*-dodecyl) ether ($C_{12}E_6$) and octaethylene glycol mono(*n*-dodecyl) ether ($C_{12}E_8$) molecules in a micelle-like aggregate with PAA were also determined by the time-resolved fluorescence method [22]. From conductivity measurements, a theoretical model was elaborated, giving information about the shape and size of the PAA coil in the presence of C_nE_8 [23–26].

In this paper, the interaction of homogeneous $C_{12}E_6$, $C_{12}E_8$, and octaethylene glycol mono(*n*-decyl) ether ($C_{10}E_8$) with poly(methacrylic acid) (PMA) was investigated in comparison with the PAA counterparts. Previously, it was known by dye solubilization method that, in contrast with PAA, some nonionic surfactants demonstrated higher T_1 than the cmc with PMA [27]. Moreover, the interaction of PMA with cationic surfactants showed significant difference from PAA [28, 29]. PMA is known to possess hydrophobic microdomains (HMD) in aqueous solution in the lower pH range due to the sequence of hydrophobic parts in the polymer [28–31]. Therefore, its interaction with surfactants was discussed in this paper regarding the influence of HMD on T_1 . The HMD were often found in hydrophobically modified polymers in water [32, 33], but in those cases, the domains are formed with particular hydrophobic side groups locally introduced in the polymer chain.

Experimental

Materials PMA was made by Polysciences and had a molecular weight of 90,000 g/mol (degree of polymerization about 1,050). PAA was the same as used before [19]. It had a molecular weight of 150,000 g/mol (degree of polymerization about 2,100). Both polymers were used without further purification. Polymer concentration was expressed in monomer unit mole per liter. Homogeneous $C_{12}E_6$ and $C_{12}E_8$ were supplied from Nikko Chemicals, Tokyo, and octaethylene glycol mono(*n*-decyl) ether ($C_{10}E_8$) was from Fluka, Switzerland and used as received. Yellow OB, an oil-soluble dye, was obtained from Wako Pure Chem., Osaka and purified by repeated recrystallizations from methanol. Pyrene was made by E. Merck, Germany and purified as before [19]. The water used had electrical conductivity lower than 1.5 μ S/cm.

Methods Yellow OB solubilization and the absorption measurement were done as follows: A small quantity of Yellow OB powder was mixed with each surfactant or polymer + surfactant solution in a closed ampoule and stirred well occasionally for 4 weeks in dark at 25 °C. An aliquot was taken from the filtered solution and diluted appropriately with methanol. The amount of dissolved dye was spectrophotometrically determined at 440 nm with a Perkin–Elmer Lambda 35 spectrophotometer from the calibration curve. Surface tension measurements were made by the platinum ring method using the same procedure and corrections as previously described [19]. The error was ± 0.5 mN/m. Fluorescence measurements were done as reported previously [19]. Viscosity was determined with an Ostwald viscometer having a flow time for water of about 200 s. pH was measured with an Orion pH meter (model 420A) with an error of less than 0.5%.

Results and discussion

Dye solubilization

Figure 1 illustrates the solubilization of oil-soluble dye Yellow OB in the absence and presence of 1.02×10^{-2} M PMA as a function of $C_{12}E_8$ concentration. The systems shown in Fig. 1 were all clear at 25 °C, but those with $1.5 \sim 2 \times 10^{-3}$ M $C_{12}E_8$ were turbid around 27–28 °C. For comparison, the result of the corresponding PAA system is shown. In the polymer absence, the dye solubilization increased abruptly at 8.5×10^{-5} M $C_{12}E_8$, which is taken as the cmc. In the presence of PAA, the abrupt increase began at almost the same or a little lower concentration than the cmc, and this point was considered the cac or T_1 .

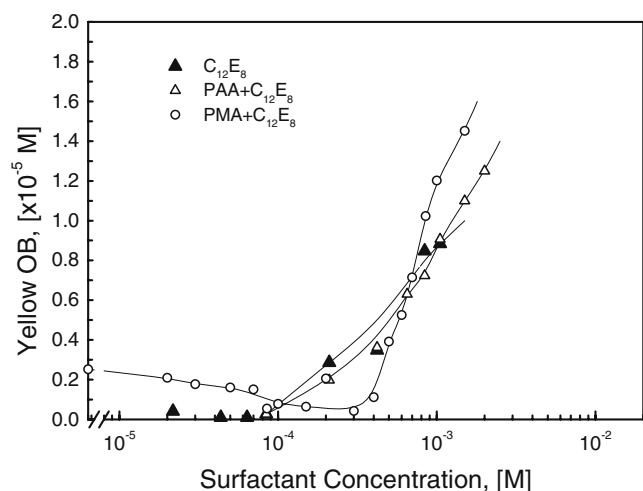


Fig. 1 Yellow OB solubilization in $C_{12}E_8$ solutions without and with 1.02×10^{-2} M PMA and with 1.02×10^{-2} M PAA, at 25 °C. pH is the initial value

Different from PAA, the more hydrophobic PMA solution without surfactant had a small dye solubility, which is ascribed to the hydrophobic conformation of PMA coil or HMD. The dye solubility in PMA without surfactant decreased with pH rise from 3.6 up; beyond pH 4.5, it became zero, at which pH PMA was more hydrophilized, and its conformation responsible for the dye solubility is supposed to be lost.

With small increase in $C_{12}E_8$ concentration, the dye solubility in PMA solution tended to decrease; passing through a shallow bottom from 3.5×10^{-4} M $C_{12}E_8$ up, it turned to rise remarkably, and this point is taken as T_1 . This T_1 is much higher than the cmc, which may seem improbable [1].

A similar dye solubilization relation was previously observed in the interaction of PMA with polydispersed PEO nonionic surfactants [27]. Different from the PAA systems [15, 19, 20], T_1 was in some cases higher than the cmc. The molecular weight PMA employed is not the reason because T_1 for PAA is independent of its molecular weight, except for a very low one [4]. Even with very low molecular weight PAA, T_1 is lower than cmc [34]. Hence, the higher T_1 than cmc for PMA is originated from the structure of PMA coils in water.

Surface tension

The surface tension method was employed in PMA + nonion systems for determining the critical concentrations. As shown in Figs. 2 and 3, without polymer, the surface tension isotherm took the typical shape for surfactant solution, and the initial descending curve was followed by a leveling-off, whose sharp break point was the onset of micellization (cmc). In the presence of PMA, changes in

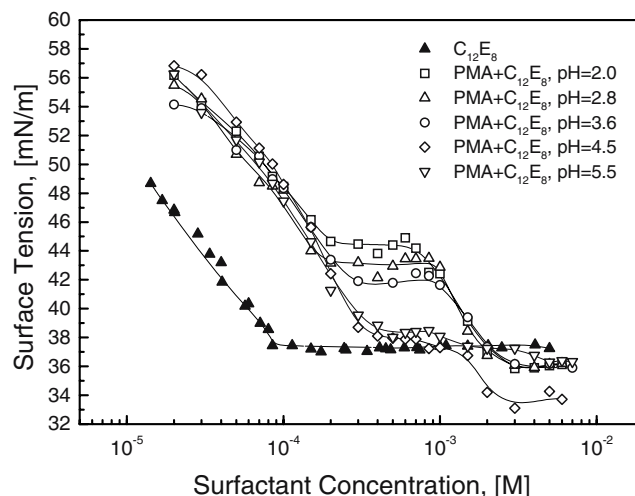


Fig. 2 Surface tension isotherms of $C_{12}E_8$ without and with 1.02×10^{-2} M PMA at various initial pH values and at 25 °C. The surface tension value of the PMA alone solution at pH 3.6 is 64 mN/m

surface tension isotherm occurred, and several regions and critical concentrations T_1 , T_2' , and T_2 appeared, as explained before in PAA + nonion systems [19–21]. With increasing surfactant concentration, the surface tension curve turns quasi-horizontal, and the plateau starts at T_1 and ends at T_2' . T_1 determined by the surface tension method is taken as the initiation concentration of micelle-like aggregation (cac) on the polymer (complex formation) [35]. Increasing the surfactant concentration, the micellar aggregates begin to contact each other on the polymer chain at T_2' , and binding is saturated at T_2 . For consistency reason, we used the T_n notation in this paper.

$C_{12}E_8$

It is known that the solution properties of polyacids depend on pH. Their pH is changed by the addition of nonionic

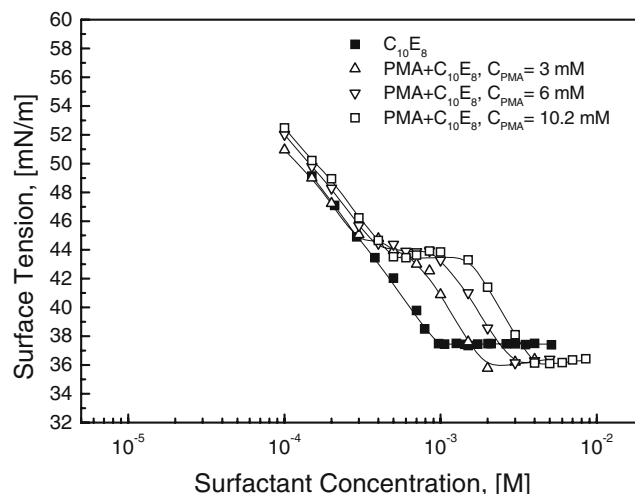


Fig. 3 The effect of PMA concentration on the surface tension of $C_{10}E_8$ at 25 °C

surfactants [19], but if not specially noted, it means the initial pH. Figure 2 shows the surface tension isotherms of 1.02×10^{-2} M PMA plotted against $C_{12}E_8$ concentration at initial pH values 2.0, 2.8, 3.6, 4.5, and 5.5, modified from its original 3.6 value by a small addition of HCl or NaOH. These systems were all clear except at pH values 2.0 and 2.8, at which the system was clear below T_1 and also above T_2 but turbid or partially precipitated between T_1 and around T_2' , its degree of precipitation being increased at pH 2.0. At pH 3.6, the surface tension of PMA+ $C_{12}E_8$ system below T_1 was much higher than that of the surfactant alone solution, and the level of the plateau for the PMA systems was evidently higher by about 5 mN/m. However, the surface tension isotherms of $C_{10}E_8$, $C_{12}E_8$, and $C_{14}E_8$ without and with PAA, respectively, overlapped below the respective T_1 [19, 20], and PAA does not coexist with $C_{12}E_8$ on the surface layer below T_1 [36]. Compared with the corresponding PAA system, PMA is a little more surface-active than PAA (64 against 70 mN/m). Thus, PMA may coexist on the surface, and it may affect the availability of the surface tension method. In this system, however, the possibility of coexistence of PMA on the surface below T_1 seems less significant because at higher pH values, especially at pH 5.5 (mentioned below), more hydrophilized and therefore less surface-active PMA showed similar, almost overlapped surface tension curves below T_1 to that at pH 3.6. In addition, the break points attributed to T_1 and T_2' were observed sharply, and T_1 agreed with that by the dye solubilization method within experimental error.

In Fig. 2, below the respective T_1 , the higher surface tension curve for PMA+ $C_{12}E_8$ system at initial pH 3.6 than that of surfactant alone solution implies that surfactants are bound to the HMD of PMA in a non-cooperative way, whereas no surfactants are bound to PAA below T_1 [19].

Similar higher surface tension values for polymer–surfactant system than those for surfactant alone solution were obtained for partially sulfonated polystyrene + $C_{12}E_5$ and bovine serum albumin + $C_{12}E_6$ systems [37–39]. It was considered that the polymer or protein did not bind to the surfactant layer; instead, it removes the surfactant from the

surface to form bulk complexes in which the hydrophobic groups of polymer are less exposed to water.

The critical concentrations T_n at 1.02×10^{-2} M PMA by the surface tension method are summarized in Table 1. T_1 is much higher than the cmc. The relevant data for PAA are included for comparison.

Higher T_1 than cmc was also observed in un-neutralized hydrophobically modified alkali-soluble emulsions (HASE)+ $C_{12}E_9$ system [40]. By isothermal titration calorimetry and dynamic light scattering, it was found for 0.1% HASE latex a T_1 of about 1.0×10^{-3} M, much higher than the $C_{12}E_9$ cmc (8×10^{-5} M). Such bigger difference between T_1 and cmc for this system than that for the present PMA+ $C_{12}E_8$ system (the cmc of $C_{12}E_8$ is similar with that of $C_{12}E_9$, and PMA concentration is about 0.1%) could be due to the higher hydrophobicity of HASE latex. In the present viewpoint, this means that more or bigger HMD may exist in which more nonionic surfactant monomers could fix non-cooperatively, leading to a much higher T_1 .

With pH increase, PMA is more dissociated and hydrophilized, and above pH 8, no interaction takes place [30]. We investigated this effect by means of surface tension method, noting the dependence of T_1 on pH. As will be mentioned in “Fluorescence”, PMA below pH 4 is hydrophobic, but at pH 5.5, it is hydrophilic [30], and the surface tension of PMA at pH 5.5 (70 mN/m) is the same as of PAA at pH 3.4. In Fig. 2, from initial pH 2.0 to 5.5, the level of the plateau was lowered; above pH 2.8, T_1 and T_2' were increased (see “ T_1 ”), and T_2 remained almost unchanged. The low surface tension around T_2 may be due to a disturbance in the surface layer by the PMA complex.

In the PAA+ $C_{12}E_8$ system, T_1 was independent of the initial pH between 2.75 and 4.5. At the same time, T_2' and T_2 were not clearly observed at pH 4.5 [21].

$C_{12}E_6$

The surface tension isotherms of $C_{12}E_6$ alone and with 1.02×10^{-2} M PMA at pH 3.6 and their tendency were similar to that of $C_{12}E_8$ (figure not shown). The T_n values were included in Table 1. T_1 was 2.4×10^{-4} M and higher than the

Table 1 The critical concentrations of $C_{10}E_8$, $C_{12}E_6$, and $C_{12}E_8$ in the interaction with 1.02×10^{-2} M PAA and PMA by the surface tension method, at 25 °C. Surfactant concentrations are expressed in M

	$C_{10}E_8$ (cmc= 1×10^{-3})				$C_{12}E_6$ (cmc= 7×10^{-5})				$C_{12}E_8$ (cmc= 8×10^{-5})			
	T_1	T_2'	T_2	$T_2'-T_1$	T_1	T_2'	T_2	$T_2'-T_1$	T_1	T_2'	T_2	$T_2'-T_1$
PAA	7×10^{-4a}	1.3×10^{-3a}	4×10^{-3a}	0.6×10^{-3}	5×10^{-5b}	1×10^{-3b}	3×10^{-3b}	1×10^{-3}	7×10^{-5b}	1.2×10^{-3b}	4.5×10^{-3b}	1.2×10^{-3}
PMA	5×10^{-4}	1.5×10^{-3}	4×10^{-3}	1×10^{-3}	2.4×10^{-4}	1.2×10^{-3}	2.5×10^{-3}	1×10^{-3}	2.3×10^{-4}	9×10^{-4}	3×10^{-3}	0.7×10^{-3}

^a Taken from ref [20]

^b Taken from ref [21], a little revised from ref [19]

cmc (7×10^{-5} M). Compared with the $C_{12}E_8$ counterpart with cmc of 8×10^{-5} M, T_1 and T_2' were only a little higher.

Higher T_1 for a shorter PEO surfactant with the same hydrophobic moiety was found in PMA + PEO-octylphenyl surfactants system [27] (see “ T_1 ”). In PAA systems, however, T_1 was almost independent of PEO chain length when the hydrophobic moiety was the same [15, 19].

$C_{10}E_8$

Figure 3 shows the surface tension isotherms of $C_{10}E_8$ without and with various PMA concentrations (regarding the initial pH values at various PMA concentrations, see “Critical concentrations at various PMA concentrations”). The surface tension curve with 1.02×10^{-2} M PMA in the lower surfactant concentration region was closer to that of the surfactant alone solution than that in PMA+ $C_{12}E_8$ (Fig. 2), in which the isotherm was much higher than that of the surfactant alone solution. It is estimated that non-cooperative binding of $C_{10}E_8$ to PMA below T_1 is less than that of $C_{12}E_8$. In contrast to the $C_{12}E_8$ and $C_{12}E_6$ systems, T_1 (5×10^{-4} M) in that with $C_{10}E_8$ was lower than the cmc (1×10^{-3} M) and also lower than T_1 for PAA (7×10^{-4} M) [20, 21]. In this respect, the PMA+ $C_{10}E_8$ system looks like normal. The critical concentrations are listed in Table 1.

Fluorescence

The fluorescence spectrum of the pyrene probe in aqueous solution at low concentration has considerable fine structure, whose relative peak intensity depends on the polarity of the medium. The ratio (I_1/I_3) of the intensity of the first peak (I_1) to the third peak (I_3) correlates with micropolarity sensed by the probe in the environment. Figure 4 shows the ratio (I_1/I_3) for both 1.02×10^{-2} M PAA and PMA as a

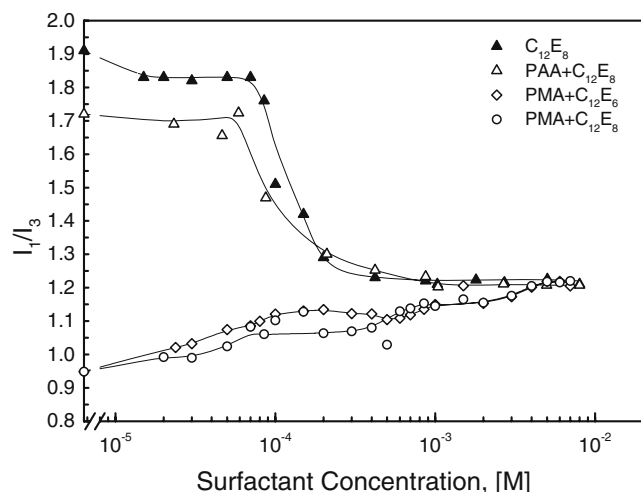


Fig. 4 Fluorescence intensity ratio (I_1/I_3) for the pyrene probe in $C_{12}E_8$ and $C_{12}E_6$ solutions without and with 1.02×10^{-2} M PMA and PAA, at 25 °C

function of $C_{12}E_8$ concentration. In the absence of polymer, the ratio showed a break point, which is the cmc of the surfactant. In the presence of PAA, the break point shifted to a slightly lower surfactant concentration than the cmc, and this concentration is taken as T_1 [19].

Different from PAA, in the PMA solution without surfactant, the ratio (I_1/I_3) around 1.0 demonstrates that the HMD in PMA coils are semi-nonpolar regions like ethyl ether or *n*-pentanol with similar polarity values [41, 42]. With initial pH rise from 4 up to 7, the ratio increased, and beyond pH 7, the nonpolar region disappeared [30]. As mentioned in “Dye solubilization”, as no Yellow OB was soluble in PMA above pH 4.5, the dye method is not sensitive for detecting HMD.

In Fig. 4, with increase in $C_{12}E_8$ concentration in the presence of PMA, the ratio rose only slightly, and with further increase, it was close to that of surfactant alone solution and also to that of the PAA + surfactant solution and merged finally with both. A similar curve was obtained on PMA+ $C_{12}E_6$. The gentle slope in the dilute region implies that the surfactant is bound to PMA even below T_1 determined by the surface tension method. Although the slope for both surfactants turned flat around $1 \sim 4 \times 10^{-4}$ M, no clear singular point appeared corresponding to T_1 , and therefore, no T_1 was decisively detected on PMA by the fluorescence method. These results may be, as compared with those in the PAA systems, attributable to the HMD.

Viscosity

Compared with PAA, PMA in water is more coiled up due to its more hydrophobic nature, and because of its lower polymerization degree, it had lower relative viscosity (Fig. 5, the left ordinate). By addition of $C_{12}E_8$, the relative viscosity curve for 1.02×10^{-2} M PMA solution showed a basin passing through T_1 (2.3×10^{-4} M) and T_2' (9×10^{-4} M)

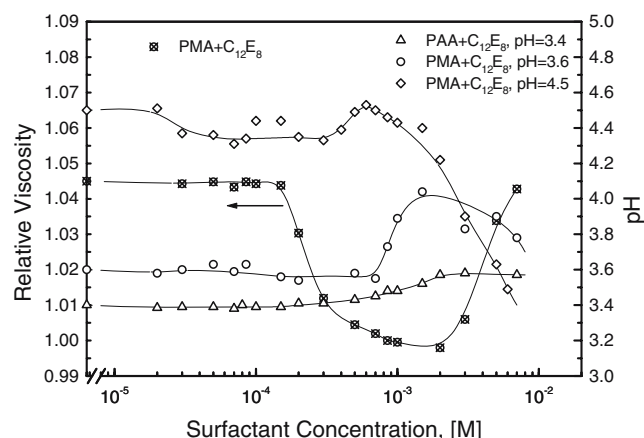


Fig. 5 Relative viscosity (the left ordinate) of PMA and pH change (the right ordinate) of PMA and PAA at 1.02×10^{-2} M plotted against $C_{12}E_8$ concentration, at 25 °C

then turning upward even beyond T_2 (3×10^{-3} M) to the level of the initial PMA solution. This trend is in contrast with the PAA system at pH 3.4 [21], in which T_1 was at the beginning of a downward curve. Generally, the critical concentrations in PAA systems were not clearly reflected by viscosity change [20, 21] because the viscosity appearance of interaction between both multifunctional long-chain polymers (PAA and PEO of surfactant) is affected by complex factors. Like in the $C_{12}E_8$ system, in PMA+ $C_{10}E_8$ system (Fig. 6, the left ordinate), the relative viscosity decreased from below T_1 (5×10^{-4} M) up, although the surface tension results (Figs. 2 and 3) suggest that below T_1 , $C_{10}E_8$ is bound to PMA less than $C_{12}E_8$. Above T_2 , the relative viscosity of the PMA system by both surfactants increased. This rise was observed also in PAA systems and attributed to some conformation change of the complex above the binding saturation [24]. The rise in the PMA case seems to be ascribed, furthermore, to some additional change in the complex structure as will be described in the next pH result.

pH

In PMA system, the dissociation degree (α) of 1.02×10^{-2} M PMA solution estimated from its pH value 3.6 was 2.5%, whereas that of PAA was 4%. At T_2' in PMA system, α was 1%, whereas in PAA it was 3%.

$C_{12}E_8$

When nonionic surfactants are bound to polyacids, hydrogen and hydrophobic bondings suppress dissociation of carboxyls and together contract the polymer chain, leading to pH rise. Figure 5 illustrates pH change (the right ordinate) for 1.02×10^{-2} M PAA and PMA plotted against $C_{12}E_8$ concentration at various initial pH values. In both

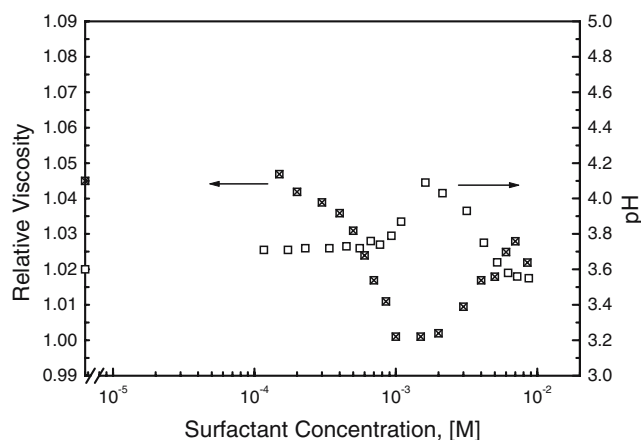


Fig. 6 Relative viscosity (the left ordinate) and pH change (the right ordinate) of PMA at 1.02×10^{-2} M plotted against $C_{10}E_8$ concentration, at 25 °C

systems, the pH increase was small and smooth below T_2' , probably because the micellar binding prevails over hydrogen bondings. In PMA system at initial pH 3.6, the pH rose from about T_2' (9×10^{-4} M) up, and a peak (pH 4.0) appeared around T_2 (3×10^{-3} M). At initial pH 4.5, no pH peak came out. As shown already, pH rise tends to suppress the interaction, but the appearance of a peak may lie in another reason. It is probably due to some change in the HMD structure in PMA around T_2 . As mentioned in “Viscosity”, in the PAA system, although at high concentration around T_2 the relative viscosity rise occurred, no pH peak accompanied it.

$C_{12}E_6$

The feature of the pH change by addition of $C_{12}E_6$ to 1.02×10^{-2} M PMA at initial pH 3.6 was similar with $C_{12}E_8$ (figure not shown).

$C_{10}E_8$

The pH change by addition of $C_{10}E_8$ to 1.02×10^{-2} M PMA at initial pH 3.6 is presented in Fig. 6 (the right ordinate). The trend is like that of the PMA+ $C_{12}E_8$, but the peak (pH 4.1) took place around T_2' (1.5×10^{-3} M) and was higher than the pH for $C_{12}E_8$ at its T_2' .

The critical concentrations of $C_{12}E_8$ and $C_{10}E_8$ at various PMA concentrations

The T_1 , T_2' , and T_2 of $C_{12}E_8$ and $C_{10}E_8$ at various PMA concentrations were determined from the surface tension isotherms in Figs. 7 and 3, respectively. As plotted in Fig. 8, for $C_{12}E_8$, they were dependent on PMA concentration; in extrapolating them to zero PMA concentration,

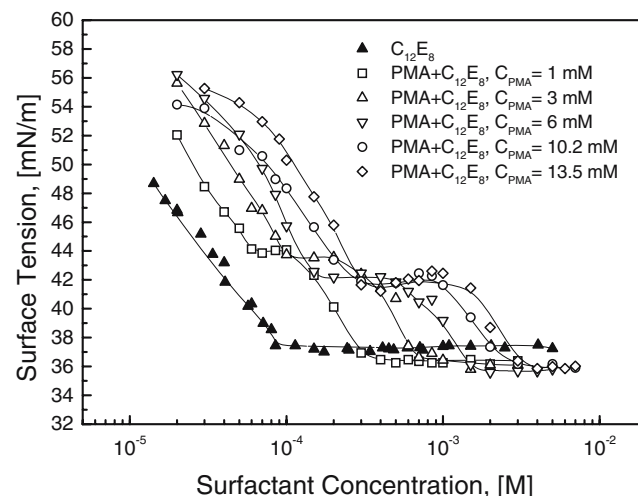


Fig. 7 Surface tension isotherms of $C_{12}E_8$ without and with various PMA concentrations, at 25 °C

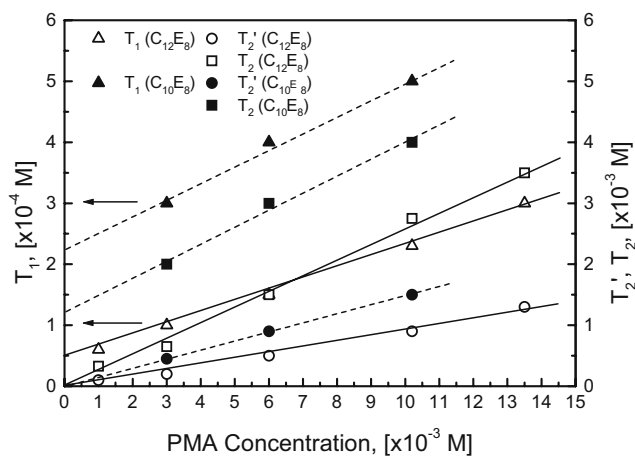


Fig. 8 The critical concentrations T_1 (the left ordinate), T_2' , and T_2 (the right ordinate) of $C_{12}E_8$ and of $C_{10}E_8$ (broken lines) with various PMA concentrations, at 25 °C

the T_1 line (the left ordinate) crossed the ordinate at 5×10^{-5} M $C_{12}E_8$, and T_2' and T_2 relations (the right ordinate) converged to the origin. Although increase in PMA concentration accompanied pH drop (from pH 4.4 to pH 3.5 from 1×10^{-3} to 13.5×10^{-3} M PMA, respectively), which caused lowering of the critical points to some extent (see Fig. 2) probably due to tightening of the HMD structure, the overall effect of PMA concentration increase resulted in raising them.

Figure 8 shows also the critical concentrations of $C_{10}E_8$ plotted against PMA concentration. The T_1 relation (the left ordinate) crossed the ordinate at 2.2×10^{-4} M $C_{10}E_8$, the T_2' (the right ordinate) at the origin, and the T_2 (the right ordinate) at 1.2×10^{-3} M $C_{10}E_8$. This positive T_2 value at zero PMA concentration seems to be due to its high cmc compared with that of $C_{12}E_8$ (see “ T_2' and T_2 ”).

In the PAA+ $C_{12}E_8$ counterparts, T_2' and T_2 converged to zero. T_1 was too small to be indicated in the figure ordinate but independent of polymer concentration [21].

The critical concentrations in the presence of PMA

T_1

The present and previous results show that, in contrast to the PAA systems, the surfactant binding to PMA starts below T_1 and that T_1 's of $C_{12}E_8$ and $C_{12}E_6$ in the PMA counterparts are higher than the respective cmc and dependent both on the hydrophobic and hydrophilic moieties of the surfactants, on polymer concentration, and also on temperature [27], whereas T_1 of $C_{10}E_8$ is lower than the cmc.

These distinctive phenomena in PMA are to be attributable to the existence of HMD in the polymer chain. The dye solubilization result in Fig. 1 is explained as follows. In

aqueous PMA, a small amount of the oil-soluble dye is contained in the HMD; when surfactants are added, they replace the dyes therefrom, and with further increase in surfactant concentration, they form micelle-like aggregates on the PMA chain that solubilize the dye markedly. Thus, the dye solubilization takes place in two steps with respect to surfactant concentration [27]: In the low concentration region, the solubilization ability is very poor, and in the higher concentration region, it is remarkable and allows T_1 determination. The HMD may admit some amount of surfactant molecules without growing to micelle-like aggregates (HMD+surfactant complex). With increasing concentration, the surfactants are bound cooperatively on PMA (above T_1). In this way, T_1 for PMA has a different meaning from that for PAA and should be called apparent T_1 . Similar two-step binding mechanisms have been proposed in the interaction of PMA with nonions [31] and of PMA in low charge densities with cationic surfactants [28, 29].

The structure of HMD in PMA chain in water may be supposed as follows. As PMA chains are more hydrophobic than PAA, in the lower pH range, they are coiled up tightly and form regions called HMD, probably inside of the coils. Below pH around 3.5, the coils are compact and/or agglomerated, and with increase in pH, they are loosened. From the fluorescence evidence [30], the loosened PMA chains at pH 5.5 still keep a partially hydrophilized HMD structure; above pH 7–8, the chains are fully hydrophilic, and the HMD disappear.

In the presence of nonions in the lower pH range, surfactants penetrate into the tightly coiled HMD chain below T_1 and fix there in a non-cooperative state, and with increase in surfactant concentration, they begin abruptly to accumulate in a micelle-like form. This critical concentration is the apparent T_1 .

As shown in Fig. 2, by raising initial pH from 2.8 to 5.5, T_1 increased. Probably by pH rise until 7–8, at which PMA is fully hydrophilic, relaxation of the HMD may develop new carboxyl sites for surfactant binding. At the same time, when the acid groups are neutralized, the sites are lost. The increase in T_1 may occur in this balance. On the other hand, in PAA+ $C_{12}E_8$ system, T_1 was unchanged from pH 2.75 to 4.5 [21]. This is ascribed to lack of HMD in PAA even at low pH.

$C_{12}E_8$ From Figs. 2 and 8, it is considered that T_1 for PMA is the simple sum of two amounts, the amount of surfactants non-micellarly bound to the HMD, which is dependent on polymer concentration, and the cac in equilibrium, which is independent of it like in PAA + nonion systems [21]. In the PMA+ $C_{12}E_8$ system, the T_1 value extrapolated to zero PMA concentration in Fig. 8 is considered free from the HMD and, therefore, of cooper-

active nature and denoted intrinsic T_1 (int T_1 ; the apparent T_1 remains simply T_1). We found that the int T_1 (5×10^{-5} M) of $C_{12}E_8$ for PMA is lower than the cmc (8×10^{-5} M) and also lower than the T_1 (7×10^{-5} M) for PAA. The present result that the int T_1 for more hydrophobic PMA is lower than T_1 for PAA seems reasonable. It is reported that T_1 's of ionic surfactants in interaction with more hydrophobic polymers are lower [43].

The difference ($T_1 - \text{int}T_1$) is taken as the amount of surfactant bound to the HMD in PMA in solution, and Fig. 8 suggests that this contribution for $C_{12}E_8$ around T_1 overwhelms that of the cooperative binding.

$C_{10}E_8$ In the PMA+ $C_{10}E_8$ system (Fig. 8), int T_1 is 2.2×10^{-4} M and so ($T_1 - \text{int}T_1$) at 1.02×10^{-2} M PMA is 2.8×10^{-4} M. Therefore, the contribution of non-cooperative binding is not so much, compared to that of the cooperative binding.

When a surfactant has low cmc and its amount contained in the HMD of the polymer is relatively high, T_1 is higher than the cmc and vice versa [27]. The PMA+ $C_{12}E_6$ and + $C_{12}E_8$ systems apply to the former case because their cmcs are very low, and the amount of surfactant bound to the HMD of PMA is large. The PMA+ $C_{10}E_8$ system is the latter case because due to its high cmc, the binding to the HMD is considered small. The systems PMA + cationic decylammonium surfactants (Anghel DF, Saito S, Iovescu A, Băran A, to be published) also belong to the latter case, as T_1 in oppositely charged pairs is usually much lower than the respective cmc [44].

T_2' and T_2

$C_{12}E_8$ The results on the relative viscosity and pH change in Fig. 5 are considered as follows. In the PMA+ $C_{12}E_8$ system, at original pH 3.6 until T_2' , tightly coiled and constrained compression of the PMA chain by surfactant binding causes little pH change because of cooperative binding. As the binding proceeds beyond T_2' , the HMD will be loosened, and carboxyls inside will be exposed and will bind surfactants (pH up). Beyond T_2 , no appreciable surfactant binding takes place, but by some rearrangement of the HMD complex in high surfactant concentrations region, a small amount of carboxyls may be further exposed (pH down), accompanied by loosening of the PMA+surfactant complex (relative viscosity up). At initial pH 4.5, as the HMD are already well relaxed, no pH peak appears.

In the system PAA+ $C_{12}E_8$, as the hydrophilic PAA chain is folded rather loosely even above T_2' , few carboxyls are packed inside, and no pH peak exists.

($T_2' - T_1$) of $C_{12}E_6$ or $C_{12}E_8$ at initial pH 3.6 is free from the HMD binding; therefore, it is the total number of

surfactants cooperatively bound to the polymer at T_2' and is equal to the number (N) of surfactants in a micellar aggregate multiplied by the number of the aggregates mutually isolated on the polymer chain. From Table 1, the ($T_2' - T_1$'s) of $C_{12}E_6$ with PAA and PMA are the same, and that of $C_{12}E_8$ with PMA is lower than that with PAA. So far, N 's are known only of $C_{12}E_6$ and $C_{12}E_8$ without and with PAA [22]. By assuming roughly the same N (75) of $C_{12}E_8$ (molecular weight 522) with PAA and PMA, the micellar aggregate has a total molecular weight of around 40,000. It is interesting to estimate how much a single PAA or PMA chain with degree of polymerization at 2,100 and 1,050 for PAA and PMA, respectively, may accommodate such aggregates at T_2' or T_2 . From ($T_2' - T_1$) at 10^{-2} unit mole concentration of the polymer, the ratio of the number of micellar aggregates of $C_{12}E_8$ to one polymer chain at T_2' was found to be approximately 3 and 1 for PAA and PMA, respectively. This ratio for PAA implies that one aggregate of 75 molecules of $C_{12}E_8$ is surrounded by 700 carboxyls. A similar estimation on $C_{12}E_6$, by assuming N as 90 for PAA [22] and PMA and from Table 1, gave the ratios approximately 2.2 and 1.1, respectively. In PMA, as its chain length is half that of PAA and in addition as mentioned in " $C_{12}E_8$ ", as its effective polymer units available for micellar binding are limited because of the HMD, the ratio could be small. The determination of N 's of both surfactants with PMA is needed.

$C_{10}E_8$ In the PMA+ $C_{10}E_8$ system, different from the $C_{12}E_8$ system because the pH peak appeared around T_2' (Fig. 6), the HMD structure is possibly loosened from T_1 up to T_2' . This implies that, although below T_1 the binding to the HMD is not much, above T_1 , both this binding and cooperative binding may proceed in parallel, and the HMD may be loosened. The T_2 value is the sum of the saturated amount of binding to the polymer chain and cmc in equilibrium. When the cmc is high, its contribution to T_2 is not negligible. Thus, as seen in Fig. 8, the extrapolated T_2 value at zero PMA concentration coincides with the cmc within experimental error.

($T_2' - T_1$) of $C_{10}E_8$ with PMA is higher than that with PAA (Table 1). In the PMA systems, in view of the higher pH increase from T_1 to T_2' compared with those for $C_{12}E_6$ and $C_{12}E_8$ as mentioned in "pH", the HMD are supposed to be loosened to some extent by $C_{10}E_8$ binding by T_2' , and at the same time, T_1 may be decreased.

Conclusions

In the interaction between PMA and $C_{12}E_6$ or $C_{12}E_8$, the cac of the surfactant determined by the dye solubilization

and/or surface tension methods was higher than the respective cmc, in contrast to the case of PAA. However, in the system of PMA+C₁₀E₈, T_1 was lower than its cmc. These may be attributable to the HMD of the PMA coil in water, probably in its inside. It is considered that some surfactants are bound first to the HMD non-cooperatively, and above saturation therein (at T_1), they are abruptly bound cooperatively. This makes T_1 higher than cmc when the cmc is low, and the amount bound by the HMD is relatively large and vice versa. The systems for C₁₂E₈ and C₁₂E₆ apply to the former case and that for C₁₀E₈ to the latter. Thus, different from the PAA system, the T_1 of the PMA system is the sum of the amount of non-cooperative binding and the cac of the cooperative binding in equilibrium. Therefore, T_1 has a different meaning from that for PAA and should be called apparent T_1 . T_1 's at various PMA concentrations were plotted against PMA concentration and extrapolated to zero PMA concentration, giving the intrinsic T_1 . As the binding to the HMD depends on PMA concentration, the intrinsic T_1 is considered free from it. This value of C₁₂E₈ was found to be lower than the apparent T_1 , lower than the respective cmc, and also lower than T_1 for PAA. Above T_2' , the micelle-like aggregates on the PMA chain condensed each other until T_2 . By the surfactant addition, the pH of the PMA solution presented a maximum. This pH peak may be induced by HMD loosening with the binding increase followed by rearrangement of PMA+surfactant complex in high surfactant concentration region above T_2 . By raising pH from 2.8 to 5.5, the HMD were loosened; consequently, T_1 rose, and in the higher pH media, no surfactant binding took place.

References

- Goddard ED, Ananthapadmanabhan KP (eds) (1993) Interactions of surfactants with polymers and proteins. CRC Press, Boca Raton, FL
- Kwak JCT (ed) (1998) Polymer–surfactant systems. Marcel Dekker, New York
- Saito S, Taniguchi T (1971) Kolloid Z 248:1039
- Saito S (1979) Colloid Polym Sci 257:266
- Saito S (1989) J Am Oil Chem Soc 66:987
- Petrova T, Rashkov I, Baranovsky V, Borisov G (1991) Eur Polym J 27:189
- Baranovsky V, Shenkov S, Rashkov I, Borisov G (1991) Eur Polym J 27:643
- Baranovsky V, Petrova T, Rashkov I (1991) Eur Polym J 27:1045
- Baranovsky V, Shenkov S, Rashkov I, Borisov G (1992) Eur Polym J 28:475
- Baranovsky VY, Shenkov S (1994) Eur Polym J 30:601
- Wasserman AM, Yasina LL, Aliev II, Doseva V, Baranovsky VY (2004) Colloid Polym Sci 282:402
- Saito S (1987) Polymer–surfactant interactions. In: Schick MJ (ed) Nonionic surfactants physical chemistry. Marcel Dekker, New York, pp 881–926
- Saito S, Anghel DF (1998) Interactions of polymers and nonionic surfactants. In: Kwak JCT (ed) Polymer–surfactant systems. Marcel Dekker, New York, pp 357–408
- Anghel DF, Saito S (2004) Recent Res Devel Surface Colloids 1:301
- Saito S (1990) Rev Roum Chim 35:821
- Anghel DF, Winnik FM, Galațanu N (1999) Colloids Surf A 149:339
- Saito S (1977) Tenside 14:113
- Galațanu AN, Chronakis IS, Anghel DF, Khan A (2000) Langmuir 16:4922
- Anghel DF, Saito S, Iovescu A, Băran A (1994) Colloids Surf A 90:89
- Anghel DF, Saito S, Băran A, Iovescu A (1998) Langmuir 14:5342
- Anghel DF, Saito S, Băran A, Iovescu A (2005) Rev Roum Chim 50:570
- Vasilescu M, Anghel DF, Almgren M, Hansson P, Saito S (1997) Langmuir 13:6951
- Raicu V, Băran A, Iovescu A, Anghel DF, Saito S (1997) Colloid Polym Sci 275:372
- Raicu V, Băran A, Anghel DF, Saito S, Iovescu A, Rădoi C (1998) Progr Colloid Polym Sci 109:136
- Băran A, Iovescu A, Raicu V, Anghel DF, Saito S, Anghel C (2003) Ann West Univ Timis Ser Chem 12:909
- Băran A, Iovescu A, Raicu V, Anghel DF, Saito S (2003) Ann West Univ Timis Ser Chem 12:847
- Saito S (1994) J Colloid Interface Sci 165:505
- Kiefer J, Somasundaran P, Ananthapadmanabhan KP (1993) Langmuir 9:1187
- Katsura H, Kawamura H, Manabe M, Maeda H (2002) Colloid Polym Sci 280:30
- Chu DY, Thomas JK (1986) J Am Chem Soc 108:6270
- Baranovsky VY, Shenkov S, Borisov G (1993) Eur Polym J 29:1137
- Thuresson K, Söderman O, Hansson P, Wang G (1996) J Phys Chem 100:4909
- Zana R (1998) Polyelectrolyte–surfactant interactions: polymer hydrophobicity, surfactant aggregation number and microstructure of the systems. In: Kwak JCT (ed) Polymer–surfactant systems. Marcel Dekker, New York, pp 409–454
- D'Errico G, Ciccarelli D, Ortona O, Paduano L, Sartorio R (2004) J Colloid Interface Sci 270:490
- Goddard ED (1993) Polymer–surfactant interactions. In: Goddard ED, Ananthapadmanabhan KP (eds) Interactions of surfactants with polymers and proteins. CRC Press, Boca Raton, FL, pp 123–203
- Maloney C, Huber K (1994) J Colloid Interface Sci 164:463
- Radlinska E, Gulik T, Lafuma F, Langevin D, Urbach W, Williams CE, Ober R (1995) Phys Rev Lett 74:4237
- Asnacios A, Klitzing R, Langevin D (2000) Colloids Surf A 167:189
- Nishikido N, Takahara T, Kobayashi H, Tanaka M (1982) Bull Chem Soc Jpn 55:3085
- Dai S, Tam KC (2005) Langmuir 21:7136
- Dong DC, Winnik MA (1984) Can J Chem 62:2560
- Kalyanasundaran K, Thomas JK (1977) J Am Chem Soc 99:2039
- Lynch I, Sjöström J, Piculell L (2005) J Phys Chem B 109:4252
- Wei YC, Hudson SM (1995) J Macromol Sci Rev Macromol Chem Phys C 35:15