Micellar structure of sodium acrylamidoundecanoate and its derivatives

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Abstract

Light scattering has been measured for aqueous NaCl and propanol solutions of the polymerizable surfactants with a reactive acrylamido group. The micelle aggregation numbers for these surfactants ranged from only 2 to 6 and their micellar diameters were less than 2 nm. The anomalous small size of these micelles may be attributed to the hydrophilicity of the acrylamido group which is believed to be located close to the micellar surface. The fast rate of polymerization of these surfactants, leading to high molecular weight polysurfactants, can thus be accounted for by the proposed micellar structure.

INTRODUCTION

Several workers have investigated the polymerization of surface active monomers [1–6] which resulted in the excellent stability of latices [7], the highly compressed polymer film [8], the rapid polymerization [3], and the improvement of emulsion polymerization [9].

Polymerizable surfactants with a reactive acrylamido group (CH_2=CHCONR–) have been synthesized recently [10–12]. The micellization and the interfacial adsorption of sodium 11-(N-methyl-acrylamido)undecanoate were also examined by surface tension measurement [13]. The polymerizations of these surfactants in aqueous micellar solutions were very rapid and high molecular weight (MW) polysurfactants with a rather narrow MW distribution were obtained [10–12]. Such characteristic polymerizations may be related to the micellar structure of the surfactants. The light scattering method was thus used in this work to study the micellar structures of sodium 11-(N-ethylacrylamido)undecanoate (Na11-EAAU), sodium 11-(N-methylacrylamido)undecanoate (Na11-MAAU), and sodium 11-

acrylamidoundecanoate (Na11-AAU). The chemical structures of these surfactants are $CH_2=CHCONR(CH_2)_{10}COO^-Na^+$, where $R = C_2H_5$, CH_3, and H, respectively.

EXPERIMENTAL

The samples of Na11-EAAU, Na11-MAAU, and Na11-AAU used were the same as those previously prepared [10-13]. Water and NaCl were purified in the usual manner [14-16]. 1-Propanol of chromatographic grade was a commercial product. Aqueous 14% vol. propanol solution was prepared by mixing 1-propanol and water in the volume fraction ratio of 1:6. Measurements of the specific refractive index increment and light scattering were carried out on a differential refractometer MR-102 and a dynamic light scattering spectrophotometer DLS-700, respectively, which were manufactured by Otsuka Electronics, Osaka. The detailed method for the light scattering measurements has been described elsewhere [14-16].

RESULTS AND DISCUSSION

The observed values of the specific refractive index increment $d\tilde{n}/dc$, where $\tilde{n}$ is the refractive index and c is the surfactant concentration, are listed in Table 1 for aqueous NaCl and propanol solutions of Na11-EAAU, Na11-MAAU, and Na11-AAU at 25°C. The specific refractive

TABLE 1

Characteristics of micelles of Na11-EAAU, Na11-MAAU and Na11-AAU in aqueous NaCl and propanol solutions at 25°C

	C_s (M)	$d\tilde{n}/dc$ (cm³ g⁻¹)	CMCª (10⁻² g cm⁻³)	M	m	B_2 (10⁻³ mol cm³ g⁻²)	D_0 (10⁻⁷ cm² s⁻¹)	R_H (nm)
Aqueous NaCl solution								
Na11-EAAU	0.01	0.169	0 30(9.8)	1190	3.9	5.8	51 5	0.48
	0.5	0.161	0.37(12)	1810	5.9	1.5	27.5	0.91
Na11-MAAU	0.5	0.161	0.40(14)	1150	3.9	0.55	44.5	0.53
Aqueous propanol solution								
Na11-EAAU		0.156	0.30(9.8)	771	2.5	2.8		
Na11-MAAU		0.156	0.33(11)	697	2.4	3.7		
Na11-AAU		0.150	0.28(10)	453	1.6	2.7		

ªValues in parentheses are in mM.

index increments for Na11-EAAU decreased with increasing NaCl concentration (C_s) and were larger in NaCl solutions than in aqueous propanol solutions. The value for Na11-AAU was smaller than those for both Na11-EAAU and Na11-MAAU in aqueous propanol solutions.

Figure 1 shows the plot of the reduced scattering intensity of the micelle ($R_{90} - R^\circ_{90}$) against the surfactant concentration c, where R_{90} and R°_{90} are the reduced scattering intensities of solution and solvent, respectively, at a scattering angle of 90°. The value of the critical micelle concentration (CMC) c_0 was obtained from the intercept of the plot by extrapolating to the zero reduced scattering intensity. The CMC values for the surfactants, as shown in Table 1, were $(0.35 \pm 0.05) \cdot 10^{-2}$ g cm^{-3} in aqueous NaCl solutions and $(0.30 \pm 0.03) \cdot 10^{-2}$ g cm^{-3} in aqueous propanol solutions. These values
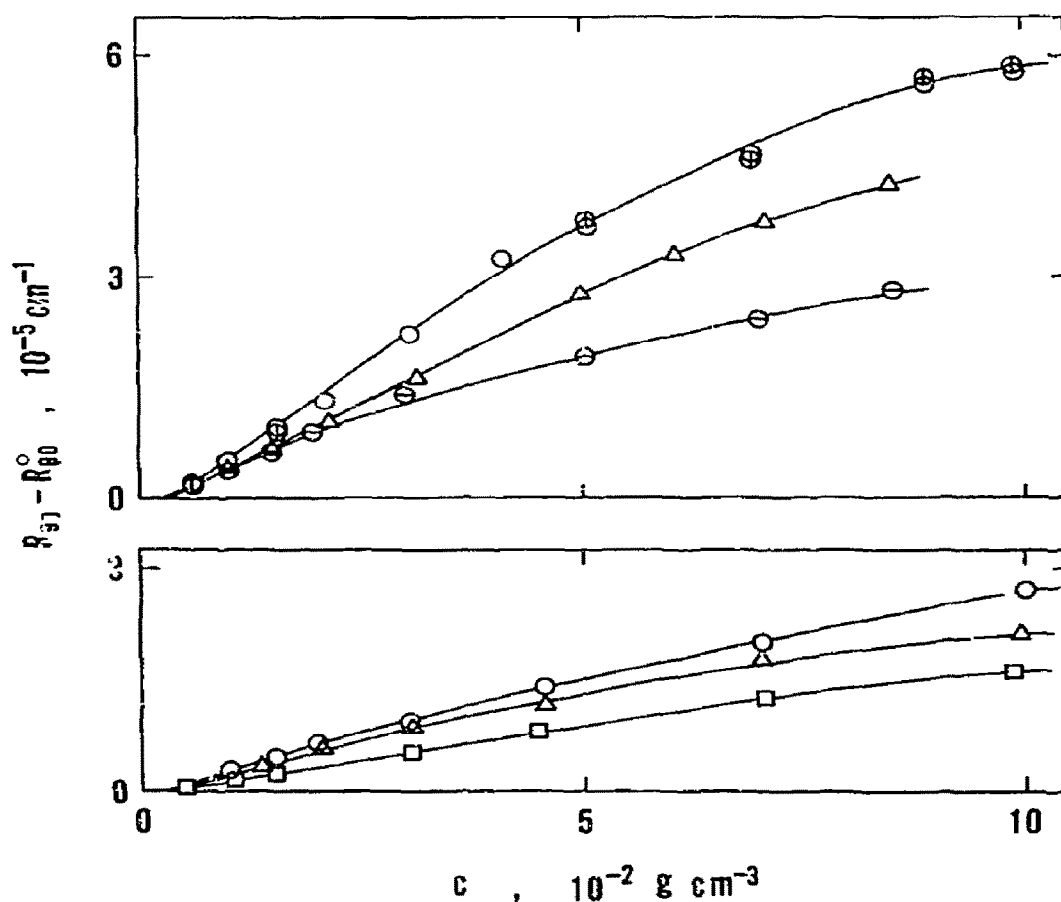

Fig. 1. ($R_{90} - R^\circ_{90}$) values plotted against c for aqueous NaCl and propanol solutions of Na11-EAAU, Na11-MAAU, and Na11-AAU. Aqueous NaCl solutions (upper): O, ⊕, Na11-EAAU in 0.5 M NaCl at 25 and 40°C, respectively; ⊖, Na11-EAAU in 0.01 M NaCl at 25°C; △, Na11-MAAU in 0.5 M NaCl at 25°C. Aqueous 14% vol. propanol solutions at 25°C (lower): O, Na11-EAAU; △, Na11-MAAU; □, Na11-AAU.

were higher than those obtained by surface tension measurements on the aqueous solutions [12,13,17].

There was no meaningful angular dependence of reciprocal scattering intensity and mutual diffusion coefficient, indicating that the micelles were of a small size. Figure 2 shows the reciprocal scattering intensity $K(c - c_0)/(R_{90} - R_{90}^{\circ})$ as a function of micelle concentration $(c - c_0)$, where K is the optical constant.

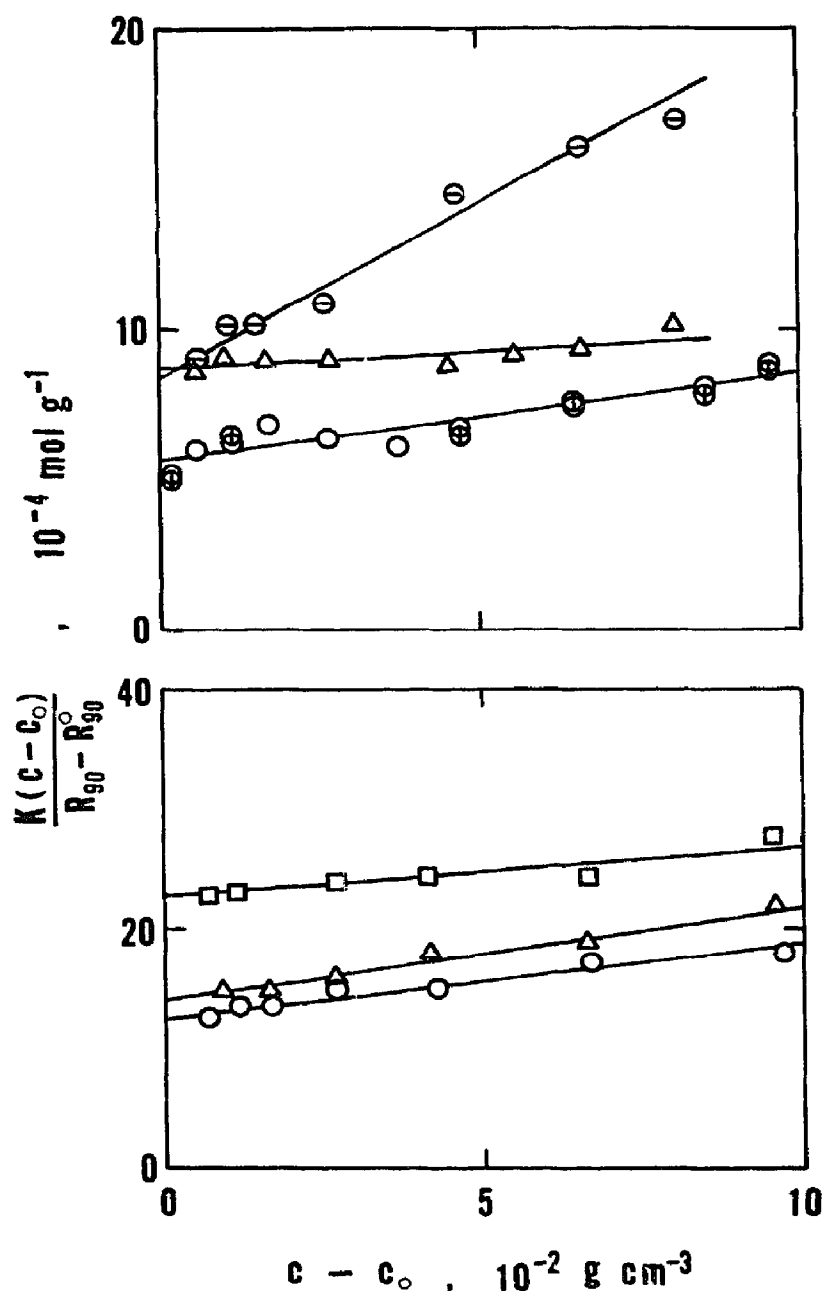The reciprocal scattering intensity of each solution exhibited a clear

Fig. 2. $K(c - c_0)/(R_{90} - R_{90}^{\circ})$ values plotted against $(c - c_0)$ for aqueous NaCl and propanol solutions of Na11-EAAU, Na11-MAAU, and Na11-AAU. Upper: in aqueous NaCl solutions. Lower: in aqueous 14% vol. propanol solutions at 25°C. The symbols have the same meanings as those in Fig. 1.

linear relationship with micelle concentration. The temperature rise from 25 to 40°C did not affect the reciprocal scattering intensity for 0.5 M NaCl solutions of Na11-EAAU. The micelle molecular weight M and the second virial coefficient B_2 were evaluated from

$$k(c - c_0)/(R_{90} - R_{90}^\circ) = 1/M + 2B_2(c - c_0) \tag{1}$$

for small micelles and are listed in Table 1. The micelle aggregation number m was calculated from the micelle molecular weight M and the molecular weight of its monomeric surfactant M_1, i.e. $m = M/M_1$. It is surprising to note that the micelle aggregation number was only 4 to 6 in aqueous NaCl solutions and 2 to 3 in aqueous propanol solutions. Although it is unusual for aggregates with aggregation number 2–6 to be called micelles, they may be referred to as "micelles" because their solutions revealed the critical micelle concentration.

The mutual diffusion coefficients of the micelles were measured at low scattering angles with higher micelle concentrations. If the average values from different micelle concentrations are regarded as the translational diffusion coefficient D_0, the hydrodynamic radii R_H of the micelles (Table 1) can then be calculated from the Einstein–Stokes relation

$$R_H = k_B T/6\pi\eta_0 D_0 \tag{2}$$

where k_B is the Boltzmann constant, T is the absolute temperature, and η_0 is the viscosity of the solvent. The hydrodynamic micellar radius thus obtained was only 0.5 to 0.9 nm in aqueous NaCl solutions. The small values of R_H and m strongly indicate that the micelles of these surfactants are abnormally small.

The anomalous small size of the micelles may be attributed to the character of the acrylamido group of the monomeric surfactant molecule. As a result of the hydrophilicity of the acrylamido group at the terminal hydrophobic portion of a surfactant molecule, this reactive group may approach the hydrophilic layer of a micelle, that is, the micelle–water interface and the air–water interface. The surfactant hydrocarbon chains at the air–water interface must be bent back on themselves to expose the acrylamido group to the aqueous phase (Fig. 3a), as deduced from the surface tension measurement [13]. However, the surfactant hydrocarbon chains in a micelle may cross over within a micelle (Fig. 3b) but they may not necessarily be bent back. Such an approach of acrylamido groups to the micellar surface causes strong geometrical hindrance on the packing in a micelle. This would allow the formation of extremely small micelles consisting of only 4 to 6 surfactant monomers in aqueous NaCl solutions. Such a micellar orientation is more evident in aqueous propanol solutions ($m = 2$ to 3)

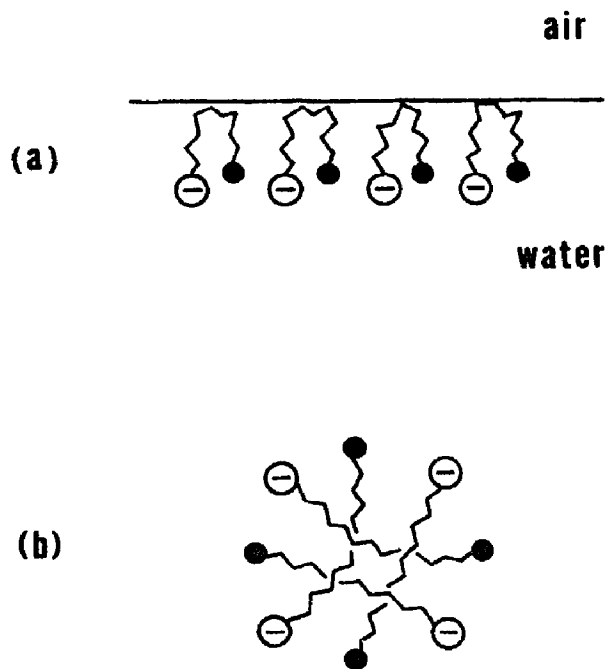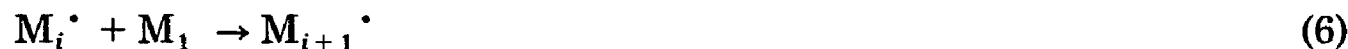**air**

(a)

water

(b)

Fig. 3. Schematic representation of the adsorption model of surfactants at the air–water interface (a) and the micellar model (b).

owing to better interactions between the acrylamido group and propanol. The micellar model with a small diameter less than 2 nm, as seen in Fig. 3b, is supported by the observed hydrodynamic micellar diameter, 1–1.8 nm.

The polymerization process of surface active monomers can be viewed generally as follows:

$$I \rightarrow R^{\bullet} \tag{3}$$

$$R^{\bullet} + M_1 \rightarrow M_1^{\bullet} \tag{4}$$

$$M_1^{\bullet} + M_1 \rightarrow M_2^{\bullet} \tag{5}$$

$$\vdots$$

$$M_i^{\bullet} + M_1 \rightarrow M_{i+1}^{\bullet} \tag{6}$$

$$M_x^{\bullet} + M_y^{\bullet} \rightarrow M_{x+y} \tag{7}$$

$$M_x^{\bullet} + M_y^{\bullet} \rightarrow M_x + M_y \tag{8}$$

where I and M_i are initiator and i-mer. $R^{\bullet}$ and $M_i^{\bullet}$ are free radicals of initiator and i-mer. The rough packing structure in a micelle with the polymerizable acrylamido groups close to the micellar surface facilitates the initiation of the polymerization (Eqn (4)) by free radicals generated in aqueous medium by potassium persulphate (Eqn (3)). The polymerization of acrylamido groups (Eqns (5, 6)) can proceed rapidly

not only within a micelle but also among micelles. This is due to the easy accessibility of the reactive sites near the micellar surfaces by free radicals and the growing polymer radicals. Since the micellar size is extremely small, the probability for a second free radical to be adsorbed on the polymerizing micelle is relatively low. Hence, the rate of radical termination (Eqns (7, 8)) in the micelle is slow. Consequently the prolonged propagation of polymerization results in the formation of high molecular weight polysurfactants with narrow MW distributions as reported [10–12].

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