Properties of Aqueous Solutions for Two Binary Mixed Systems Between Two Kinds of Bile Salts and Nonionic Surfactants

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The micellar properties of aqueous binary mixed solutions for two systems consisting of sodium cholate (NaC) -octaoxyethylene glycol mono n-decyl ether ($C_{10}E_8$) and sodium glycocholate (NaGC)-$C_{10}E_8$ have been studied on the basis of surface tensions, polarity of the micelle interior and the mean aggregation number. Application of two theoretical treatments, based on regular solution and excess thermodynamic quantities for critical micellar concentration (CMC) data from surface tension curves of two mixed systems showed that the mole fraction of each bile salt in the mixed micelles near the CMC is lower than that of the corresponding prepared mole fraction in the mixed solution. The polarity of the interior suggested that the hydrophobicity of intramicelles increased with the increase of the mole fraction of bile salt in the mixed solution and that the mixed micelles become dramatically more hydrophobic at a mole fraction of 0.68 for NaGC–$C_{10}E_8$ system and 0.75 for NaC–$C_{10}E_8$ system, respectively. This implies that the micelles become richer in the bile salt molecules and the tendency appears strongly for NaGC–$C_{10}E_8$system due to the strong cohesion between the conjugated glycines in the NaGC molecules. The decrease of aggregation number with the increase of the mole fraction of bile salts shows that the micelles approach those of the single system of each bile salt. This supports the previously mentioned facts.

KEY WORDS: **Aggregation number, excess thermodynamic quantities, octaoxyethylene glycol mono n-decyl ether, pyrene fluorescence, regular solution treatment, sodium cholate, sodium glycocholate, surface tension.**

The detergent-like properties and the propensity to form micellar aggregates are related to the most important physiological functions of bile salts. The association of bile salts' molecules in aqueous solutions is markedly different from that of aliphatic surfactants, owing to the very different chemical structure of the bile salts (1,2). Bile salts possess a rigid steroidal ring structure, one side of which is spiked with hydroxyl groups, and the other side with methyl groups, while one end possesses a short hydrocarbon chain ending in a carboxyl group conjugated by glycine or taurine. Accordingly, as bile salts' molecules with bulky structure and with strong affinity among the steroid rings are mixed with nonionic surfactants with linear molecular structure in water, the differences in the mixed properties between conjugated and unconjugated bile salts may appear on the association and the micelles may become a non-ideal mixture.

Micellar properties in aqueous solutions for bile salt have been extensively studied by many investigators (3-7). For example, according to Small and co-workers (8,9), the primary micelles are stabilized through hydrophobic interactions, whereas the formation of secondary micelles involves hydrogen bonding between the hydroxylic groups at the micelle surface. However, few studies on the mixture of bile salts and the other surfactants have been carried out because of the difficulties in confirming the properties of the mixed micelles and the surface behavior, owing to a strong cohesion among bile salt molecules.

In recent years, fluorescence techniques have been extensively applied to micellar systems in order to obtain information on the micelles. The fluorescence probes such as pyrene, which are solubilized by micelles, can provide much information on the polarity of the micelle interior (10-15). Furthermore, the mean aggregation number of micelles can be directly determined by means of the steady state quenching of fluorescent probe in a wide range of the concentrations without a restriction to the concentration near the critical micellar concentration (CMC) (16-18). These methods are completely insensitive to intramicellar interactions and can easily confirm the concentration dependence of the polarity and the mean aggregation number of micelles.

In this work, colloidal and surface properties of the mixed micelles for two combination systems consisting of sodium cholate and octaoxyethylene glycol mono n-decyl ether, sodium glycocholate and octaoxyethylene glycol mono n-decyl ether (19, 20) will be discussed based on data from surface tension and fluorescence techniques. Each component of the mixed micelles is estimated by applications of regular solution treatment (21) and the excess thermodynamic quantities (22) to CMC data from surface tension curves. Furthermore, the difference in the micellar properties between the conjugated and unconjugated bile salt will be discussed on the basis of all results.

EXPERIMENTAL PROCEDURES

Materials. Sodium cholate, NaC (Mikuni Chemicals, Tokyo, Japan), and sodium glycocholate, NaGC (Midori Chemicals, Tokyo, Japan), were purified several times by recrystallization from the mixed solvents of ethanol and methanol, and then Soxhlet extraction was performed with acetone for 72 hr. Octaoxyethylene glycol mono n-decyl ether, $C_{10}E_8$ (Nikko Chemicals, Tokyo, Japan), was purified by gel chromatography (Wakogel C-200, Wako Chemicals, Osaka, Japan) with equivalently mixed solvents of acetone and n-hexane; the product then gave a single spot on thin-layer chromatography. These surfactants were confirmed to be highly pure by the fact that there was no minimum around each of the CMCs in the surface tension vs the concentration curves.

The pyrene (Tokyo Kasei Kogyo, Tokyo, Japan) used as a probe was purified by gel chromatography with cyclohexane. The dodecylpyridinium chloride, DPCl (Tokyo Kasei Kogyo), used as a quencher was purified several times by recrystallization from the mixed solvents of acetone and isopropanol after a decolorization with activated carbon in the mixed solvents.

In order to prevent the hydrolysis of bile salts, aqueous solutions of surfactants were prepared with tris/HCl buffer solution adjusted at pH 9.0 ± 0.05 with ionic strength of 0.026.

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Methods. All surface tensions were measured by the Wilhelmy vertical plate method using a glass plate with a Shimadzu surface tensiometer ST-1 (Shimadzu, Kyoto, Japan). The data for surface tensions were taken at 15-min intervals for about 1 hr.

The pyrene fluorescence emission spectrum was measured by monitoring the spectrum from 350 nm to 500 nm, exciting the pyrene molecules near 341 nm with a Shimadzu fluorescence spectrophotometer RF-540. The pyrene concentrations solubilized in the micellar solutions were prepared in the range from 0.1×10^{-5} to 1.0×10^{-5} mol/L, depending on the surfactant concentration.

The mean aggregation number of micelles were obtained from luminescence quenching measurements (16-18). Assuming that both the probe molecule (P) and the quencher molecule (Q) are solubilized into micelles and obey the Poisson distribution among micelles and that P is luminescent only in micelle free from Q, the measured ratio of luminescence intensities (I/I^0) in the presence of Q to that in the absence of Q is given by the equation:

$$(I/I^0) = \exp(-[Q]/[M]) \qquad [1]$$

where [Q] is a concentration of quencher, and [M] is an unknown micelle concentration that can be related to the mean aggregation number, $\bar{n}$, using the measurable concentration of the surfactant, [Surf], e.g., [M] = ([Surf] – [free monomer])/$\bar{n}$. Since the free monomer concentration is approximately equal to the critical micelle concentration (CMC), Equation [1] can be rewritten using the relationship among $\bar{n}$. [Surf] and CMC in the form:

$$\ln(I^0/I) = [Q]\bar{n} / ([Surf] - CMC). \qquad [2]$$

Accordingly, from the slope of plots of $[\ln(I^0/I)]$ against [Q], the mean aggregation number can be obtained for each concentration of surfactants. The concentrations of pyrene were prepared in the range from 0.2×10^{-6} to 1.0×10^{-6} mol/L, depending on the total surfactant concentration. The concentrations of DPCl as a quencher were prepared to get the ratio of [Q] to [M] in the range from 0.5 to 1.5. Throughout this work, the temperature was kept at 25 ± 0.05°C.

RESULTS AND DISCUSSION

Surface tension of NaC-$C_{10}E_8$ and NaGC-$C_{10}E_8$. The surface tensions vs logarithm of total surfactant concentration curves for aqueous solutions of NaC, $C_{10}E_8$ and their mixtures with mole fractions of bile salt of 0.25, 0.50, 0.75, 0.90 are shown in Figure 1. Similar curves for NaGC, $C_{10}E_8$ and their mixtures are shown in Figure 2, respectively. Each curve for NaC, NaGC and $C_{10}E_8$ alone showed only one break point corresponding to the CMC, and the curves for the mixtures in each system of NaC-$C_{10}E_8$ and NaGC-$C_{10}E_8$ also showed only one break point on each curve. These CMCs are listed in Table 1. In general, when two kinds of surfactants having a large difference in the amount of each surface excess are mixed in water, a minimum usually appears near CMC on surface tension curve for the binary mixtures. However, a minimum is not found on the curves in Figures 1 and 2. This may be due to the mutual compensation for adsorption and desorption of the surfactants on the surface.

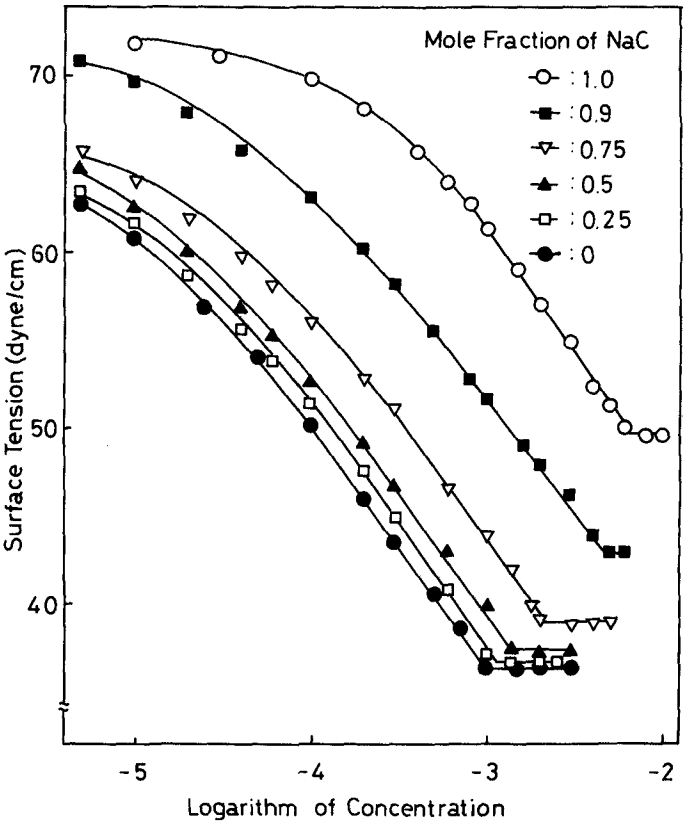

FIG. 1. Curves of the surface tension vs total surfactant concentration (in logarithmic scale) with various mole fractions of NaC.

The CMC values were used for the theoretical calculations by regular solution treatment of Rubingh (21) and excess thermodynamic quantities of Motomura (22), and for the determination of micellar aggregation number.

The composition in the mixed micelles. The composition of two surfactants in the mixed micelles varies with the change of the mole fraction of bile salts in the solutions and, in most cases, the mixed state of two surfactants are known to become non-ideal. The deviation from ideal mixing can be confirmed by analyzing the relationship of the CMC and mole fraction of bile salt using the regular solution treatment by Rubingh (21) and from excess thermodynamic quantities by Motomura and co-workers (22).

Rubingh (21) proposes that the mole fraction ($X^M_{regular}$) of bile salt in the mixed micelles of a binary system of bile salt and $C_{10}E_8$ is given by:

$$X^M_{regular}{}^2 \ln [CMC_{mix}X_{bile}/CMC_{bile}X^M_{regular}] / (1 - X^M_{regular})^2 \ln [CMC_{mix}(1 - X_{bile}) / CMC_{nonion}(1 - X^M_{regular})] = 1 \qquad [3]$$

where X_{bile} is the mole fraction of bile salt in the solution; and CMC_{bile}, CMC_{nonion} and CMC_{mix} are CMCs for bile salt, $C_{10}E_8$ and the mixed system, respectively.

On the other hand, Motomura and co-workers (22) indicate that the mole fraction (X^M_{excess}) of bile salt in the mixed micelles of a binary mixture at constant temperature and pressure is given by:

$$X_{bile} = 2X_{bile}/(X_{nonion} + 2X_{bile}) \qquad [4]$$

TABLE 1

CMC and Mole Fractions of Bile Salts in the Mixed Micelle at 25°C

Mole fraction of bile salts in the solution	Critical micellar concentration		Mole fraction of bile salt in one mixed micelle			
	CMC [mmol/L]		$X^M_{regular}$		X^M_{excess}	
X_{Bile}	NaC − $C_{10}E_8$	NaCG − $C_{10}E_8$	NaC − $C_{10}E_8$	NaCG − $C_{10}E_8$	NaC − $C_{10}E_8$	NaCG − $C_{10}E_8$
0.00	1.00	1.00	0.00	0.00	0.00	0.00
0.25	1.17	1.16	0.11	0.12	0.03	0.03
0.50	1.53	1.65	0.20	0.17	0.09	0.06
0.75	2.28	2.20	0.36	0.37	0.13	0.12
0.90	4.28	4.04	0.56	0.58	0.40	0.38
1.00	6.93	6.34	1.00	1.00	1.00	1.00

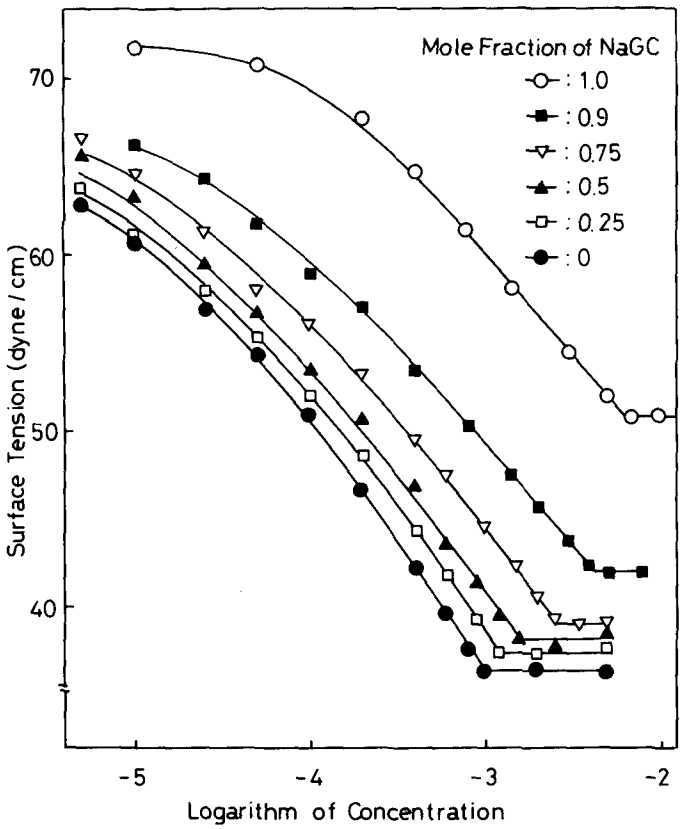

FIG. 2. Curves of the surface tension vs total surfactant concentration (in logarithmic scale) with various mole fractions of NaGG.

$$C\hat{M}C_{mix} = (X_{nonion} + 2X_{bile})CMC_{mix} \quad [5]$$

$$\hat{X}_{nonion} = 1 - \hat{X}_{bile} \quad [6]$$

and

$$X^M_{excess} = X_{bile} - (\hat{X}_{nonion}\hat{X}_{bile}/C\hat{M}C_{mix})(\partial C\hat{M}C_{mix}/\partial \hat{X}_{bile})_{T,P} \quad [7]$$

where $\hat{X}_{bile}$, $C\hat{M}C_{mix}$ and $\hat{X}_{nonion}$ are defined as the variables considering the dissociation of the bile salts instead of the variable X_{bile}, CMC_{mix} and the mole fraction of $C_{10}E_8$ (X_{nonion}), respectively. The values for mole fraction of bile salt in the mixed micelle can be determined by analyzing the data applied to both theories using a computer. The values of each component are listed in Table 1. Figure 3 shows each plot of the calculated mole fraction of bile salts in the mixed micelles as a function of the prepared mole fraction of bile salts in the solutions for these two mixed systems. The values for NaC-$C_{10}E_8$ system calculated by the regular solution treatment deviated positively form an ideal line-(a) and also for NaGC-$C_{10}E_8$ system from an ideal line-(b). However, these values for both systems calculated by the excess thermodynamic quantities deviated remarkably negatively from each ideal line. Comparing the values of both analyses, there is a large difference between $X^M_{regular}$ and X^M_{excess} in the curves of Figure 3, and a slight distortion in the curves of $X^M_{regular}$ is observed in the range of the low X_{bile}. It is generally accepted that regular solution treatment of Rubingh (21) can be applied to a series of homologous surfactants and undissociated surfactants. On the other hand, the treatment on the basis of excess thermodynamic quantities by Motomura (22) is not restricted to its application by the nature of the surfactants or their counterions and can be used to describe the behavior of the binary surfactant mixtures, which are of widely different structures. Accordingly, this latter should give the actual composition of the mixed micelles in binary mixtures of bile salt and $C_{10}E_8$ than the former. Therefore, $X^M_{excess} - X_{bile}$ curves for the mixed systems deviated negatively from the ideal line suggest that, and the ratio of bile salts in the mixed micelle is very small, the bile salt molecules are solubilized in an excess amount of $C_{10}E_8$ molecules. It appears that there may be a break point in the curves at about 0.7 mole fraction.

Microenvironment of intramicelles. Some information about the solubilization site of pyrene in the mixed micelles for both mixed systems can be obtained from the measurements of the ratio of the first and third vibronic peak, I_1/I_3, in a monomeric pyrene fluorescence emission spectrum. This ratio is known to be an excellent index of the polarity in the probe microenvironment (10-15). In the case of low I_1/I_3 values, the microenvironment of the solubilized pyrene is non-polar, as in hydrocarbon solvents. For example, it is about 0.6 for solvents such as cyclohexane and n-hexane. On the other hand, for more polar microenvironment, the values are higher—1.05 for isopropanol, 1.23 for ethanol, 1.75 for polyoxyethylene (ethyleneoxide units are 400), and 1.83 for H_2O, respectively.

Figures 4 and 5 show dependence of I_1/I_3 values on total surfactant concentrations for both single and mixed micellar systems of NaC-$C_{10}E_8$ and NaGC-$C_{10}E_8$. The I_1/I_3 values of the mixed micellar systems in each figure are close to ones near that of $C_{10}E_8$ in the range of the total surfactant concentration near the CMC. This means that the solubilization site of pyrene and the microenvironment of the intramicelles are considered to be nearly the same as those of $C_{10}E_8$

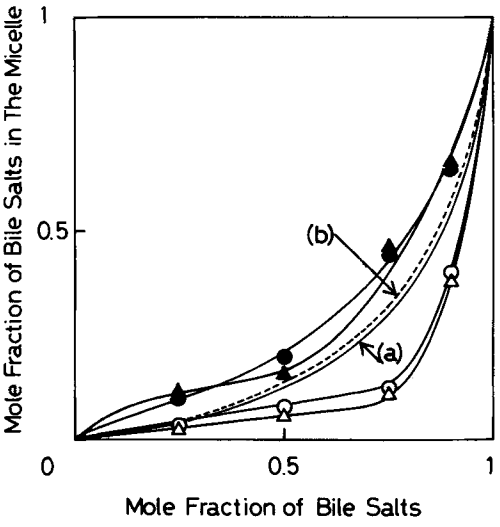

FIG. 3. Curves of the mole fraction of bile salts in the mixed micelle vs the mole fraction of bile salts in the solution. The closed plots are calculated by regular solution theory and the open plots are calculated by excess thermodynamic quantities. Line-(a), an ideal time for the NaC-$C_{10}E_8$ system; line-(b), an ideal time for NaGC-$C_{10}E_8$ system; (●,○), NaC-$C_{10}E_8$ system; and (▲,△), NaGC-$C_{10}E_8$ system.

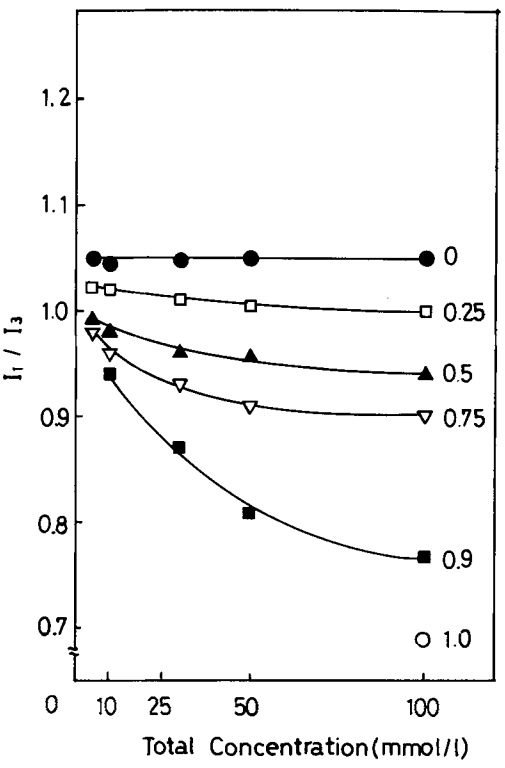

FIG. 4. Curves of the I_1/I_3 vs total surfactant concentration with various mole fraction: mole fraction of NaC = 0.00 (●), 0.25 (□), 0.50 (▲), 0.75 (▽), 0.90 (■), and 1.00 (○).

micelles near the CMC, and the mole fraction of NaC or NaGC in mixed micelle of each system is much lower than the prepared mole fraction of NaC or NaGC.

Figure 6 shows plots of I_1/I_3 values for various mole fractions of bile salts at the constant total surfactant concentration of 100 mmol/L, as a function of the mole fraction of bile salt. Open plots show the values for NaC-$C_{10}E_8$ system and closed plots for NaGC-$C_{10}E_8$ system. These values are listed in Table 2.

The I_1/I_3 values for single system of bile salt were 0.69 for NaC, and 0.74 for NaGC, respectively. These values indicate that the solubilized pyrene is located in the micelles of bile salts with a microenvironment which is nearly as non-polar as hydrocarbon solvents (23), and the difference of I_1/I_6 values between NaC and NaGC indicates that a carboxyl group conjugated by glycine influences the solubilization site of pyrene in the micelles. On the other hand, the value for single system of $C_{10}E_8$ was 1.05, and was close to the value of polar solvents, such as isopropanol. This means that pyrene molecules are solubilized into the micellar palisade layer of $C_{10}E_8$. Owing to slight surface activity of pyrene, the I_1/I_3 values are as high as that in micelles of ordinary surfactants.

In the case of the mixed NaC-$C_{10}E_8$ or NaGC-$C_{10}E_8$, the I_1/I_3 values decreased slightly with the increase of the mole fraction of bile salt and show a break point at the mole fraction of 0.75 for NaC- $C_{10}E_8$ and 0.68 for NaGC-$C_{10}E_8$, respectively. Above these mole fractions the values decrease more steeply. The break points in each curve may correspond to a transition point in hydrophobicity of the intramicelles or to a change of micellar shape, e.g., from spherical to lamellar micelles. The I_1/I_3 values for the mixed systems in the range of the mole fraction of bile salt from 0 to the values of each break point are near 1.05, which is that of pure $C_{10}E_8$ micelles. This means that the hydrophobicity inside the mixed micelles resembles that of the $C_{10}E_8$ in this range of the mole fraction. Above mole fraction of 0.75 for NaC or 0.68 for NaGC, the hydrophobicities or the micellar shapes approach that of the single micelle of NaC or NaGC, and show that the ratio of bile salt in the mixed micelle increase. It should be noticed that the mole fractions of bile salts corresponding to each break point of I_1/I_3 values for each mixed system coincide with the ones on the curves of X^M_{excess} and X_{bile} obtained from theoretical calculations in Figure 3. Accordingly, from the results of the analyses of the micelle composition, the values obtained from the excess thermodynamic quantities by Motomura (22) may approach the real system for the mixed micelles in the binary mixtures of bile salts and nonionic surfactant.

Further, as shown in Figure 6, the mole fraction corresponding to a break point for NaC-$C_{10}E_8$ system deviates slightly to a larger value than that for NaGC-$C_{10}E_8$ system. This may be due to the affinity between glycine groups conjugated in the NaGC molecules.

The mean aggregation number. The mean aggregation numbers for both single systems and the mixtures were measured in the range of the total surfactant concentration from 20 mmol/L to 50 mmol/L in order to solubilize thoroughly pyrene molecules in the single and mixed micelles. The mean aggregation number, $\bar{n}$, at various mole fractions of bile salt as a function of total surfactant concentration are shown in Figure 7 for NaC-$C_{10}E_8$ system and in Figure 8 for NaGC-$C_{10}E_8$ system.

The values of $\bar{n}$ for $C_{10}E_8$ alone were almost constant across the whole range of total surfactant concentrations.

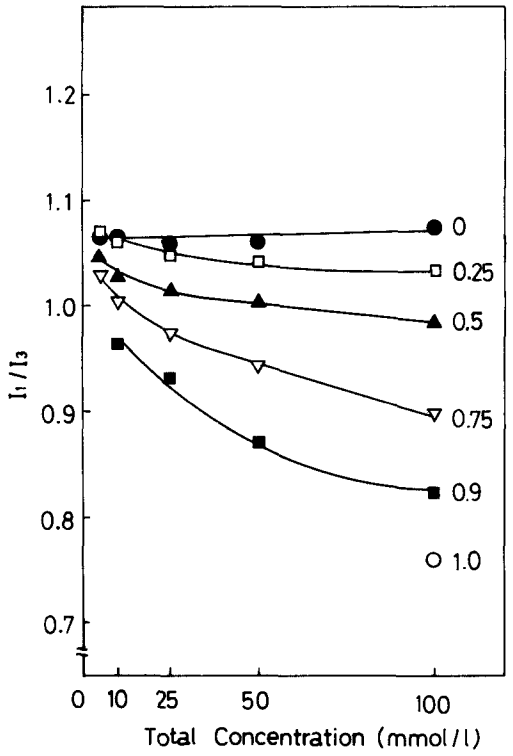

FIG. 5. Curves of the I_1/I_3 vs total surfactant concentration with various mole fraction: mole fraction of NaGC = 0.00 (●), 0.25 (□), 0.50 (▲), 0.75 (▽), 0.90 (■), and 1.00 (○).

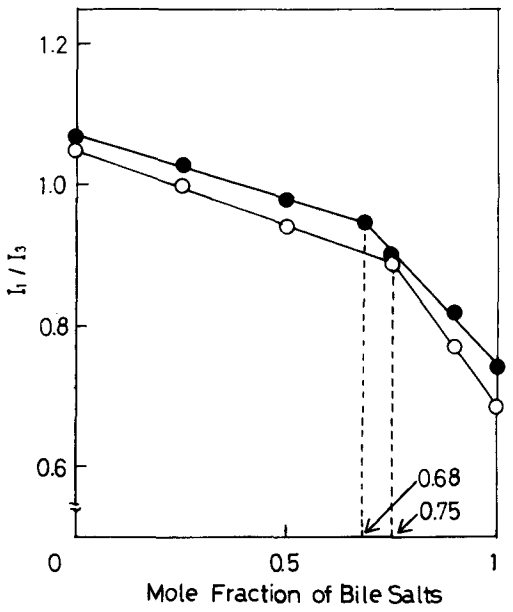

FIG. 6. Plots of the I_1/I_3 values vs mole fraction of bile salts; (○), NaC-$C_{10}E_8$ system; and (●) NaGC-$C_{10}E_8$ system.

However, the values of $\bar{n}$ for the mixed micellar systems in both Figures decreased more extensively than those for the single micellar system of $C_{10}E_8$ with the increase of the total surfactant concentration. This suggests that the properties of the mixed micelles are very close to that of the single micelle of bile salts having small aggregation number, although the bile salt molecules have intermolecular strong affinity between the steroid rings. Furthermore, the $\bar{n}$ values for mixed micellar systems showed gradually lowering tendencies with the increase of the total surfactant concentration from 20 mmol/L to 50 mmol/L as with I_1/I_3 measurements.

Figure 9 shows plots of $\bar{n}$ values for all mixed systems at the constant total concentration of 50 mmol/L as a function of mole fraction of bile salt. Open plots are NaC-$C_{10}E_8$ system and closed plots are NaGC-$C_{10}E_8$ system, and the

TABLE 2

The Values of I_1/I_3 and the Mean Aggregation Number with Various Mole Fractions at 25°C

Mole fraction of bile salts in the solution	The first/third peak in a monomeric pyrene fluorescence emision spectrum		Mean aggregation number	
	I_1/I_3		$\bar{n}$	
X_{Bile}	NaC-$C_{10}E_8$	NaGC-$C_{10}E_8$	NaC-$C_{10}E_8$	NaGC-$C_{10}E_8$
0.00	1.05	1.05	69	69
0.25	1.00	1.03	37	36
0.50	0.94	0.98	29	32
0.75	0.90	0.90	23	23
0.90	0.77	0.82	16	18
1.00	0.69	0.74	15	14

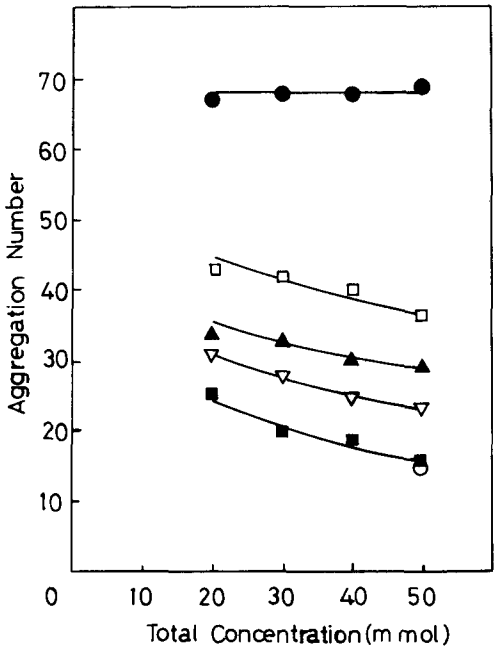

FIG. 7. Curves of the mean aggregation number vs total surfactant concentration with various mole fraction: mole fraction of NaC, 0.00 (●); 0.25 (□), 0.50 (▲), 0.75 (▽), 0.90 (■), and 1.00 (○).

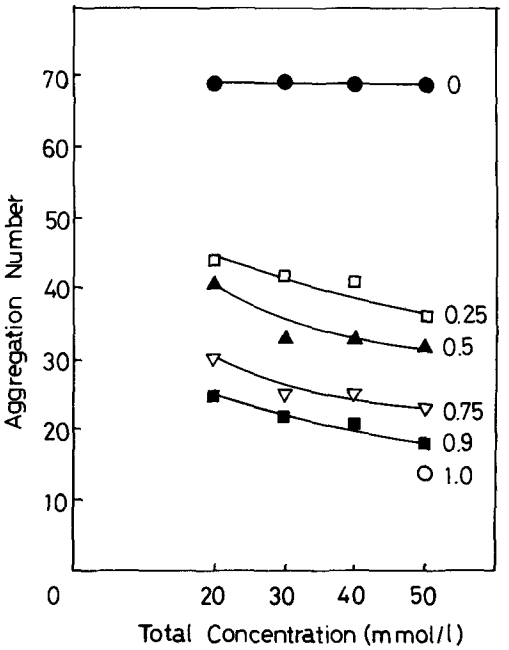

FIG. 8. Curves of the mean aggregation number vs total surfactant concentration with various mole fraction: mole fraction of NaGC 0.00 (●); 0.25 (□), 0.50 (▲), 0.75 (▽), 0.90 (■), and 1.00 (○).

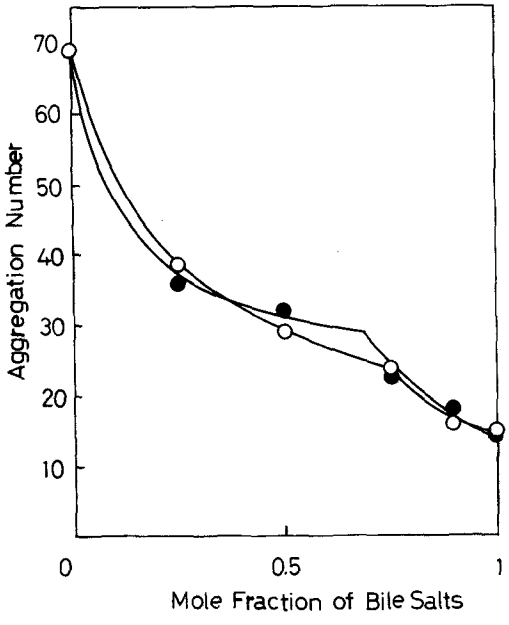

FIG. 9. Plots of the mean aggregation number vs mole fraction of bile salts; (○), NaC-$C_{10}E_8$ sytem; and (●), NaGC-$C_{10}E_8$ system.

data are listed in Table 2. In both mixed systems, an additional effect of a trace of NaC or NaGC on the micellar solution of $C_{10}E_8$ can be observed in the range of the mole fraction from 0 to 0.25, as shown in Figure 9. This abrupt decrease of $\bar{n}$ may be explained on the basis of the differences in the cohesions or the shapes between bile salt and $C_{10}E_8$. The $\bar{n}$ value of 15 for single micellar system of NaC and 14 for NaGC are very small, as shown in Table 2, and the $\bar{n}$ values for each mixed micelle may become smaller due to an incorporation of $C_{10}E_8$ molecules into the micelles of each bile salt with small $\bar{n}$ value.

Furthermore, the $\bar{n}$ values for each mixed micellar system showed a break point near the mole fraction of 0.75 for NaC-$C_{10}E_8$ system and 0.68 for NaGC-$C_{10}E_8$ system that was similar to the break point that appeared on the curve in Figure 6. This means that micellar shapes of mixed micelles change from similar structure to the micelle of $C_{10}E_8$ to the ones similar to the micelle of bile salt. The difference in the values of $\bar{n}$ on the break point between NaC-$C_{10}E_8$ system and NaGC-$C_{10}E_8$ system on the curves may be caused by the difference in the intermolecular affinity between the conjugated bile salt and free bile salt. Accordingly, as the values of I_1/I_3 changes with an increase of the mole fraction of bile salt combined to this result, it seems that by a terminal glycine group, NaGC molecules tend to aggregate in the binary mixture and strongly exclude $C_{10}E_8$ molecules from the mixed micelles.

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