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ORIGINAL CONTRIBUTION

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# A circular dichroism study of the interaction between *n*-decanoyl-*N*-methylglucamide and surface active agents in mixed micelles

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**Abstract** The interaction between MEGA-10 and surface active agents was studied by means of circular dichroism. The molecular ellipticity of MEGA-10 varied with the addition of surface active agents, but its peak wavelength did not. The carbonyl group of MEGA-10 did not interact with the nonionic surface active agents nor the catanionic surfactant (of which the anionic and cationic portions were decanesulfonate and decyltrimethylammonium, respectively). It did, however, interact with the ionic surfactants, and also strongly with the ammonium group and the benzene ring. The interaction between MEGA-10 and ionic surfactant charges did not differ according to the sign of the charge. Circular dichroism spectra are a useful tool for performing research into the interaction between an optically active carbonyl group and an additive.

**Keywords** n-Decanoyl-*N*-methylglucamide · Micelle · Interaction · Mixture · Circular dichroism

## Introduction

Micellar and microemulsion systems, which are microheterogeneous in nature, are well-known, and have an enormous number of technical applications. In fundamental and applied (pharmaceutical, technological and industrial) fields, solubilization in the micelle is important. A micellar surface is a field of highly concentrated hydrophilic groups. Solubilization of an organic substrate in a micelle depends on hydrophobicity, hydrophilicity, and charge of the substrate. Micellar and microemulsion systems provide vital information about the solute-solute and solute-solvent interactions in surfactant solutions, and have therefore led to extensive structural, kinetic, and thermodynamic studies.

The nonionic surfactant *n*-decanoyl-*N*-methylglucamide (MEGA-10) has been used to solubilize membrane proteins [1, 2]. Since MEGA-n has hydroxyl and carbonyl groups, it is a model compound for fundamental research into the interactions between a hydrophilic group and a biosubstance such as a carbohydrate or a peptide. A study of the interactions between MEGA-10 and surfactants is significant for research into the interactions between carbonyl and other polar groups.

The physicochemical properties of MEGA-n have been investigated by several workers [3, 4, 5, 6, 7, 8]. Circular dichroism (CD) is preferable to UV absorbance when studying interactions with carbonyl groups in aqueous solutions, because sample solutions contain dissolved carbon dioxide, which affects the UV absorbance in the vicinity of 200–250 nm but not the optical activity. In this paper we report on the interaction between carbonyl and various hydrophilic groups, as studied by CD.

## Experimental

### Materials

MEGA-10 was purchased from Dojin Kagaku Co. and was recrystallized five times from a diethylether-

ethanol mixture following extraction with hot acetone. Some surface active agents [dodecyldimethylphosphine oxide (C12PO), sodium dodecanesulfonate (SC12S), octylammonium octanesulfonate (C8AC8S), heptylammonium dodecanesulfonate (C7AC12S), and butylammonium tetradecanesulfonate (C4AC14S)] were prepared in our laboratory [9, 10]. Decyltrimethylammonium decanesulfonate (C10TAC10S) was prepared by double decomposition of silver decanesulfonate and decyltrimethylammonium bromide in ethanol. Dodecylammonium chloride (C12TACl) was obtained by neutralization of dodecylamine by hydrochloride in ethanol. Decyltrimethylammonium bromide, dodecyltrimethylammonium bromide (C12TABr), and hexadecylpyridinium chloride (C16PCl) were purchased from Tokyo Kasei Kogyo Co. These surfactants were recrystallized five times from acetone-ethanol. Octanol (C8OH) and soft-type sodium dodecylbenzenesulfonate (SC12BS) were commercial products (Tokyo Kasei Kogyo Co.) and were used without further purification.

### Methods

The CD spectra of MEGA-10 were measured with the surface active agent by a JASCO J-720 spectropolarimeter. The measurement was carried out at 30 °C in a constant concentration of MEGA-10, about 0.1 mol/kg. The CD spectra of pure MEGA-10 solutions were also measured at 30 °C at several concentrations below and above the critical micelle concentration (CMC).

## Results and discussion

### General aspects

The absorption spectrum of MEGA-10 consists of one major peak at 220 nm due to the secondary amide group [1]. CD spectra of pure MEGA-10 at different concentrations are shown in Fig. 1. The molecular ellipticity of pure MEGA-10 does not have a peak, and is negative at 210–240 nm below the CMC, which is about 0.005 mol/kg [4]; however, it becomes positive, and its CD spectra has a peak in the vicinity of 225 nm above the CMC; as shown in Fig. 1. The peak of the CD spectra results from the Cotton effect due to the $n$-$\pi^*$ transition of the carbonyl group.

The CD spectra of MEGA-10 with several surface active agents were measured at a constant concentration of MEGA-10. We assumed that MEGA-10 mixed completely with the additives in a micelle. The CD spectra of MEGA-10 with some additives could not be measured at high mole fractions because of turbidity or gelation. The peak of the CD spectra at 225.6 nm does not shift for all of the additives, but the molecular ellipticity of MEGA-10 generally decreases with their addition, as shown in Fig. 2.

The reduction in the molecular ellipticity depends on the type of hydrophilic group and the mole fraction. The initial slope of the molecular ellipticity when plotted against the mole fraction, of which the upper limit is 0.2, is listed with the type of additive in Table 1. With a low mole fraction of additive, it is approximated that the molecular ellipticity changes linearly with the mole fraction. The strength of the interaction between

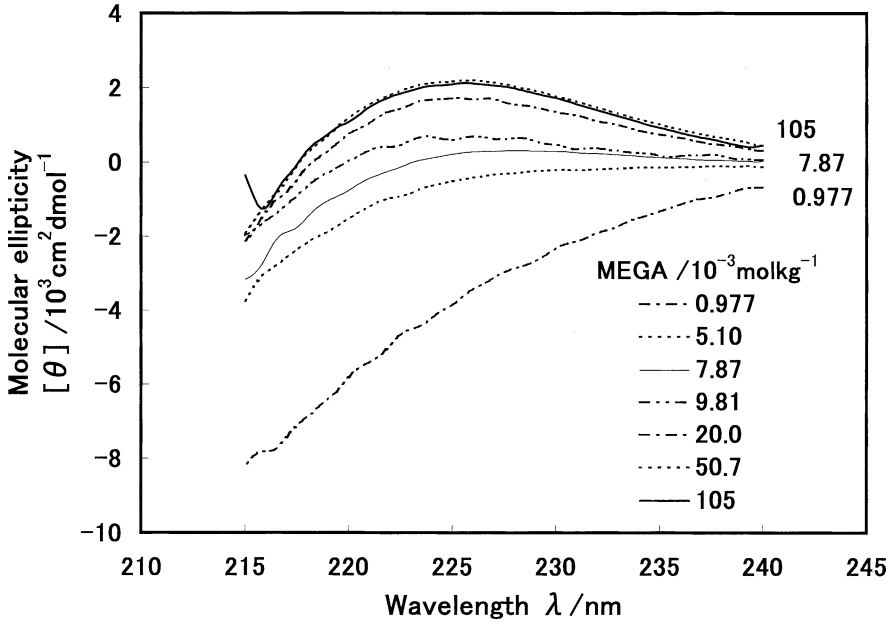


**Fig. 1** CD spectra of different molalities of pure MEGA-10

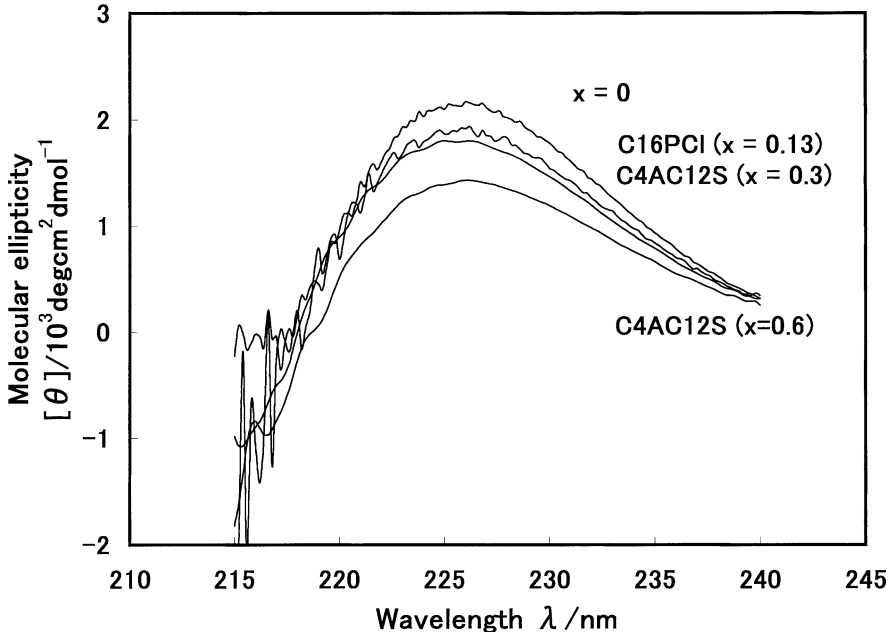


**Fig. 2** Samples of CD spectra of MEGA-10 with some additives; the concentration of MEGA-10 is 0.1 mol/kg, and the symbol $x$ is the mole fraction of the additive

MEGA-10 and the additive is estimated from the reduction in the molecular ellipticity.

## Charge effect of hydrophilic group

The molecular ellipticities of MEGA-10 at 225.6 nm with some of the additives (the cationic surfactant C12TABr, the anionic surfactant SC12S, the catanionic surfactant C10TAC10S, and the nonionic surface active agents C12PO and C8OH) are shown in Fig. 3, to show the charge effects of the hydrophilic groups.

The anionic and cationic surfactants have similar effects on the reduction of the molecular ellipticity, while the molecular ellipticity is not affected by addition of the catanionic and nonionic surface active agents. These facts show that the interaction between the carbonyl group of MEGA-10 and a hydrophilic group on an additive does not depend on the sign of its charge, but rather on the charge density in the micelle.

## Effect of the species of hydrophilic group

The molecular ellipticity of MEGA-10 depends on the type of hydrophilic group on the additive, as shown in Figs. 3 and 4. The additives with ammonium and benzenesulfonate hydrophilic groups exhibit a greater reduction in the molecular ellipticity than SC12S and C12TABr, as shown in Fig. 4 and Table 1. It is thought that the carbonyl group of MEGA-10 interacts with benzene ring $\pi$-electrons. It is also thought that the carbonyl group interacts with ammonium hydrogen, because trimethylammonium salt interacts weakly with MEGA-10.

The hydrated dipole does not interact with the carbonyl group of MEGA-10, because the hydroxyl and dimethylphosphine oxide groups do not affect the molecular ellipticity, as shown in Fig. 3. These are related to the interactions between hydrophilic groups in proteins or on a cell surface.

## Effect of the ammonium group

The molecular ellipticity of MEGA-10 with ammonium compounds decreases as their mole fractions are increased, and this reduction is larger than that with C12TABr, as shown in Fig. 5. The molecular ellipticity hardly changes with the addition of C10TAC10S, but it decreases with addition of C8AC8S, as shown in Table 1

**Table 1** Effect of additives on the molecular ellipticity of MEGA-10, when the upper limit of the mole fraction is 0.2

| Additive | Slope/$10^3$degree cm$^2$ dmol$^{-1}$ | Standard error |
|---|---|---|
| SC12BS | −3.50 | 0.42 |
| C12ACl | −2.37 | 0.15 |
| C8AC8S | −1.82 | 0.08 |
| C4AC14S | −0.92 | 0.10 |
| C7AC12S | −0.71 | 0.18 |
| C16PCl | −0.66 | 0.16 |
| C12TABr | −0.47 | 0.09 |
| SC12S | −0.32 | 0.13 |
| C12PO | 0.01 | 0.03 |
| C10TAC10S | 0.10 | 0.02 |
| C8OH | 0.17 | 0.15 |

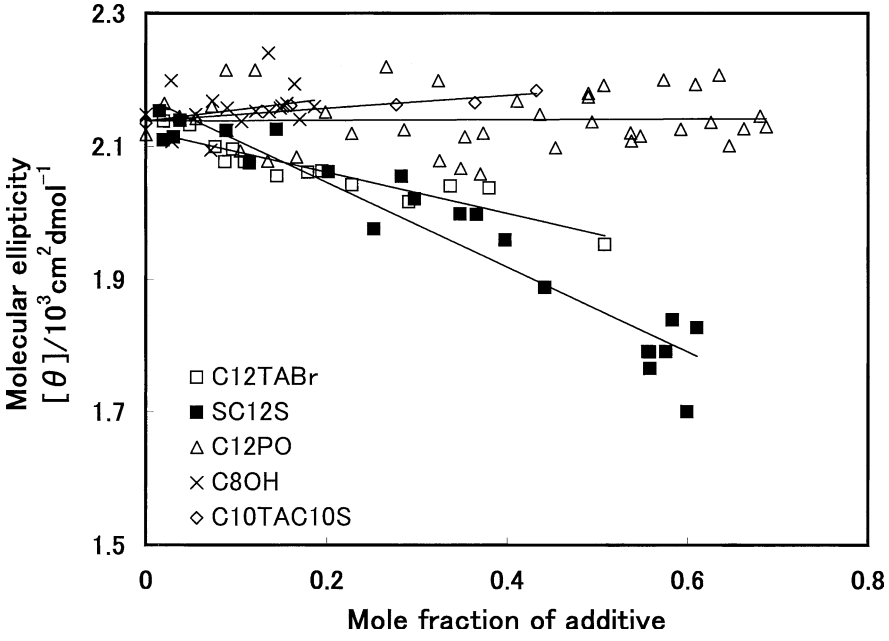


**Fig. 3** Effect of additive charge on the molecular ellipticity of MEGA-10; investigated by adding nonionic, ionic, and catanionic surfactants. The concentration of MEGA-10 is 0.1 mol/kg

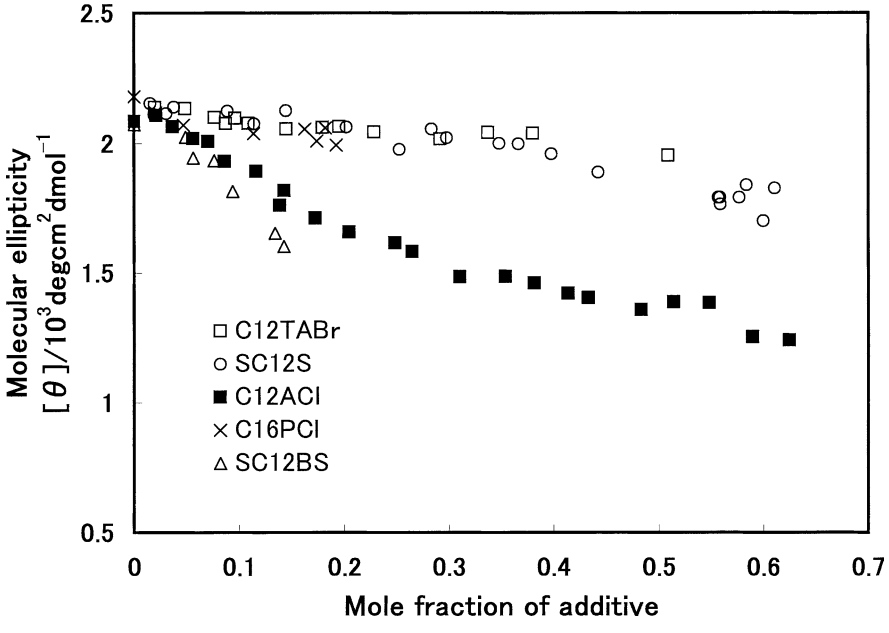


**Fig. 4** Effect of additives on the molecular ellipticity of MEGA-10; plotted by hydrophilic group type. The concentration of MEGA-10 is 0.1 mol/kg

and Fig. 5. The catanionic surfactants C10TAC10S and C8AC8S do not give a charge effect to MEGA-10. The difference between them leads to the view that an ammonium group has a characteristic interaction with MEGA-10 other than the charge effect.

The reduction of the molecular ellipticity with C8AC8S is similar to that with C12ACl. The dependence of the molecular ellipticity on the mole fractions of C4AC14S and C7AC12S is very small for low mole fractions (lower than 0.15), as shown in Fig. 5. Their molecular ellipticities are similar to that with SC12S, which is not expected to undergo any characteristic interaction with MEGA-10 except for the charge effect. Their counterions dissociate completely from micelles in which the charge density is low. This agrees with the view that the counterion of an ionic surfactant dissociates completely from the mixed micelle of nonionic and ionic surfactants when the micellar composition of the ionic surfactant has a mole fraction lower than 0.1 [11, 12].

The molecular ellipticities of MEGA-10 with the three sulfonates show interesting behavior, as shown in Fig. 5, when their mole fractions are high. The reduction

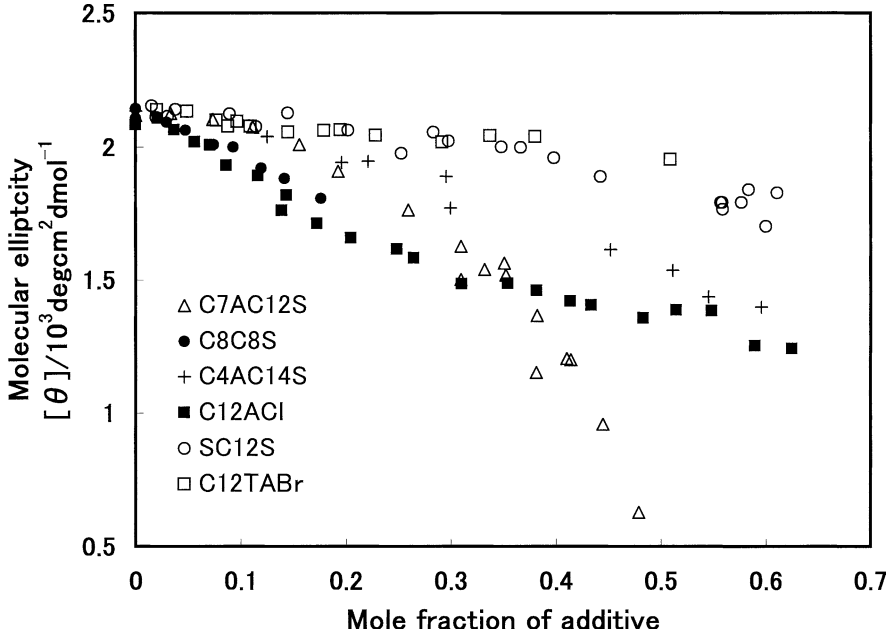


**Fig. 5** Effect of the ammonium group of the additive on the molecular ellipticity of MEGA-10; investigated by adding cationic and catanionic surfactants and counterions. The concentration of MEGA-10 is 0.1 mol/kg

of the molecular ellipticity with C8AC8S is linearly related to its mole fraction, though it is insoluble above a mole fraction of 0.2. The reduction with C4AC12S is smaller than that with C12ACl, and gradually approaches it with an increase in the mole fraction. Butylammonium is hydrophobic and forms a mixed micelle [9, 10]. However, it dissociates from the micelle of low charge density because it has weaker hydrophobicity than octylammonium. The reduction with C7AC12S is similar to that with C4AC12S when the mole fraction is low, but it expands greatly when the mole fraction is higher than 0.3. Then its reduction becomes larger than that with C12ACl. Gelation of the solution of MEGA-10 and C7AC12S take place when the mole fraction is 0.5. It is presumed that the structure of the micelle changes above a mole fraction of 0.3. It is concluded that the ammonium group at the micellar surface interacts strongly with the carbonyl group of MEGA-10.

## Conclusions

In conclusion, the carbonyl group of MEGA-10 does not interact with nonionic surface active agents nor with the catanionic surfactant in which the anion and cation are decanesulfonate and decyltrimethylammonium, respectively. It does, however, interact with ionic surfactants. It also interacts significantly with benzene rings and ammonium groups. These interactions were observed by CD spectra, without the interference of carbon dioxide. CD spectra are a useful tool for research into the interaction between an optically active carbonyl and a hydrophilic group in aqueous solution. Information on the interactions between the optically active carbonyl and ammonium groups will be useful when studying the behavior of counterions and surfactant ions on micellar surfaces.

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