Journal of Inclusion Phenomena and Molecular Recognition in Chemistry **28:** 213–221, 1997.

Surface Tension and ^{1}H NMR Studies on Inclusion Complexes of β-Cyclodextrin with Sodium Alkyl Sulfonate

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(Received: 15 May 1996; in final form: 13 November 1996)

Abstract. The inclusion complexes of β-CD with sodium octyl sulfonate (C_8As), sodium dodecyl sulfonate (C_{12}As), and sodium hexadecyl sulfonate (C_{16}As) in aqueous solutions have been studied by surface tension measurement at the air/water interface and ^{1}H NMR spectroscopy at 323 K.

At fixed concentrations of the surfactants, the surface tensions first increase with the increase of β-CD concentrations, then they attain a maximum. The surface tension curves of the surfactants in the presence of β-CD are higher than those in the absence of β-CD. The values increase with increasing β-CD concentrations for each surfactant. The apparent critical micelle concentrations (CMC) of the surfactants vary linearly with β-CD concentrations.

A ^{1}H NMR study shows that the signals of the inner H-3 and H-5 of β-CD shift upfield upon addition of the surfactants. The magnitude of the chemical shift changes ($\Delta\delta = \delta_{CD} - \delta_{obs}$) varies as a function of the concentrations of the surfactants. From the relationships between the chemical shift changes of H-3 or H-5 inside the β-CD cavity and guest/host molar ratios, a 1 : 1 stoichiometry for each inclusion complex is assumed. The association constants of the inclusion complexes have been determined by ^{1}H NMR spectroscopy.

Key words: β-Cyclodextrin, surfactants, inclusion complexes, NMR, surface tension.

1. Introduction

Cyclodextrins (CDs) are a family of macrocylic oligosaccharides consisting of six, seven, or eight D-(+) glucopyranose units called α-, β-, γ-CDs, respectively. The shape of CDs is like a truncated cone with a hydrophilic exterior and a hydrophobic interior. A significant property of CDs is their ability to include other organic or inorganic compounds into their cavities, both in the solid state and in solutions to form inclusion complexes. The driving force for guest-CD inclusion complex formation has been explained in terms of van der Waals interactions, hydrogen bonding, hydrophobic interactions, and the release of high energy water molecules or of steric strains on complexation [1–3]. A number of studies have reported the complexation of CDs with surfactants. The association constants of such complexes have been investigated mainly by UV-visible spectroscopy and conductivity

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** This work was supported by the Director Foundation of our Institute.

[4–10]. It is difficult, however, to determine the association constants by spectroscopic methods if the systems have no chromophoric groups. The difference in electric conductivity between associated and unassociated surfactant ions is not always very significant, especially when higher-order association is present [11], which limits the utility of the conductometric method in determining association constants for CD-surfactant complexes. Furthermore, the magnitude of association constants reported by different authors using spectroscopic or conductometric methods are still controversial. For example, the association constants for sodium dodecyl sulfate (SDS) with β-CD are reported to be: 300 [12], 356 [6], 1300–7230 [7], 3630 [13], 3200–18 000 [14], and 25 600 [11], respectively. In recent years, ^{1}H NMR and surface tension methods have been developed to study the complexing of CDs with surfactants [6, 15–23]. But there is no report about the complexation of CDs with alkyl sulfonate using these two methods.

C_8As, $C_{12}As$, and $C_{16}As$ are anionic surfactants with relatively high Krafft temperatures (above 313 K). To date, only a few papers have dealt with the interaction of CDs with C_8As and $C_{12}As$ below 313 K using the conductometric method [11, 13, 24, 25].

The purpose of our work is to systematically investigate the formation, guest/host molar ratios, and the association constants of β-CD – CnAs (n = 8, 12, and 16) systems at 323 K (above their Krafft temperatures) by surface tension and ^{1}H NMR measurements. The results demonstrate that adding β-CD decreases the surface activity and increases the CMC value of each surfactant. A ^{1}H NMR study shows that the guest/host molar ratios of each inclusion complex is 1 : 1. The chemical shift changes of H-3 or H-5 between pure β-CD and each inclusion complex (Q) have been determined by multivariate statistical analysis of the NMR data. The association constants of the inclusion complexes inferred from NMR results show that the longer the hydrocarbon chain of the surfactant, the larger is the association constant.

2. Experimental

2.1. Materials

β-CD is a product of our laboratory, and has been recrystallized twice in deionized water and dried at 363 K *in vacuo* for 24 h before being used. CnAs (n = 8, 12, and 16) was purchased from Fluka (purity >99%) and has been used without further purification. D_2O (deuterium content 99.9%) and DSS were purchased from Aldrich. For surface tension measurements, deionized water was used. The surface tension of pure water is 69 mN m^{-1} at 323 K.

2.2. Methods

Surface tension measurements were made using a FACE CBVP-A3 surface tensiometer. The standard deviation of surface tension from the mean values is less

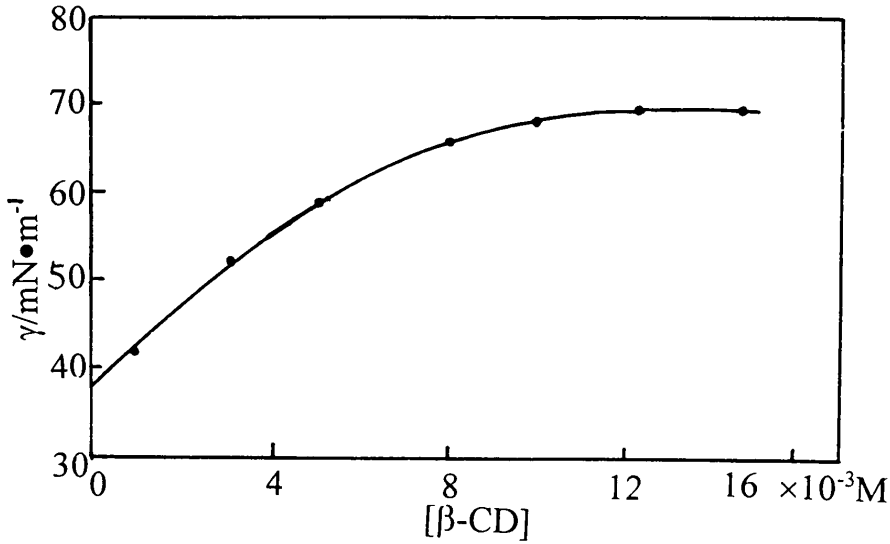

Figure 1. Surface tension variations of $C_{12}As$ with β-CD concentrations (the concentration of $C_{12}As$ is fixed at 6.02×10^{-3} M, 323 K).

than ± 0.2 mN m^{-1}. ^{1}H NMR spectra were recorded with a Bruker AM-400 NMR spectrometer with DSS as external reference. All measurements were carried out at 323 K. The deviation of temperature is less than ± 0.1 °C.

Each of the solutions was prepared by weighing the same amount of surfactant and adding a certain amount of β-CD stock solutions (1.0×10^{-2} M, if inclusion complexes are studied), then diluting with deionized water to the desired volume. This is because the Krafft temperatures of CnAs (n = 8, 12, and 16) are rather high. So it is difficult to prepare uniform stock solutions at higher concentrations at room temperature.

3. Results and Discussion

3.1. Surface tension measurement

Figure 1 shows the variation of surface tension with β-CD concentrations at a fixed concentration of $C_{12}As$. The surface tension values first increase with the increase of β-CD concentrations, and then they reach a maximum. This maximum value is the surface tension of pure water. This indicates that inclusion complexes are formed, the surface activity of the surfactant is decreased with the addition of β-CD, and that the aqueous solutions of β-CD and the inclusion complexes do not have any surface activity. The same results are found for C_8As and $C_{16}As$ upon the addition of β-CD solutions.

The influences of β-CD on varied concentrations of CnAs (n = 8, 12, and 16) have also been studied by surface tension measurements. Figures 2, 3, and 4 display

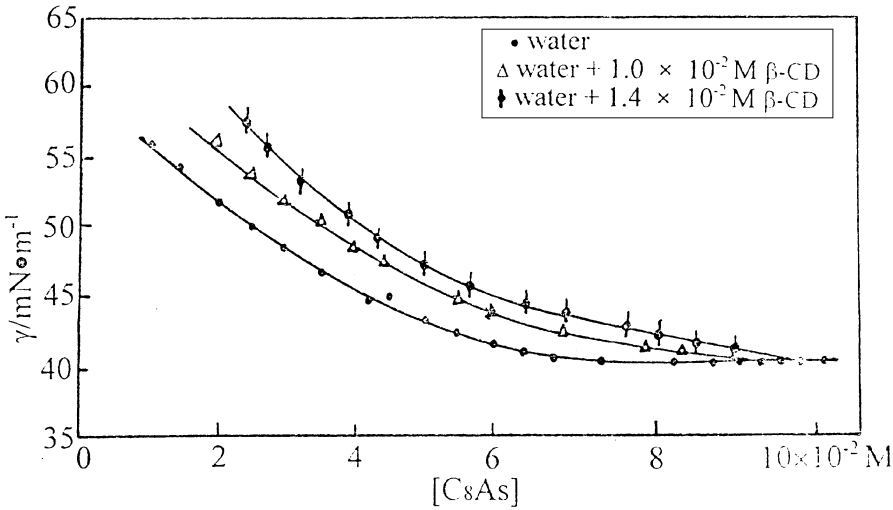

Figure 2. Surface tension results for C_8As in the presence and in the absence of β-CD.

variations of the surface tensions for CnAs (n = 8, 12, and 16) in the presence of β-CD. It can be seen that the surface tension curves of CnAs (n = 8, 12, and 16) in the presence of β-CD are higher than that in the absence of β-CD. The values increase with increasing β-CD concentrations. The apparent critical micelle concentration (CMC) of each surfactant varies linearly with the increase of β-CD concentration (Figure 5). This result demonstrates that the total concentration of the surfactant is divided into two parts: one included in the β-CD cavity, the other existing in the free state. The latter one may form micelles if the concentration of free surfactant is large enough. In the absence of β-CD, the total concentration of the surfactant needed to form micelles (apparent critical micelle concentration, CMC) is CMC_0. If β-CD is added to the solution when the concentration of the surfactant equals CMC_0, micelles cannot form since some surfactant molecules are included in the β-CD cavities. The total concentration of the surfactant (CMC) must be increased to form micelles in the presence of β-CD. The higher the β-CD concentration, the larger is the apparent critical micelle concentration (CMC), so CMCs are directly proportional to β-CD concentrations. The increase of CMC values caused by the presence of β-CD indicates that the formation of β-CD – CnAs (n = 8, 12, and 16) complexes decrease the ability of CnAs (n = 8, 12, and 16) to form micelles. The surface tension values of each surfactant above CMC in the presence of β-CD remain the same as that of the surfactant without β-CD. This also indicates that the complexes have no surface activity.

3.2. ^{1}H NMR MEASUREMENT

The representative ^{1}H NMR spectrum of β-CD in D_2O consists of six kinds of protons [26–28]. The proton resonances of inner H-3 and H-5 of β-CD shift

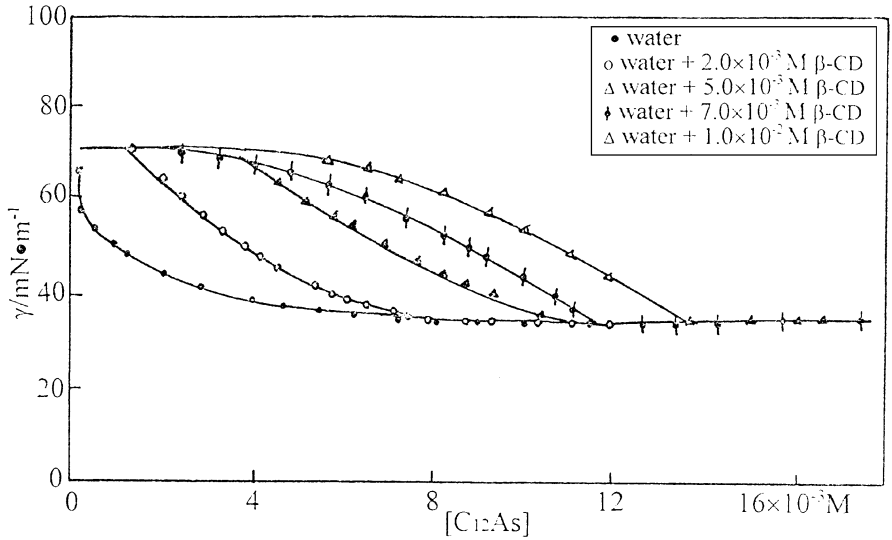

Figure 3. Surface tension results for $C_{12}As$ in the presence and in the absence of β-CD.

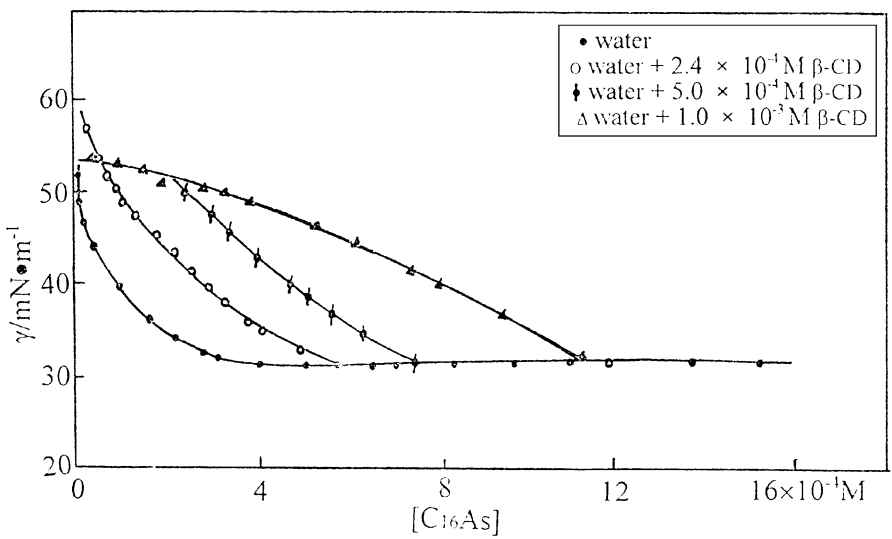

Figure 4. Surface tension results for $C_{16}As$ in the presence and in the absence of β-CD.

upfield upon addition of the surfactants. The magnitude of the chemical shift changes ($\Delta\delta = \delta_{CD} - \delta_{obs}$) depends on the concentrations of the surfactants. These results are shown in Figures 6 and 7. The molar ratio of β-CD to the surfactant at the point of intersection (dashed lines) for each complex is around unity, indicating that the stoichiometry for each inclusion complex is 1 : 1.

The association constants (K_a) are evaluated using the modified Hildebrand–Benesi equation [29, 30]. With this method, the concentrations of β-CD for CnAs

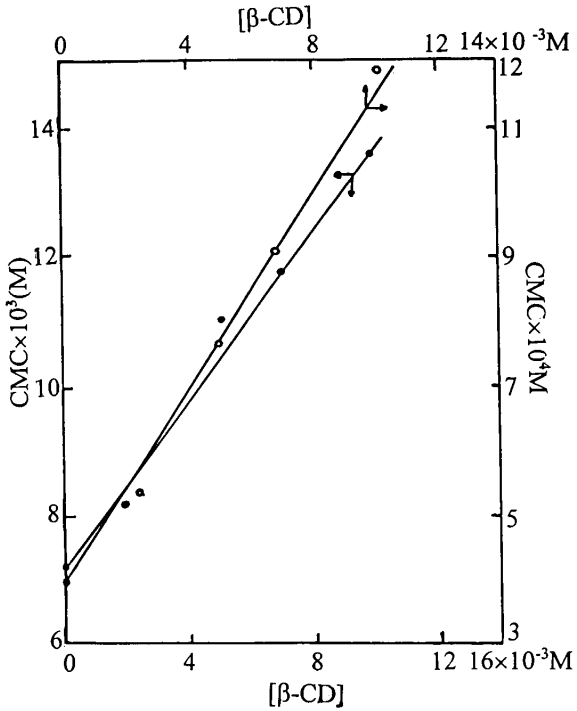

Figure 5. Dependence of apparent critical micelle concentrations (CMC) of $C_{12}As$ and $C_{16}As$ on β-CD concentrations (● $C_{12}As$ + β-CD, ○ $C_{16}As$ + β-CD).

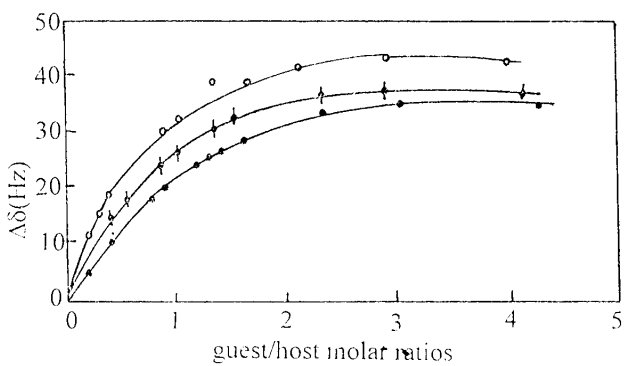

Figure 6. H-3 chemical shift changes of β-CD ($\Delta\delta = \delta_{CD} - \delta_{obs}$) plotted against the guest/host molar ratios with fixed concentrations of β-CD (○ $C_{12}As$ + 5.0 × 10^{-3} M β-CD, ◐ $C_{16}As$ + 1.0 × 10^{-3} M β-CD, ● C_8As + 2.0 × 10^{-3} M β-CD).

(n = 8, 12 and 16) are fixed at 2.0 × 10^{-3} M, 5.0 × 10^{-3} M, and 1.0 × 10^{-3} M, respectively, and the concentrations of the surfactants are varied. The quantitative expression of each complex in the premicellar region is:

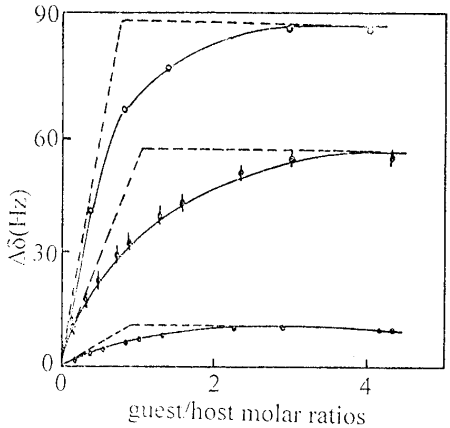

Figure 7. H-5 chemical shift changes of β-CD ($\Delta\delta = \delta_{CD} - \delta_{obs}$) plotted against the guest/host molar ratios with fixed concentrations of β-CD (○ $C_{12}As$ + 5.0×10^{-3} M β-CD, ● C_8As + $2.0 \times 10^{-3} M$ β-CD, ● $C_{16}As$ + 1.0×10^{-3} M β-CD).

CD+S=CDS

$$K_a = [CDS]/[CD][S] \tag{1}$$

$$CD_0 = [CD] + [CDS] \tag{2}$$

$$S_0 = [S]+[CDS] \tag{3}$$

where CD_0 and S_0 are the total concentrations of β-CD and the surfactant. Thus

$$K_a = [CDS]/\{S_0 - [CDS]\}/\{CD_0 - [CDS]\}. \tag{4}$$

In the mixture of CD and surfactant, the observed chemical shift (δ_{obs}) of H-3 or H-5 for β-CD is a weighted average of that for the monomer (δ_{CD}) and that for the complex (δ_{CDS}):

$$\delta_{obs} = \frac{[CD]}{CD_0} \cdot \delta_{CD} + \frac{[CDS]}{CD_0} \cdot \delta_{CDS} \tag{5}$$

$$\delta_{obs} = \frac{CD_0 - [CDS]}{CD_0} \cdot \delta_{CD} + \frac{[CDS]}{CD_0} \cdot \delta_{CDS}. \tag{6}$$

Equation (6) can be transformed to:

$$\delta_{CD} - \delta_{obs} = \frac{[CDS]}{CD_0} \cdot (\delta_{CD} - \delta_{CDS}). \tag{7}$$

Letting $\delta_{CD} - \delta_{obs} = \Delta\delta$, $\delta_{CD} - \delta_{CDS} = Q$, we obtain:

$$\Delta\delta = \frac{[CDS]}{CD_0} \cdot Q \tag{8}$$

Table I. Chemical shift changes of H-3 and H-5 between β-CD and the complexes (Q).

Proton of β-CD / Ka / System	H-3	H-5
C_8As+β-CD	35.00	53.80
$C_{12}As$+β-CD	42.20	85.80
$C_{16}As$+β-CD	36.40	9.70

Table II. Association constants (K_a) of β-CD with CnAs (n = 8, 12, and 16) (323 K).

Proton of β-CD / Ka / System	H-3	H-5
C_8As+β-CD	$(2.52 \pm 0.23) \times 10^3$	$(2.23 \pm 0.23) \times 10^3$
$C_{12}As$+β-CD	$(2.98 \pm 0.55) \times 10^3$	$(4.10 \pm 0.39) \times 10^3$
$C_{16}As$+β-CD	$(9.67 \pm 0.59) \times 10^3$	$(9.81 \pm 0.50) \times 10^3$

$$\frac{1}{K_a} = \frac{S_0 \cdot Q}{\Delta\delta} + \frac{\mathrm{CD}_0 \cdot \Delta\delta}{Q} - (\mathrm{CD}_0 + S_0). \tag{9}$$

Equation (9) is rearranged to:

$$S_0 = \frac{\Delta\delta}{Q} \cdot \mathrm{CD}_0 + \frac{Q}{\Delta\delta} \cdot S_0 - \left(\mathrm{CD}_0 + \frac{1}{K_a}\right). \tag{10}$$

The chemical shift difference of H-3 or H-5 between β-CD and 'pure' β-CD inclusion complex (Q) is determined by regression of S_0 against $\Delta\delta$ and $S_0/\Delta\delta$ (Table I). Association constants (K_a) of β-CD with CnAs (n = 8, 12, and 16) are calculated from Equation (9), and the K_a values are listed in Table II. It can be seen that association constants of β-CD with CnAs (n = 8, 12, and 16) increase with the length of the hydrocarbon chain of the surfactants. This result indicates that the interaction of β-CD with surfactants having long hydrocarbon chains is stronger than that with shorter ones.

4. Conclusion

The aim of this study was to determine the influence of β-CD on the surface tension of CnAs (n = 8, 12, and 16) and to infer association constants of the inclusion complexes. The surface tensions of the surfactants change as a function of β-CD concentrations. The critical micelle concentrations (CMC) of CnAs (n = 8, 12, 16) vary linearly with β-CD concentrations. The chemical shift changes of H-3 and H-5 of β-CD shift upfield upon addition of CnAs (n = 8, 12, and 16). The magnitude of the shifts is a function of the concentrations of the surfactants. Chemical shift changes (Q) of H-3 and H-5 between β-CD and the complexes have been determined by the regression method. Association constants (K_a) for the complexes are also calculated. K_a increases with the length of the hydrophobic chain of the surfactants.

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