Interaction of sodium carboxymethylamylose with aqueous surfactants in both the presence and the absence of added salt: mixed micelles and inclusion complexes

Zhen Zhen and Chen-Ho Tung*
Institute of Photographic Chemistry, Academia Sinica, Beijing 100101, China
(Received 16 October 1990; accepted 2 January 1991)

Fluoresence probe techniques have been employed to monitor interactions of sodium carboxymethylamylose (NaCMA) with cationic and anionic surfactants in aqueous solution in both the absence and the presence of added salt. The changes of the I_1/I_3 ratio of the fluorescence of pyrene in NaCMA solution were measured as a function of hexadecyltrimethylammonium chloride (HTAC) and sodium dodecyl sulphate (SDS) concentration. In the absence of added salt, mixed micelle formation of NaCMA with both HTAC and SDS was observed with an apparent critical micelle concentration (CMC) of 1×10^{-4} and 3×10^{-3} M respectively. These are the first observations of mixed micelle formation between an anionic surfactant and an anionic polyelectrolyte. The average aggregation numbers of the mixed micelles were measured by the analysis of the fluoresence decay curve of the micelle-solubilized pyrene to be smaller than that for the micelles in the absence of NaCMA. In the presence of 2% NaCl the apparent CMC values of the surfactants are greater than those in the absence of NaCMA, suggesting that NaCMA forms inclusion complexes with both HTAC and SDS. The association constant of NaCMA with HTAC is 4.1×10^4 M^{-1}, and the maximum amount of bound HTAC per anhydroglucose residue is 0.014. This result is consistent with the model of interrupted 6-helix conformation of NaCMA.

(Keywords: polyelectrolyte; surfactant; interactions; sodium carboxymethylamylose; salt effect; conformation; inclusion complexes; mixed micelles)

INTRODUCTION

Sodium carboxymethylamylose (NaCMA) is a polymer with many interesting properties and commercial applications. This polymer is a water-soluble derivative obtained by chemical functionalization of amylose. Although the conformation of amylose in solution and its interaction with polar and non-polar compounds have been extensively investigated in connection with the biological significance of the amylose structure[1–6], reports on NaCMA are relatively few[7,8]. Preliminary studies suggest that in aqueous solution the NaCMA polymer chain exists as random coils and behaves like a polyelectrolyte. In aqueous solution of salt, NaCMA can form inclusion complexes with a variety of organic molecules.

There is extensive literature on the interaction of surfactant and polyelectrolyte in aqueous solution[9–11]. Classical studies of bulk solution properties (viscosity, surface tension, conductivity, equilibrium dialysis) indicate that ionic surfactants commonly bind to polyelectrolytes with opposite charge at surfactant concentrations below their normal critical micelle concentration (CMC)[12,13]. The binding process has been reported to be highly cooperative. Electrostatic interactions alone were insufficient to understand the results. Hydrophobic interactions between bound surfactants and polymer were also important in the determination of solution properties. Newer techniques, such as luminescence probe studies, provided information about the microenvironment of the surfactant–polyelectrolyte complexes[14–18]. There are also many studies dealing with the interaction of surfactant with water-soluble non-ionic polymers such as poly(ethylene oxide) (PEO), poly(*N*-vinylpyrrolidone) (PVP) and hydroxypropylcellulose (HPC)[19–25]. For example, in the sodium dodecyl sulphate–poly(ethylene oxide) (SDS–PEO) system, there is no interaction between SDS and PEO for SDS concentrations below a certain value (termed C_1). Above C_1 (which is a lower concentration than the CMC of SDS) the PEO–SDS association process starts abruptly and then saturates abruptly at a concentration C_2 (which is a higher concentration than the CMC of SDS). The micelles formed in the range between C_1 and C_2 are smaller than in the absence of polymer[24]. Many factors affect the interaction of surfactants with non-ionic polymers. Cationic detergents tend to experience weaker interactions than anionic detergents[23]. The size of the head-group appears to be very important[19]. For example, no interaction has been observed between hexadecyltrimethylammonium chloride (HTAC) and PEO or PVP, both of which form mixed micelles with SDS[21]. Polymer hydrophobicity is also important. Methylcellulose interacts with SDS below the normal SDS CMC, while hydroxyethylcellulose does not form mixed micelles with SDS[26]. Fluorescence probe studies, however, suggest that HPC interacts with both SDS and HTAC[25].

* To whom correspondence should be addressed

0032-3861/92/040812-05

A number of investigations have suggested that in aqueous solution of salt the NaCMA polymer chain behaves like amylose, and can form an inclusion complex with many compounds ranging from fairly large aromatic molecules such as phenyl alkyl ketones and viologen dications to various functionalized molecules bearing linear hydrocarbon chains[7,8,27,28]. The driving force for inclusion complex formation is hydrophobic interactions. The inclusion process is accompanied by conformational changes of the NaCMA polymer chain from random coils to interrupted helices. An interesting feature of the helical cavities is that the size can be adjusted according to the substrate. Thus, a 6-unit/turn helix with an internal cross-sectional area of 16 $Å^2$ is indicated as the most stable structure and the host for aliphatic hydrocarbons and benzene derivatives. A '7-helix' having 38 $Å^2$ as the cross-sectional area can accommodate naphthalene derivatives[29,30].

In the present study we examine the interaction of NaCMA with SDS and HTAC. We carry out fluorescence probe experiments with pyrene at very low concentrations ($\sim 10^{-7}$ M) in the presence of surfactant and polymer. We examine the influence of environment on the vibrational fine structure of the pyrene fluorescence and use this information to determine the apparent *CMC* of the micelles[21,24,25]. We will demonstrate that in the absence of added salt NaCMA indeed behaves like other polyelectrolytes and interacts strongly with both HTAC and SDS to form mixed micelles, i.e. micelles that bind to the polymer. The mixed micelles have smaller aggregation numbers (number of surfactant molecules per micelle) than those of the surfactant micelle itself. On the other hand, in the presence of added salt, NaCMA forms inclusion complexes with HTAC and SDS.

EXPERIMENTAL

Materials

SDS was obtained from Aldrich and was recrystallized twice from methanol–ether. HTAC was purchased from Eastman Kodak Co. and was used without further purification. Water was distilled twice. Pyrene was sublimed under vacuum. NaCMA was kindly supplied by Professor G. Z. Ji, Shanghai Institute of Organic Chemistry, Academia Sinica. The average molecular weight as measured by the viscosity method was 5.2×10^4, and the degree of polymerization (*DP*) was 320. The degree of substitution (the number of carboxymethyl groups per glucose unit) was 0.41. Iodine was sublimed before use.

Samples for spectroscopic analysis

A solution of NaCMA and/or surfactant was prepared in pyrene-saturated water, previously filtered to remove pyrene microcrystals. The pyrene concentration was $\sim 3 \times 10^{-7}$ M. The solutions were allowed to stand typically for 24 h before they were used. Samples for steady-state fluorescence measurements were not degassed. Control experiments on samples degassed by passing nitrogen through the solutions indicated negligible differences in fluorescence intensities[25].

Methods

Steady-state fluorescence spectra were run on a Hitachi EM-850 fluorescence spectrometer and are fully corrected. The ratio I_1/I_3 of the intensities of the first and third vibrational peaks of the fluorescence spectrum of micelle-solubilized monomeric pyrene was measured as peak heights. Fluorescence decay measurements were made with a Horiba NAES-1100 time-correlated single-photon-counting instrument, and prior to the measurements the solutions were bubbled with nitrogen for about 20 min for deoxygenation. The micelle aggregation number N was obtained from the analysis of the fluorescence decay curve of the micelle-solubilized pyrene in the condition where the [pyrene]/[micelle] concentration ratio is around unity[31].

RESULTS

Fluorescence spectra in the absence of added salt

The variation of I_1/I_3 in the pyrene fluorescence spectra was measured for aqueous solutions containing fixed concentrations of NaCMA and variable concentrations of HTAC. The results are shown in *Figure 1*. It is well documented that changes in I_1/I_3 reflect micelle formation, in both the absence and the presence of polymer[21–25]. In the absence of NaCMA, HTAC forms well defined micelles above the *CMC* of $\sim 1.4 \times 10^{-3}$ M, and the ratio I_1/I_3 is ~ 1.34, which is very close to the literature value (1.4)[32]. When HTAC is added to a 0.4% (in g/100 ml of solution) solution of NaCMA, interaction of pyrene with HTAC is first observed at $\sim 5 \times 10^{-6}$ M, and saturation is achieved at $\sim 1 \times 10^{-4}$ M. A plateau region is clearly shown in the range from 1×10^{-4} M to 3.5×10^{-3} M. Above 3.5×10^{-3} M, the solution becomes turbid, which prevents determination of I_1/I_3. The ratio I_1/I_3 is ~ 1.32 in the plateau region, which is close to the value above *CMC* in the absence of NaCMA.

Figure 2 shows the plot of I_1/I_3 as a function of SDS concentration at fixed NaCMA concentration. The *CMC* of SDS itself occurs[32] at 8×10^{-3} M. In the presence of 1.6% NaCMA, the interaction of pyrene with SDS seems more sharply defined, with an apparent *CMC* of $\sim 3 \times 10^{-3}$ M. Above this concentration, the value of

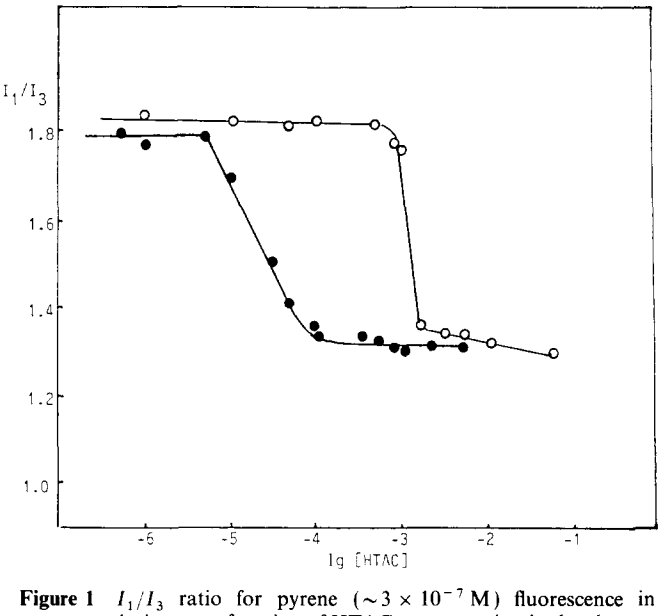

Figure 1 I_1/I_3 ratio for pyrene ($\sim 3 \times 10^{-7}$ M) fluorescence in aqueous solutions as a function of HTAC concentration in the absence of added salt: (○) in the absence of NaCMA; (●) in the presence of 0.4% NaCMA

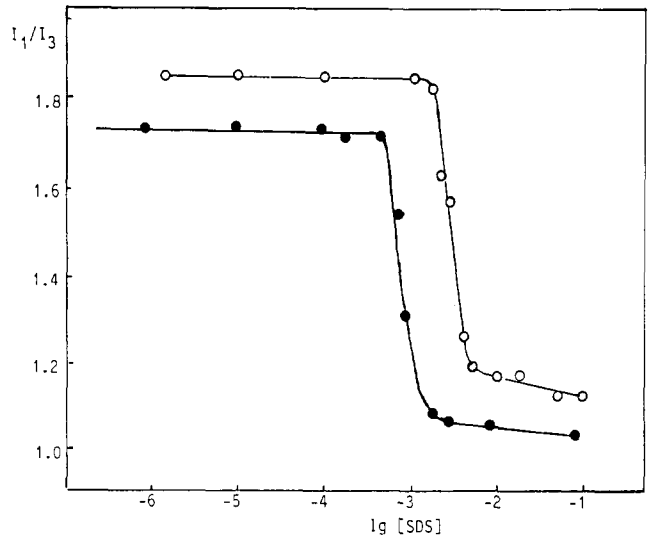

Figure 2 I_1/I_3 ratio for pyrene ($\sim 3 \times 10^{-7}$ M) fluorescence in aqueous solutions as a function of SDS concentration in the absence of added salt: (○) in the absence of NaCMA; (●) in the presence of 1.6% NaCMA

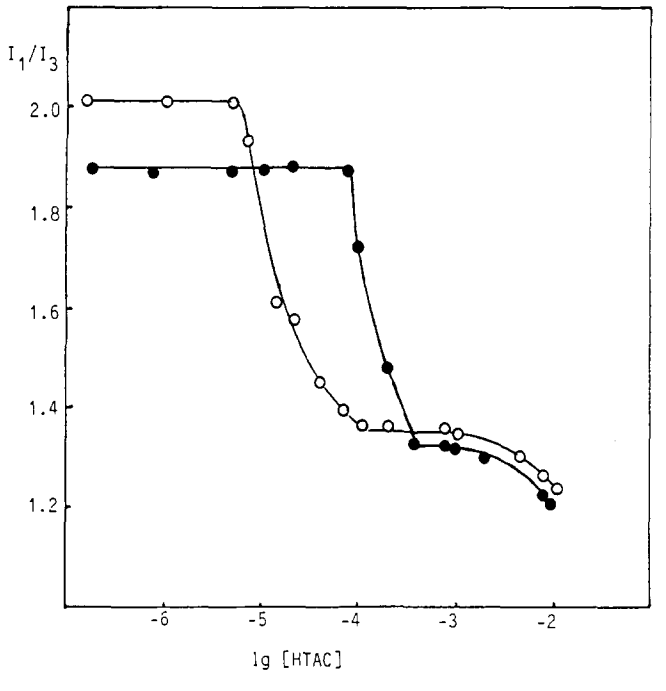

Figure 3 I_1/I_3 ratio for pyrene ($\sim 3 \times 10^{-7}$ M) fluorescence in aqueous solutions as a function of HTAC concentration in the presence of 2% NaCl: (○) in the absence of NaCMA; (●) in the presence of 0.4% NaCMA

I_1/I_3 ($\sim$0.9–1.02) is evidently smaller than that for the SDS micelle ($\sim$1.20).

Even in the range where no interaction between pyrene and surfactant occurs, the ratio I_1/I_3 in the presence of NaCMA ($\sim$1.78) is evidently different from that in the absence of NaCMA ($\sim$1.87)[33].

Fluorescence spectra in the presence of added salt

Figure 3 shows the plot of I_1/I_3 as a function of HTAC concentration in the presence of 0.4% NaCMA and 2% NaCl. Three significant features in the profiles are evident. First, addition of salt to surfactant aqueous solution results in the decrease in *CMC*. In the presence of 2% NaCl, the *CMC* of HTAC is $\sim 5 \times 10^{-5}$ M, which is about 30 times smaller than that in the absence of salt. Secondly, the *CMC* of NaCMA–HTAC mixed micelle ($\sim 3 \times 10^{-4}$ M) is greater than that of HTAC itself. This is contrary to the case in the absence of salt where NaCMA causes the decrease in *CMC*. Finally, above 2×10^{-3} M, the ratio of I_1/I_3 decreases slightly with increase in HTAC concentration. Again, in the low HTAC concentration range, I_1/I_3 values in the presence of NaCMA are smaller than that in the absence of NaCMA.

The plot of I_1/I_3 as a function of SDS concentration in the presence of 1.6% NaCMA and 2% NaCl is given in *Figure 4*. The results are similar to those for the NaCMA–HTAC system. The *CMC* of NaCMA–SDS mixed micelle and SDS itself are $\sim 2.5 \times 10^{-4}$ and $\sim 1.2 \times 10^{-4}$ M respectively.

Aggregation number of NaCMA–surfactant mixed micelle

The aggregation numbers N for the NaCMA–HTAC mixed micelles with the NaCMA concentration of 0.4% and various HTAC concentrations were determined in both the presence and the absence of added salt by using time-resolved fluorescence analysis of micelle-solubilized pyrene[31,34]. In the absence of added salt, the NaCMA–HTAC mixed micelles have smaller size than the micelle of HTAC itself. The N value of the HTAC micelle at HTAC concentration of 2×10^{-2} M is $\sim$120, which is in agreement with the literature value[32]. The N value of the NaCMA–HTAC mixed micelle at HTAC concentration of 1×10^{-3} M is $\sim$61. In the presence of 2% NaCl, NaCMA does not affect the aggregation number. The N value of the HTAC micelle at HTAC concentration of 3×10^{-3} M is $\sim$147. Addition of 0.4% NaCMA results in no change of N value ($\sim$152) within the experimental error.

For the NaCMA–SDS systems in the absence of added salt, the N value of the SDS micelle at SDS concentration of 2.5×10^{-2} M is $\sim$67[32]. The NaCMA–SDS mixed micelles at SDS concentration of 5×10^{-3} M and 1.6%

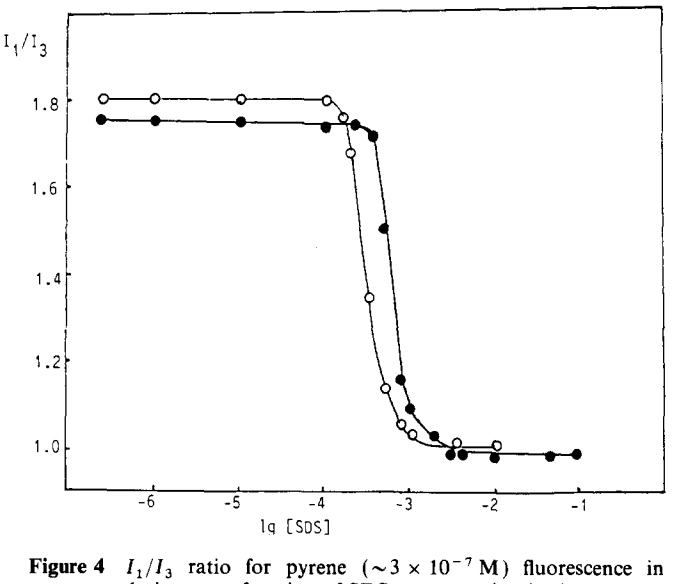

Figure 4 I_1/I_3 ratio for pyrene ($\sim 3 \times 10^{-7}$ M) fluorescence in aqueous solutions as a function of SDS concentration in the presence of 2% NaCl: (○) in the absence of NaCMA; (●) in the presence of 1.6% NaCMA

NaCMA have smaller size (~47). In aqueous solution of 2% NaCl, the aggregation numbers of micelles in the absence and presence of NaCMA are ~413 and ~260 respectively.

DISCUSSION

In the absence of added salt

The data in *Figure 1* indicate that there is no significant NaCMA–HTAC interaction at [HTAC] below 5×10^{-6} M. However, the ratio I_1/I_3 (1.78) is evidently smaller than that in the absence of NaCMA (1.87). It has been established that the pyrene probe provides information on the effective polarity of the molecular environment surrounding the probe[33]. The small change in the ratio I_1/I_3 (1.78 vs. 1.87) suggests that the pyrene molecules loosely associate with the polymer, and the polarity surrounding the polymer is a little smaller relative to water. At HTAC concentration above 1×10^{-4} M clusters of HTAC molecules (termed pre-micelles) cooperatively associate with the polymers to form mixed micelles. The driving force for the association is obviously the electrostatic interactions between the anionic polyelectrolyte and the cationic surfactant. Furthermore, hydrophobic interactions between NaCMA and HTAC and between the bound HTAC molecules may play an important role in the formation of the mixed micelles. The aggregation number of the mixed micelles is 50% smaller (61) than that for HTAC micelles in the absence of NaCMA (120). This observation is analogous to the mixed micelles of SDS and PEO[24]. In general, the pyrene probe bound to smaller micelles should experience a more hydrophilic environment, since for smaller micelles water penetration is expected to be greater. However, the ratio I_1/I_3 for the NaCMA–HTAC mixed micelles (1.32) is slightly smaller than that for the HTAC micelles (1.34). This result suggests that HTAC molecules tightly aggregate along the polymer strand, thus protecting the micelle from water penetration.

For the NaCMA–SDS system the interaction between the surfactant and the polymer does not seem as strong as that for NaCMA–HTAC. At NaCMA concentration of 1.6% the apparent *CMC* of NaCMA–SDS mixed micelle is only 2.7 times smaller than the *CMC* of SDS itself, while at NaCMA concentration of 0.4% the *CMC* of NaCMA–HTAC is 14 times smaller than the *CMC* of HTAC. This result may be attributed to the difference in the driving force for the polymer and the surfactant association. The driving force for NaCMA–SDS association is the hydrophobic interaction, while that for NaCMA–HTAC is the combination of the electrostatic interaction and the hydrophobic interaction. The NaCMA–SDS mixed micelles have smaller size (47) than that of the micelles of SDS itself (67). The pyrene probe in the mixed micelles experiences a less polar environment than that in SDS micelles. This, again, suggests that association of SDS with NaCMA protects the micelle from water penetration.

In the presence of added salt

Addition of 2% NaCl to the aqueous solution of HTAC results in a decrease in the *CMC* from 1.4×10^{-3} M in the absence of NaCl to 5×10^{-5} M, and an increase in aggregation number from 120 to 147. The profile of the I_1/I_3 vs. [HTAC] in the presence of 0.4% NaCMA shifts to higher surfactant concentration (*Figure 3*) compared to that in the absence of NaCMA. The apparent *CMC* in the presence of 0.4% NaCMA is 3×10^{-4} M. It has been established that in the presence of salt with higher concentration NaCMA behaves like a non-ionic polymer and can form inclusion complexes with various long-chain substrates[7,8,27,28]. We believe that the shift of the profile in the presence of NaCMA in *Figure 3* originates from the formation of the inclusion complex of NaCMA with HTAC. Since the HTAC molecules included in the NaCMA helices do not contribute to the formation of micelles, additional HTAC molecules are required for micelle formation. To confirm the formation of the inclusion complex, we have examined the effect of the surfactant on the inclusion complex between NaCMA and iodine. In 2% NaCl aqueous solution NaCMA forms a blue-coloured complex with iodine[35,36]. This complex evidently consists of linear I_x^- ($x = 3$ or 5) incorporated into helical cavities formed by the NaCMA molecule[28,35]. The complex has a sharp absorption with $\lambda_{max} = 600$ nm, and is stable over time. The colour was bleached by the addition of HTAC owing to the replacement of polyiodide ions by an HTAC chain. The helical cavity of NaCMA can be a 6-helix or 7-helix, which have the approximate internal diameters of 4.5 and 7.0 Å respectively[29,30]. The 6-helix is the most stable form and can incorporate long-chain substrates like HTAC. The aggregation number (147 vs. 152) and I_1/I_3 value at [HTAC] greater than 3×10^{-4} M are almost identical with that for the HTAC micelle, indicating that the inclusion complexes do not interact with HTAC micelles.

Since the HTAC bound to NaCMA cannot contribute to the formation of micelles (thus to I_1/I_3), the concentration of the included HTAC is equal to the difference in the HTAC concentration required to give the same I_1/I_3 on the two curves in *Figure 3*. The binding equilibrium of the NaCMA–HTAC system is written as:

$$A + HTAC_f = HTAC_b \quad (1)$$

where A represents the binding site of NaCMA. $HTAC_f$ and $HTAC_b$ are the free and bound HTAC, respectively. The Scatchard equation for the above reaction is given by:

$$r/C_f = K(n - r) \quad (2)$$

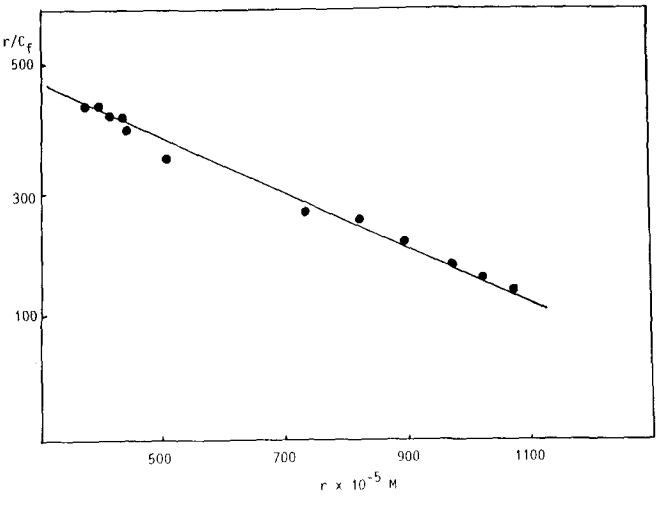

Figure 5 Linear relationship between r/C_f and r for the NaCMA–HTAC system in the presence of 2% NaCl. Correlation coefficient $r = 0.98$

where r is the ratio of bound HTAC to total NaCMA concentration in anhydroglucose residue units, n is the maximum amount of bound HTAC per anhydroglucose residue, C_f is the concentration of free HTAC, and K is the apparent equilibrium constant. The plot of r/C_f vs. r is shown in *Figure 5*. The values of K and n were evaluated from the intercept and the slope of the straight line. The K value is $\sim 4.1 \times 10^4\ M^{-1}$, and the n value is ~ 0.014. These are in reasonable agreement with the literature data measured by the surface tension method[7]. The n value of 0.014 suggests that to complex one HTAC molecule requires about 71 anhydroglucose residues, which corresponds to an average helical length of 92 Å if the helical structure is with six residues per turn[37]. The Corey–Pauling–Koltun (CPK) molecule model suggests that the fully extended length of HTAC is about 25 Å (including the counterion). Obviously the observed behaviour would not be consistent with a model of end-to-end packing of extended HTAC molecules in the cavity of a six-fold helix. An extensive body of evidence supports the proposal that the structure of NaCMA in aqueous solution in the presence of salt is composed of the six-fold helix regions with intervals of random coils between them[7,8,27,28]. Based on the length of the HTAC molecule (25 Å) and the NaCMA helical length available to each HTAC molecule (92 Å), one can obtain that only about 27% anhydroglucose residues in the NaCMA molecule are in helix regions and the others are in random-coil conformation.

Similar results were observed for the NaCMA–SDS system. However, the interaction is not as strong as that for NaCMA–HTAC. In the presence of 1.6% NaCMA, the *CMC* of the mixed micelle is only twice as great as that of SDS itself. The experiments with iodine also demonstrated that NaCMA forms an inclusion complex with SDS in the presence of NaCl. The aggregation numbers of the micelles in both the absence and presence of NaCMA are greater than 250. It should be mentioned that, for an N value greater than 200, the fluorescence probe method involving pyrene excimer formation and time-resolved fluorescence analysis of micelle-solubilized pyrene cannot be used as an accurate and reliable method for determining micelle aggregation number[38].

SUMMARY

In the absence of added salt both HTAC and SDS form mixed micelles with NaCMA. The apparent *CMC* values for NaCMA–HTAC and NaCMA–SDS systems are 14 and 2.7 times smaller, respectively, than those in the absence of NaCMA. The mixed micelles are smaller in size than those formed by the surfactants themselves. The aggregation numbers of the HTAC–NaCMA and SDS–NaCMA mixed micelles are 50% and 70% of those in the absence of NaCMA, respectively. In the presence of 2% NaCl, NaCMA forms inclusion complexes with both HTAC and SDS. The association constant (K) with HTAC is $4.1 \times 10^4\ M^{-1}$, and each NaCMA molecule includes about 3.5 HTAC molecules. The inclusion complex is most likely in an interrupted helical conformation and does not interact with the surfactant micelles.

ACKNOWLEDGEMENT

We thank the National Science Foundation of China for support of this work.

REFERENCES

1 Nishimura, N. and Janado, M. *J. Biochem.* 1975, **97**, 421
2 Nakatani, H., Shibata, K.-I., Kondo, H. and Hiromi, K. *Biopolymers* 1977, **16**, 3263
3 Hui, Y.-Z., Cheng, X.-N., Gu, J.-H. and Jiang, X.-K. *Sci. Sinica (Engl. Edn.), Ser. (B)* 1982, **25**, 698
4 Yamamoto, M., Sano, T. and Yasunaga, T. *Bull. Chem. Soc. Japan* 1982, **55**, 1886
5 Hui, Y., Russell, J. C. and Whitten, D. G. *J. Am. Chem. Soc.* 1983, **105**, 1374
6 Bulpin, P. V., Cutler, A. N. and Lips, A. *Macromolecules* 1987, **20**, 44
7 Hui, Y.-Z. and Gu, J.-H. *Acta Chim. Sinica* 1981, **39**, 309
8 Hui, Y.-Z., Gu, J.-H. and Jiang, X.-K. *Acta Chim. Sinica* 1981, **39**, 376
9 Lewis, R. E. and Robinson, C. P. *J. Colloid Interface Sci.* 1970, **32**, 539
10 Hayakawa, K. and Kwak, J. C. T. *J. Phys. Chem.* 1982, **86**, 3866
11 Hayakawa, K., Santerre, J. P. and Kwak, J. C. T. *Macromolecules* 1983, **16**, 1642
12 Goddard, E. D. *Colloids Surf.* 1986, **19**, 301
13 Leung, P. S. and Goddard, E. D. *Colloids Surf.* 1985, **13**, 47
14 Chandar, P., Somasundaran, P. and Turro, N. J. *Macromolecules* 1988, **21**, 950
15 Chu, D. Y. and Thomas, J. K. *J. Am. Chem. Soc.* 1986, **108**, 6270
16 Chu, D. Y. and Thomas, J. K. *Macromolecules* 1987, **20**, 2133
17 Abuin, E. B. and Sciano, J. C. *J. Am. Chem. Soc.* 1984, **106**, 6274
18 Ananthapadmanabhan, K. P., Leung, P. S. and Goddard, E. D. *Colloids Surf.* 1985, **13**, 63
19 Nagarajan, R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1981, **22**, 33
20 Turro, N. J. and Arora, K. S. *Polymer* 1986, **27**, 783
21 Turro, N. J., Baretz, B. H. and Kuo, P.-L. *Macromolecules* 1984, **17**, 1321
22 Turro, N. J. and Kuo, P.-L. *Langmuir* 1985, **1**, 352
23 Zana, R., Lang, J. and Lianos, P. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1982, **23**, 39
24 Zana, R., Lianos, P. and Lang, J. *J. Phys. Chem.* 1985, **89**, 41
25 Winnik, F. M., Winnik, M. A. and Tazuke, S. *J. Phys. Chem.* 1987, **91**, 594
26 Goddard, E. D. and Hannan, R. B. in 'Micellellization, Solubilization and Microemulsion' (Ed. K. L. Mittal), Plenum New York, 1977, Vol. 2
27 Hui, Y., Winkle, J. R. and Whitten, D. G. *J. Phys. Chem.* 1983, **87**, 23
28 Suddaby, B. R., Dominey, R. N., Hui, Y. and Whitten, D. G. *Can. J. Chem.* 1985, **63**, 1315
29 Sundarajan, P. R. and Rao, V. S. R. *Biopolymer* 1969, **8**, 313
30 Bender, M. L. and Komiyama, M. in 'Cyclodextrin Chemistry', Springer Verlag, Berlin, 1978
31 Atik, S., Nam, M. and Singer, L. *Chem. Phys. Lett.* 1979, **67**, 75
32 Lianos, P., Viriot, M. and Zana, R. *J. Phys. Chem.* 1984, **88**, 1098
33 Kalyanasundaram, K. and Thomas, J. K. *J. Am. Chem. Soc.* 1977, **99**, 2039
34 Tachiya, M. *Chem. Phys. Lett.* 1975, **33**, 289; *J. Chem. Phys.* 1982, **76**, 340
35 Teitelbaum, R. C., Ruby, S. L. and Marks, T. J. *J. Am. Chem. Soc.* 1978, **100**, 3215
36 Reddy, J. M., Knox, K. and Robbin, M. B. *J. Chem. Phys.* 1964, **40**, 1082
37 Jane, J. L. and Robyt, J. F. *Carbohydr. Res.* 1984, **132**, 105
38 Lianos, P. and Zana, R. *J. Phys. Chem.* 1980, **84**, 3339