Study the effect of α,β,γ-cyclodextrins on the critical micelles concentration (c.m.c.) of sodium dodecyl sulphate (SDS) by using...

Article *in* Colloids and Surfaces A Physicochemical and Engineering Aspects · September 2009

CITATIONS
0

READS
12

1 author:

Alsayed A M Elsherbini
Cairo University
59 PUBLICATIONS **411** CITATIONS

SEE PROFILE

Colloids and Surfaces A: Physicochem. Eng. Aspects 352 (2009) 1–4

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Study the effect of α,β,γ-cyclodextrins on the critical micelles concentration (c.m.c.) of sodium dodecyl sulphate (SDS) by using 1-methyl-4-[4′-aminostyryl]pyridinium iodide

El-Sayed A.M. Al-Sherbini*

Department of Measurements and Environmental Applications, National Institute of Laser Enhanced Science (NILES), Cairo University, P.O. Box 12613, Cairo 202, Egypt

ARTICLE INFO

Article history:
Received 19 July 2009
Accepted 6 September 2009
Available online 11 September 2009

Keywords:
Critical micelles concentration (c.m.c.)
Cyclodextrin (CD)

ABSTRACT

The study of the effect of α,β,γ-cyclodextrins on the critical micelles concentration (c.m.c.) of sodium dodecyl sulphate (SDS) has been carried out by UV–vis spectroscopic measurements. The results reveal that, the complex formation between α,β,γ-cyclodextrins and SDS micelles shifts c.m.c. to higher values depending on the cavity size. It was 1.24×10^{-2}, 1.4×10^{-2}, and 1.61×10^{-2} mol dm^{-3} for α,β,γ-cyclodextrins, respectively.

1. Introduction

Amphiphilic molecules such as surfactants can self-associate to a variety of structured assemblies in aqueous solutions. One of these assemblies is known as micelles [1–3], where the hydrophobic part of the aggregates forms the miceller core and the polar head groups which are located at the micellar surface. In aqueous solutions the point at which the micelles start to aggregate is known as critical micelle concentration (c.m.c.). The shape of the micelles depends upon the surfactant concentration. At low concentrations the micelles were spherical with small diameters (15–30 Å) [4,5] containing about 40–100 monomers whereas, they have rod-like shapes at higher concentrations. Most results of microscopic polarities of micelles were obtained from the absorption and fluorescence spectroscopy. Some suggestions indicated that lots of water molecules penetrate into the spherical ionic molecules leading the interior of the micelles to be relatively polar [6].

Several alternatives are available including changing the cell size by using a microcell, changing of geometry and changing the affinity of organic compounds. One of these alternatives is a cyclic oligosaccharide produced from starch by enzymatic degradation and named cyclodextrins. These cyclic products consisting of six, seven or eight glucose units known as α,β,γ-cyclodextrins together with small amount of higher analogous of cyclodextrins [7–9]. Numerous investigations were carried out illustrating that cyclodextrins (CDs) form inclusion complexes with a variety of hydrophobic and amphiphilic species. Physicochemical properties of organic molecules included in the cavity of cyclodextrin provide a hydrophobic environment for guest molecules while remaining in aqueous solution. Moreover, complicated behavior of formation of the inclusion complex has been observed [10] especially when the solubility of hydrophobic molecules in cyclodextrin solution is poor compared with other systems such as aqueous micelles. These factors are considered to be serious disadvantage of cyclodextrin systems. Another approach to improve this system is by adding a third component to the host–guest systems which gave more hydrophobic environment [8,11–13]. It is expected that the third molecule, which contains a hydrophobic moiety, can interact with cyclodextrin to increase the hydrophobicity of the cyclodextrin by excluding water molecules from the cavity. This may lead to the different organizations of the host–guest systems.

In the present study, the aggregation of the surfactant molecules have been investigated spectrophotometrically in a variety of aqueous solutions of α,β,γ-cyclodextrins by using 1-methyl-4-[4′-aminostyryl] pyridinium iodide (M=$^{+}NH_2$)I^{-} (Fig. 1).

2. Experimental methods

2.1. Materials

SDS (Fluka) was used after purification according to the literature procedure [14]. An aqueous stock solution of 10^{-2} dm^{-3} SDS was freshly prepared. α,β,γ-Cyclodextrins (Fluka, >99%) were used without further purification. Double distilled water was used for all the measurements.

* Tel.: +20 2 5729499; fax: +20 2 5729499.
E-mail address: elsayed_s2000@yahoo.com.

0927-7757/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.colsurfa.2009.09.018

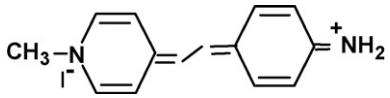

Fig. 1. 1-methyl-4-[4′-aminostyryl] pyridiniumiodide, $(M{=}^{+}NH_2)I^{-}$.

2.2. Synthesis of 1-methyl-4-[4′-aminostyryl] pyridinium iodide $(M{=}^{+}NH_2)I^{-}$

p-Amino benzaldehyde 1.21 gm (10 mmol) dissolved in a minimum amount of absolute ethanol was added dropwise to 2.35 g (10 mmol) of 1-methyl picolinium iodide dissolved in 25 ml of absolute ethanol. 1.5 ml of piperidine was added and the mixture was stirred for 20 h at room temperature and then refluxed for half an hour. The obtained light brown precipitate was filtered and recrystallized twice in distilled water. The melting point was 278–280 °C. The elemental analyses are as follows:

	C	H	N	I
Found (%):	49.49	4.32	8.04	37.24
Calculated (%):	49.72	4.47	8.28	37.53

2.3. Instrumentation

UV–vis absorption spectral measurements were carried out on a *PerkinElmer Lambda-17* spectrophotometer with matched quartz cells with path length 1 cm.

3. Results and discussions

3.1. Micellar formation in aqueous micellar solution

At the critical micelle concentrations aggregation begins with the formation of relatively small micelles. These small micelles grow rapidly and remain approximately constant in size with further increasing in the concentrations. Fig. 2A indicates the absorption spectra of the dye in aqueous solution at different concentrations of SDS. Within the range between 4×10^{-2} and 8×10^{-3} mol dm^{-3} the absorption spectra exhibit a significant red shifts from λ_{max} = 402 nm in H_2O to λ_{max} = 440 nm in micellar solution and the optical density slightly decreases. The observed red shifts suggest that the dye incorporated into the micelle interface. With gradual decreasing in SDS concentrations between 7×10^{-3} and 5×10^{-3} mol dm^{-3}, the absorption spectra decrease remarkably with slightly blue shift in the absorption spectra. At the range between 1×10^{-4} and 1×10^{-6} mol dm^{-3} the absorption maxima of the dye showed the same spectra as in aqueous medium, λ_{max} = 402 nm. The figure showed that the dye has two absorption bands; one of them is in aqueous phase and the other is in the micellar phase. These results reveal that above the c.m.c. the electrostatic and hydrophobic force interactions between the micelles and the dye increase. In this case the dye may be present in the inner layer of the micellar interface. With gradual dilution the electrostatic and hydrophobic forces decrease, the micelles disaggregate and the dye behaves the same as spectral properties as in aqueous medium. The critical micelle concentration was calculated from the normalized absorption spectra at λ_{max} = 440 nm (Fig. 2B) and was $8.1 \times 10^{-3} \pm 0.0002$ mol dm^{-3}. The aggregation number is equal to ~64 and was calculated according to the following [15]:

$$N = \frac{R(C - \text{c.m.c})}{(M{=}^{+}NH_2)I^{-}} \quad (1)$$

where R is equal to unity at low concentration of the dye generally around 10^{-5} mol dm^{-3}, C = concentration of surfactant, c.m.c. = critical micelles concentration, $(M{=}^{+}NH_2)I^{-}$ = concentration of the dye and $N = 1 \times (0.01 - 8.1 \times 10^{-3} \pm 0.0002/3 \times 10^{-5}) = \sim 64$.

3.2. Micellar formation in aqueous solution of cyclodextrins–amphiphilic complex system

Fig. 3 illustrates the absorption spectra of 3×10^{-5} mol dm^{-3} of $(M{=}^{+}NH_2)I^{-}$ dye in water and 1×10^{-2} mol dm^{-3} of α,β,γ-cyclodextrins. The red shift observed from λ_{max} = 402 nm in aqueous solution to λ_{max} = 415 nm in α-CD, λ_{max} = 412 nm in β-CD, and λ_{max} = 404 in γ-CD nm indicate that the dye was inserted or partially inserted into the cavities. In case of γ-cyclodextrin the absorption spectra of the dye is nearly the same as that in aqueous solution. The slight difference in the optical density and the red shift (2 nm) means that the dye is rattle in the cavity with a very slight effect. For β-cyclodextrin the red shift (~10 nm) illustrates that the dye was more included into the cavity. In case of α-CD the significant red shift observed (13 nm) suggests that the dye fits snugly in the cavity. The formation and dissociation constant of the inclusion complexes of α,β,γ-cyclodextrins is determined by the spectral changes between the free and complex molecules (Table 1). Fig. 4 illustrates the absorption spectra of $(M{=}^{+}NH_2)I^{-}$ dye in aqueous solution, and at different concentrations of α-CD. At concentration 1×10^{-1} mol dm^{-3} α-CD a significant changes in both optical density and absorption band observed compared to that in aqueous solution. A well defined isosbestic point at λ = 419 nm indicated that the dye forms an inclusion complex with α-CD. With gradual dilution the spectral bands shows blue shifts toward the same position as in aqueous medium.

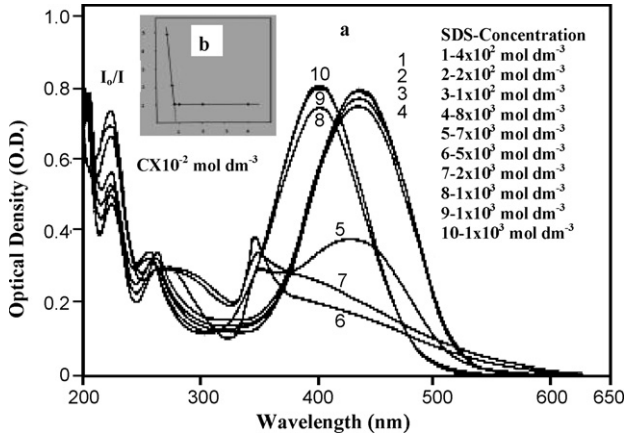

Fig. 2. (A and B) Absorption and normalized spectra of 3×10^{-5} mol dm^{-3} 1-methyl-4-[4′-aminostyryl] pyridinium iodide in different concentration of SDS.

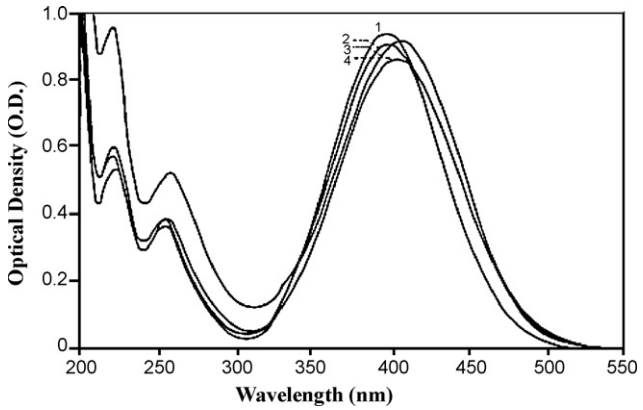

Fig. 3. Absorption spectra of 3×10^{-5} mole dm^{-3} of 1-methyl-4-[4′-aminostyryl] pyridinium iodide in 1-H_2O, and 1×10^{-2} mol dm^{-3} 3-α,4-β, 2-γ-cyclodextrins.

Table 1
Illustrate the critical micelles concentration, formation constants, and aggregation number of 1-methyl-4-[4′-aminostyryl] pyrimidinium iodide in different medium.

Medium	λ_{max}	c.m.c. $\times 10^{-2}$ mol dm^{-3} [a]	K_f [b]	N_d [c]
H_2O	402	–	–	–
1-SDS	440	0.81 ± 0.0002	3.35×10^4	64 ± 2
2-α-CD	419	–	3.33×10^5	–
3-B-CD	412	–	0.33×10^5	–
4-γ-CD	404	–	0.34×10^5	–
5-α-CD + SDS	435	1.24 ± 0.0002	∼126	94 ± 2
6-B-CD + SDS	435	1.4 ± 0.0002	–	106 ± 2
7-γ-CD + SDS	435	1.61 ± 0.0002	–	122 ± 2

[a] Critical micelles concentration.
[b] Formation constant.
[c] Aggregation number.

It is well known that the inclusion process in the cyclodextrin cavity, which is similar to that in micellar solution, is a dynamic equilibrium process and can be illustrated by the following equation:

$$CD + (M{=}^{+}NH_2)I^- \underset{K_f}{\overset{K_d}{\longleftrightarrow}} CD - (M{=}^{+}NH_2)I^- \quad (2)$$

where CD is cyclodextrin concentration $(M{=}^{+}NH_2)I^-$ = Is guest molecule CD–$(M{=}^{+}NH_2)I^-$ = Is the inclusion complex.

The stability of the inclusion complex can be described in terms of the formation constant (K_f) or dissociation constant (K_d) as defined in the above Eq. (1):

$$K_f = \frac{[CD - (M{=}^{+}NH_2)I^-]}{[CD][(M{=}^{+}NH_2)I^-]} \quad (3)$$

and $K_d = 1/K_f$.

Table 1 shows the formation constants of the inclusion complexes. The results reflect the stability of the inclusion complex for all cavities but in case of α-cyclodextrin it is higher than β,γ-cyclodextrins.

It is expected that the third molecule contains a hydrophobic moiety which can interact with α,β,γ-cyclodextrins to increase the hydrophobicity of the cavity by excluding internal water molecules. The influence of SDS concentrations on the CD–SDS complex was studied by varying SDS concentrations between premicellization value 0.4×10^{-2} mol dm^{-3} and postmicellization value 1.8×10^{-2} mol dm^{-3}. Fig. 5 shows a red shift in the absorption spectra of the dye in aqueous medium, λ_{max} = 402 nm and in case of a mixture of 1.8×10^{-2} mol dm^{-3} SDS and 1×10^{-2} mol dm^{-3} of α-cyclodextrin, λ_{max} = 435 nm. The absorption maxima at 435 nm corresponding to the incorporation of the dye in the micellar interface. With gradual decrease in the concentrations of SDS, at the same concentration of α-cyclodextrin, a dramatic shift was observed in both of absorption spectra and optical density. These changes can be divided into four domains. In the first one, at concentration of 0.4×10^{-2} mol dm^{-3} SDS, the absorption spectra is approximately the same as in aqueous solution, $\lambda_{max} \sim$ = 404 nm. In this case, most of SDS monomers may complex with CD (SDS–CD) with displacement of $(M{=}^{+}NH_2)I^-$ dye to aqueous medium [15] (Fig. 5A). In the second domain, with increasing the concentrations of SDS between 0.6 and 1×10^{-2} mol dm^{-3}, the ratio of CD–SDS complex increases and some of small micelles or clusters begin to form due to the increasing in the SDS monomers and associated with $(M{=}^{+}NH_2)I^-$ dye. The observed significant decrease in the optical density with slight red shift in the absorption spectra, λ_{max} = 406 nm, suggests the increasing in the interaction of α-CD with favorable hydrocarbon tail with more SDS_{mon} associated with the dye. It may assume that, some SDS_{mon} increases with increasing the surfactant concentrations before the micellization, while above the micellization point, SDS_{mon} remains constant due to the dynamic equilibrium between the micelles and SDS_{mon}. Hence, with increasing the SDS concentrations the hydrophobicity increases and the micellization process begins in small micelles, and the association between $(M{=}^{+}NH_2)I^-$ dye with the small micelles starts. This can be understood from the decreasing in the optical density at the concentrations between 0.6×10^{-2} and 1×10^{-2} mol dm^{-3} of SDS (Fig. 5B). With increasing the concentration above the micellization process most of CDs depleted, and the small micelles grow due to the inhibition of the association of the micelles by CD. Hence the dye is incorporated in to the micellar interface. So the red shift observed in the absorption spectra to λ_{max} = 437 nm at 1.2×10^{-2} mol dm^{-3} of SDS may due to the growing in the micellar size. The excluding water molecules originally from the micellar core leading to a more hydrophobic environment and gave the dye strong interaction with the micelles (Fig. 5C). In the fourth domain, with further increasing the concentrations of SDS between 1.4×10^{-2} and 1.8×10^{-2} mol dm^{-3} the optical density at λ_{max} = 437 nm increases and remain approximately constant. This may be due to the growing of the micelles and may turn to wormlike micelles (Fig. 5D).

The equilibrium between SDS surfactant and cyclodextrin (CD) is defined according to the following reaction:

$$SDS + CD \underset{K_d}{\overset{K_f}{\longleftrightarrow}} CD - SDS \quad (4)$$

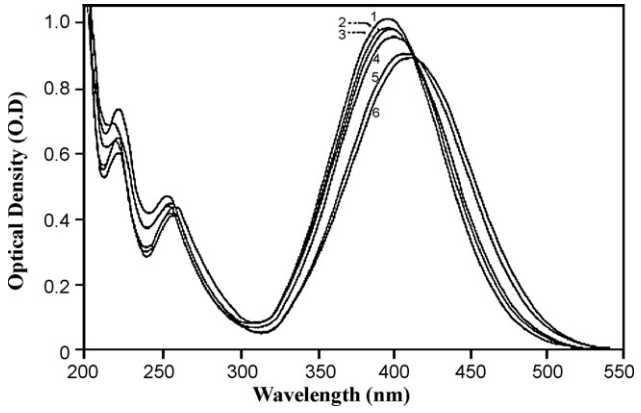

Fig. 4. Absorption spectra of 3×10^{-5} mol dm^{-3} of 1-methyl-4-[4′-aminostyryl] pyridinium iodide in different concentrations of α-cyclodextrins.

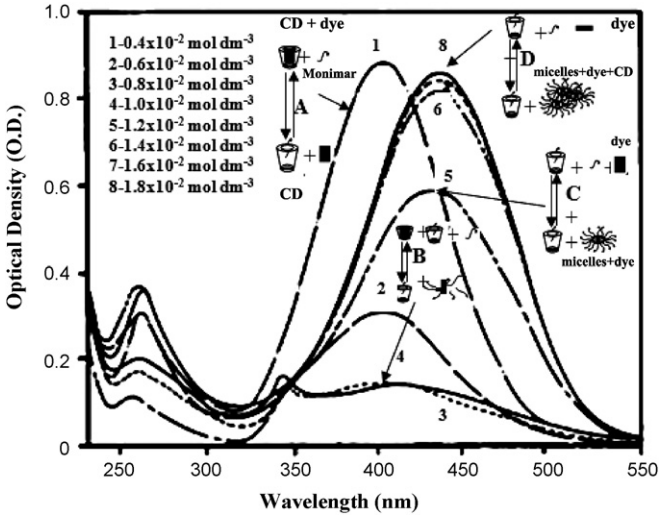

Fig. 5. Absorption spectra of 3×10^{-5} mol dm^{-3} 1-methyl-4-[4′-aminostyryl] pyridinium iodide in 1×10^{-2} mol dm^{-3} of α-CD at different concentrations of SDS.

and

$$K_f = \frac{[CD - SDS]}{[SDS][CD]} \quad (5)$$

where [SDS], [CD], and [CD–SDS] indicate the concentration of free SDS monomer, free CD, CD–SDS complex, respectively.

This equation is used only to determine the formation constant with only one complexation step that can be observed from the absorption spectra at 1:1 complex. The concentration of CD–SDS complex calculated from the spectral behavior at premicellization process according to the following:

$$CD - SDS = C_2(SDS) - C_1(SDS) \quad (7)$$

The decreasing in the optical density may due to the replacement of the dye from the CD cavity. Then CD associates with SDS monomer giving the CD–SDS complex. By subtraction of CD–SDS complex from the total concentration of CD_T we get the residual of CD_f.

At point (1) on the absorption spectra:

$$CD_{f1} = CD_T - [C_1(SDS) + C(dye)] \quad (8)$$

and at point (2):

$$CD_{f2} = CD_T - [C_2(SDS) + C(dye)] \quad (9)$$

$$[CD - SDS] = CD_{f2} - CD_{f1} = C_2(SDS) - C_1(SDS) \quad (10)$$

$$SDS_f = C_2(SDS) - C(CD - SDS) \quad (11)$$

$K_f = 0.2 \times 10^{-2}/[0.397 \times 10^{-2}][0.4 \times 10^{-2}] = \sim 126\ mol\ dm^{-3}$.

Table 1 summarizes the results obtained in this study and showed that the association constant of the inclusion complex of CD–SDS is lower than both CD–dye and SDS–dye complexes. However, at high concentration of CD the inclusion complex starts in case of SDS–CD with expulsion of the dye to aqueous medium. With increasing the SDS concentration it replaces the dye from CD cavity. Moreover, with increasing the SDS concentrations the number of monomer increases to the point which start to begin to aggregate with the dye. At the c.m.c. the dye prefer to associate with the micelles, because the inclusion complex of CD–dye is lower than that of SDS–dye. The critical micelle concentration (c.m.c.) was calculated from the spectral changes at λ_{max} = 437 nm above c.m.c. and the aggregation number was calculated relative to the aggregated number of aqueous micellar solution (Table 1). The results of c.m.c. and aggregation numbers illustrated that, the micelle is grown in the presence of α,β,γ-cyclodextrin cavities. The increasing in c.m.c. values was studied by using different techniques [13,16–20]. The results obtained assumed that 1:1 surfactant–CD complex is formed; and the presence of CD has no effect on existing SDS micelles but raise the c.m.c. point.

4. Conclusion

The presence of α,β,γ-cyclodextrins affects c.m.c. of SDS. The c.m.c. increases with increasing the size of the cavity.

Acknowledgments

The author gratefully acknowledges the help of Prof. Dr. Lotfia El-Nadi and Prof. M.A. El-Sayed for several fruitful discussions and revision of this manuscript.

References

[1] M.B. Lay, C.J. Drummond, P.J. Thistlethwhite, F. Grieser, J. Colloid Interface Sci. 128 (1989) 602.
[2] A. Chakraborty, S. Basak, J. Colloids Surf. B: Biointerfaces 63 (2008) 83.
[3] K.A. Hobson, F. Griser, T.W. Healy, J. Phys. Chem. 98 (1994) 274.
[4] L.J. Magid, R. Triolo, J.S. Johnson, J. Phys. Chem. 88 (1978) 5730.
[5] K. Kalyanasundram, Photochemistry in Microheterogeneous Systems, Academic Press, New York, 1987, p. 25.
[6] C. Ramachandran, R.A. Pyter, P. Mukerjee, J. Phys. Chem. 86 (1982) 3198.
[7] J.C. Fendlar, J. Phys. Chem. 84 (1980) 1485.
[8] M.H. Maeso, S.P. Gonzïalez, C.B. Dïıaz, E.G. Romero, Colloids Surf. A: Physicochem. Eng. Aspects 249 (2004) 29.
[9] H. Gharibi, S. Lalili, T. Ragabi, J. Colloids Surf. 175 (2000) 361.
[10] W.G Herkstroeter, P.A. Martie, S. Farid, J. Chem. Soc. Perkin Trans. 2 (1984) 1453.
[11] M.H. Maesoa, S.P. Gonzïaleza, C.B. Dïıazb, E.G. Romeroa, J. Colloids Surf. A: Physicochem. Eng. Aspects 249 (2004) 29.
[12] S. Hashimoto, J.K. Thomas, J. Am. Chem. Soc. 107 (1985) 4655.
[13] J.W. Park, H.J. Song, J. Phys. Chem. 93 (1989) 6454.
[14] T.T. Herskovits, J.P. Harrington, Biochemistry 25 (1972) 4800.
[15] Y. Marcus, Chem. Soc. Rev. 409 (1993).
[16] T. Okubo, H. Kitano, N. Ise, J. Phys. Chem. 80 (1976) 2661.
[17] M. Shimada, A. Harada, S. Takahashi, J. Chem. Soc. Chem. Commun. 263 (1991).
[18] L. Garcia-Rio, J.R. Leis, J. Phys. Chem. B: 101 (1997) 7383.
[19] D.J. Jobe, R.E. Verrall, E. Junquera, E. Aicart, J. Phys. Chem. 97 (1997) 1243.
[20] D.J. Willem, V. Jenny, H.M.B. Petra, Biochem. J. 330 (1998) 667.