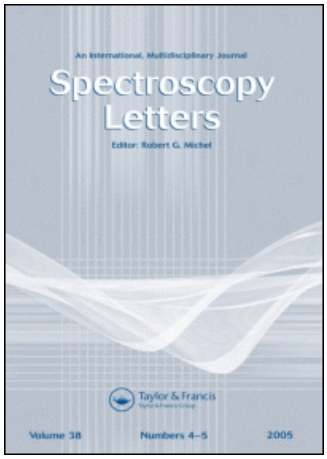

Spectroscopy Letters
An International Journal for Rapid Communication
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

β-Cyclodextrin Effect on Micellization of Cetyltrimethyl ammonium Bromide in Aqueous Solution. Probed by Dual Fluorescence of Sodium P-Dimethylaminobenzoate

Li-Rong Lin [a]; Yun-Bao Jiang [a]; Xian-Zhi Huang [a]; Guo-Zhen Chen [a]
[a] Department of Chemistry and Research Laboratory of SEDC of Analytical Science for Material and Life Chemistry, Xiamen University, Xiamen, People's Republic of China

Online Publication Date: 01 December 1997
To cite this Article: Lin, Li-Rong, Jiang, Yun-Bao, Huang, Xian-Zhi and Chen, Guo-Zhen (1997) 'β-Cyclodextrin Effect on Micellization of Cetyltrimethyl ammonium Bromide in Aqueous Solution. Probed by Dual Fluorescence of Sodium P-Dimethylaminobenzoate', Spectroscopy Letters, 30:8, 1551 - 1560
To link to this article: DOI: 10.1080/00387019708006743
URL: http://dx.doi.org/10.1080/00387019708006743

SPECTROSCOPY LETTERS, 30(8), 1551-1560 (1997)

β-Cyclodextrin Effect on Micellization of Cetyltrimethylammonium Bromide in Aqueous Solution. Probed by Dual Fluorescence of Sodium P-Dimethylaminobenzoate

Keywords: β-cyclodextrin, Micellization, Cetyltrimethylammonium bromide, Twisted intramolecular charge Transfer(TICT), Sodium p-dimethylaminobenzoate

Li-Rong Lin, Yun-Bao Jiang *, Xian-Zhi Huang and Guo-Zhen Chen
Department of Chemistry and Research Laboratory of SEDC of Analytical Science for Material and Life Chemistry, Xiamen University, Xiamen 361005, People's Republic of China

ABSTRACT

Effect of β-cyclodextrin (β-CD) on micellization of cetyltrimethylammonium bromide (CTAB) in aqueous solution was investigated by twisted intramolecular charge transfer (TICT) dual fluorescence of sodium p-dimethylaminobenzoate (SDMAB). It was shown that β-CD induces the micellization of CTAB and the aggregation of CTAB below CMC as well. A reduced charge density at CTAB micelle interface in the presence of β-CD, due to the incorporation of 1:1 CTAB-β-CD inclusion complex in micelle, was concluded to be the reason for β-CD induced micellization of CTAB.

INTRODUCTION

Effect of β-Cyclodextrin (β-CD) on micellization behavior of surfactant in aqueous solution has been a subject of recent interest[1-12]. It appears to indicate that the kinetics of surfactant monomer-micelle exchange process is unaffected and average aggregation number of micelle unchanged by the presence of β-CD[9,10,12]. The critical micelle concentration(CMC) of surfactant in the presence of β-CD has been shown to be nearly the sum of that in the absence of

the cyclodextrin and the CD concentration in solution[7]. This means that β-CD practically does not induce the micellization of surfactant. Furthermore, it was also reported that the surfactant-β-CD inclusion complex was not solubilized or incorporated into micelle[12]. All these conclusions, mainly derived by using classical techniques such as electric condutometry, ion-selective electrode, ultrasonic relaxation, etc., appears to show that β-CD has little effect on micellization process and micelle structure[5,8,9,12].

The others have shown that β-CD does have some effects on the micellization of surfactant[2,11,13-15]. Recent reports from this laboratory by using fluorescent probes capable of excited state intramolecular charge transfer(ICT), indicated that β-CD induces both the micellization[13,14]and aggregation of surfactant below CMC[15]. Twisted intramolecular charge transfer(TICT) has been a subject of intense interest since the establishment of this model in the late 1970's[16]. Typically, TICT flurophore emits dual fluorescence, one is due to the locally excited(LE) state and the other due to the TICT state. TICT state has a much larger dipole moment than the ground state does, thereby fluorescence emission from TICT state is highly sensitive to medium polarity, which makes TICT fluorophore a good fluorescent probe for the microoenvironment of organized medium[16,17]. It should be of interest to examine the effect of β-CD on the aggregation behavior of surfactant in detail by using a TICT fluorescent probe.

In the present work, a TICT flurophore, sodium p-dimethylaminobenzoate(SDMAB) is taken as a probe to examine the effect of β-CD on aggregation behavior of CTAB, a cationic surfactant, in aqueous solution with increasing CTAB concentration. SDMAB is chose as TICT probe because its TICT fluorophore does not depend on micelle concentration and the amount of fluorophore that is solubilized in micelle phase[18]. By using this TICT fluorescent probe, one would expect some new information on β-CD/CTAB systems. The results turned out to be the case indeed.

EXPERIMENTAL SECTION

SDMAB was obtained by neutralization the conjugate acid, p-(N,N'-dimethylamino)benzoic acid (DMABOA)by sodium hydroxide. DMABOA was prepared as before[19]. β-CD was used as received from Fluka. CTAB was a CP. reagent from Shanghai the First Chemicals Factory and was rescrytallized from absolute ethyl alcohol. Water was twice deionized with an electric conductivity lower than 1 us/cm.

Corrected fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer which was corrected in emission wavelength range 200-600 nm by using Rhodamine B as standard. The excitation wavelength was 280 nm, slits for excitation and emission monochromators were both 5 nm. The samples used for taking fluorescence spectra were aerated. All experiment were performed at room temperature (25 ± 2°C).

RESULTS AND DISCUSSION

Figure 1 presents the fluorescence spectra of SDMAB in 1.0×10^{-3} mol/L β-CD solution as a function of the concentration of added CTAB. Dual fluorescence typical of the presence of excited state TICT reaction can be identified from the spectra. It is important to note that the variations of fluorescence spectra of SDMAB in solutions with CTAB concentration below β-CD concentration (1.0×10^{-3}mol/L) are different from those with [CTAB] above 1.0×10^{-3}mol/L. In solutions with CTAB concentration lower than 1.0×10^{-3}mol/L, the intensities of both LE band and TICT band are slightly decreased with increasing CTAB concentration, and the TICT band is shifted to the red. While in solutions in which [CTAB] is higher than 1.0×10^{-3}mol/L, both LE band and TICT band are enhanced and shifted to the blue.

Generally speaking, in SDMAB, CTAB and β-CD mixed solutions, both SDMAB and CTAB molecular will compete cyclodextrin cavity to be included. The association constant of SDMAB/β-CD inclusion complex was determined, based on the variations of the total fluorescence intensity of SDMAB in aqueous β-CD solution with β-CD concentration by using the double reciprocal plotting[20]. The double reciprocal plot for SDMAB/β-CD system is given in Figure 2. Nice linear fitting indicates an 1:1 stoichometry in the SDMAB-β-CD inclusion complex. An association constant of 825 L/mol for the complex was calculated by dividing the intercept of the straight line by slope of the same line. It has been reported that the association constant of β-CD inclusion complex of surfactant alkyl trimethylammonium bromide (alkyl=dodecyl, tetradecyl, or hexadecyl) is at the order of 10^4L/mol or higher [4,5,7,21], which is more an order of magnitude higher than that of SDMAB-β-CD inclusion complex. Thus upon addition of CTAB to SDMAB/β-CD solution, SDMAB which is previously included in the nonpolar cyclodextrin cavity when in the absence of CTAB, will now be substituted by CTAB and be driven to the bulk aqueous phase, leading to the quenching of SDMAB fluorescence. This is really the case in solutions when CTAB concentration is not higher than β-CD concentration, as can be seen in Figure 1. Thus the sharp difference between the fluorescence spectra of the

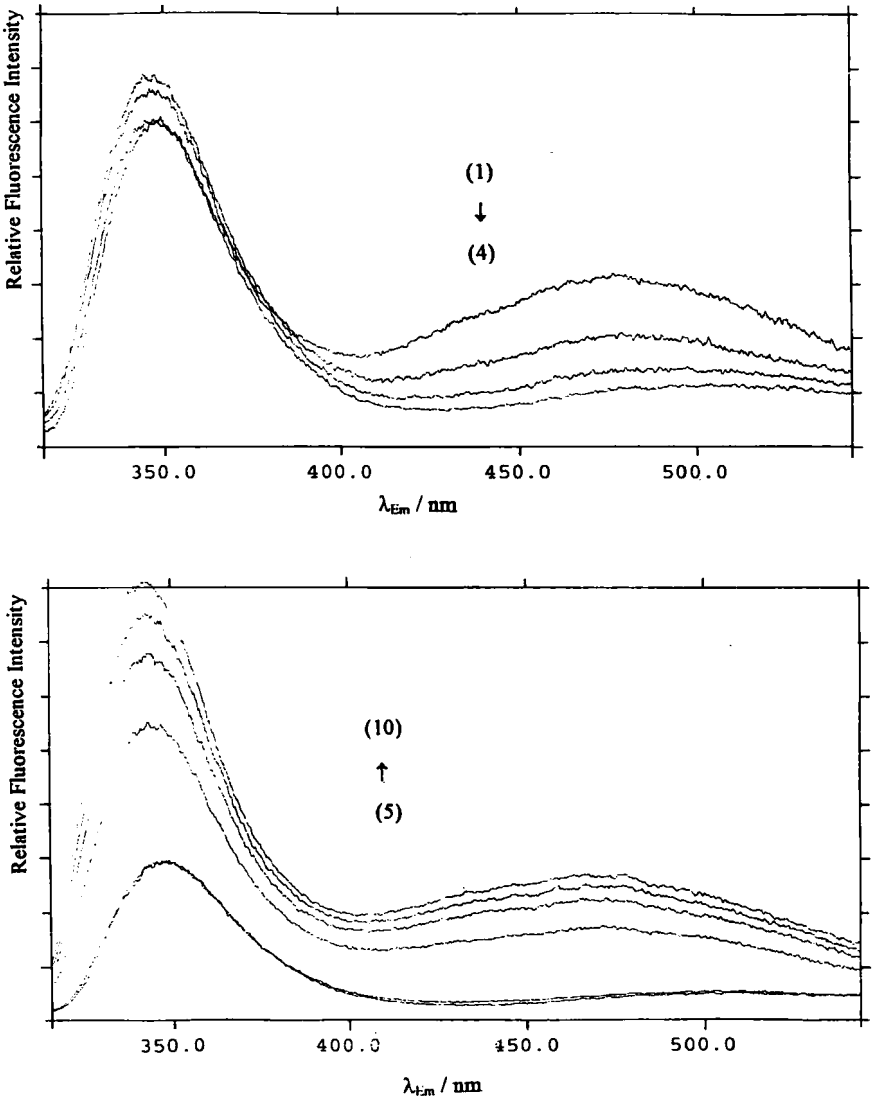

Figure 1. Fluorescence spectra of SDMAB as a function of the CTAB concentration in the β-CD aqueous solution [SDMAB]:2.5 × 10^{-5} mol.L^{-1}, [β-CD]:1.0 × 10^{-3}mol.L^{-1}. [CTAB]:(1)0.0,(2)0.5, (3)0.8, (4)1.0, (5)1.2, (6)1.5, (7)1.8, (8)2.0, (9)2.2, (10) 2.5, × 10^{-3}mol.L^{-1}

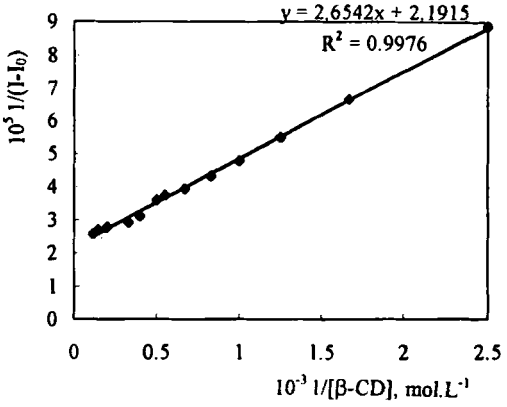

Figure 2. The double reciprocal plot of $1/(I-I_0)$ verus $1/[\beta\text{-CD}]$ for SDMAB/β-CD system. [SDMAB]:2.5×10^{-5} mol.L^{-1}

SDMAB/CTAB/β-CD solutions before and after CTAB concentration equals to β-CD concentration shall indicate that the stoichiometry in CTAB/β-CD inclusion complex is 1:1, as we have previously demonstrated[13-15].

The blue shift of the LE band and TICT band of SDMAB in SDMAB /CTAB/β-CD solutions with [CTAB] higher than [β-CD] indicates that SDMAB molecule is solubilized in a nonpolar microenvironment other than cyclodextrin cavity, since in this case the SDMAB molecules is not included in cyclodextrin cavity, as shown in the last paragraph. It is clear that in these solutions, there are 1:1 CTAB-β-CD complex, SDMAB and CTAB. Thus this blue shift could evidence that the CTAB molecules and /or CTAB plus 1:1 CTAB-β-CD complex exist in such a form that could provide SDMAB with a somewhat nonpolar environment. This environment is practically even less polar than cyclodextrin cavity as the LE band of SDMAB in these solutions is blue shifted compared to that in pure β-CD solution, as can be easily seen in Figure 1.

In order to identify the existing forms of CTAB in SDMAB/CTAB/β-CD systems with increasing CTAB concentration, we analyzed the intensity ratio of the TICT band to LE band, Ia/Ib, as a function of CTAB concentration, since it has been reported that this ratio could easily probes micelle formation[18,22]. Representative data are plotted in Figure 3. In the absence of β-CD, the variation of Ia/Ib of SDMAB with CTAB concentration is in an S-shaped orbital, with

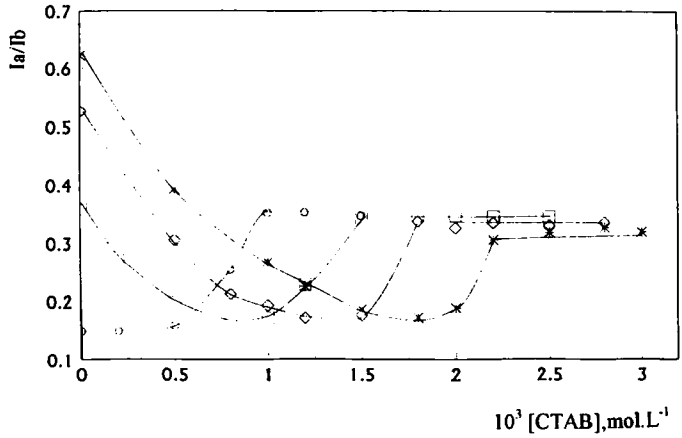

Figure 3. Variations of I_a/I_b of SDMAB in aqueous β-CD/CTAB solution with CTAB concentration.
[β-CD]:(1)-○-○-○- 0.0, (2)-□-□-□- 0.5 × 10^{-3},
(3)-◇-◇-◇- 1.0 × 10^{-3}, (4)-※-※-※ 1.5 × 10^{-3}mol.L^{-1}

a break at the CMC[18,22]. It is seen that the Ia/Ib ratio of SDMAB after micelle formation is independent of CTAB concentration, thus this constant ratio value can be taken to represent Ia/Ib of SDMAB in CTAB micelle. The Ia/Ib ratio variation curve in the presence of β-CD shows somewhat different from that in the absence of the cyclodextrin. In systems where the [CTAB]is lower than [β-CD], the Ia/Ib ratio is greatly decreased with increasing CTAB concentration, this is the result of SDMAB being driven out of cyclodextrin cavity. In higher CTAB concentration range a similar S-shaped variation of Ia/Ib with [CTAB] could be identified. From this S-shape variation, the critical micelle concentration of CTAB in the presence of β-CD, CMC*, can be vaulted from the break point in a manner similar to that used to abstract pKa or Pkb from a typical acid-base titration curve.

The difference between CMC* and concentration of β-CD in solution, CMC*-[β-CD], versus β-CD concentration is plotted in Figure 4. It is important to see that this difference slightly decreases with increasing β-CD concentration. This should mean that the presence of β-CD in CTAB solution induces micelle formation, since if there is no such inducement, the CMC* should be the sum of [β-CD]and CMC in the absence of β-CD because of the formation of 1:1

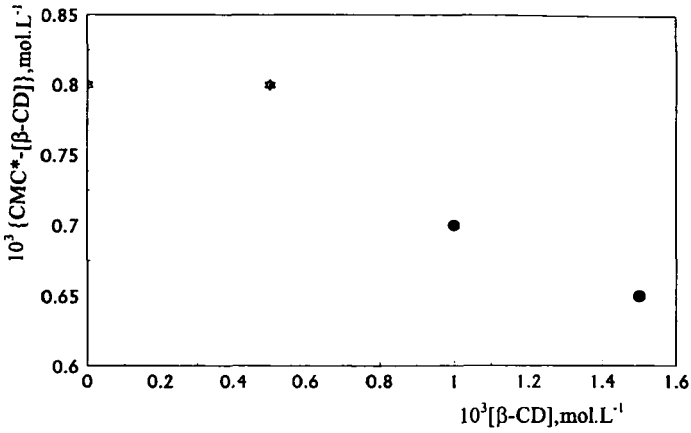

Figure 4. The difference between the CMC* and β-CD concentration, CMC*-[β-CD], as a function of β-CD concentration

CTAB-β-CD inclusion complex that decreases by [β-CD] the concentration of CTAB available for micelle formation. It is well established that micelle formation is the result of the struggle of hydrophobic interaction between alkyl chains of surfactants and electrostatic repulsion between polar heads[23]. Thus the inducement of micelle formation could be due to the enhanced hydrophobic interaction and/or reduced electrostatic repulsion. The former seems to be not likely as the presence of β-CD can only reduce the hydrophobic interaction through inclusion complex formation. Thus the reducement in the electrostatic repulsion should be the reason for enhanced formation, since it has been established[18,24] that the Ia/Ib ration of TICT fluorophore in ionic micelle could also act as a measurement for the charge density at micelle interface. In case that the medium polarity is the same, the higher the charge density, the higher the ratio. From Figure 4 we note that the Ia/Ib ratio of SDMAB in CTAB micelle decreases with increasing β-CD concentration. The TICT emission was observed to be at the same position independent of β-CD concentration, implying that the polarity of the microenvironment of SDMAB in CTAB micelle is not altered by the presence of β-CD. Thus it is not risky to conclude that the reduced Ia/Ib ratio in CTAB micelle in the presence of β-CD is an indication of the reduced charge density at micelle interface.

The conclusions that the presence of β-CD reduces the electrostatic repulsion between polar heads of surfactants in CTAB micelle and decreases the charge density at micelle interface will be instructive for understanding the origins of the β-CD effects. Then the reducement of the charge density at micelle interface could be the results of the substitution of a CTAB molecule by an 1:1 CTAB-β-CD inclusion complex[25,26,27] with cyclodextrin towards bulk aqueous phase. Thus we would conclude that it is the 1:1 CTAB-β-CD inclusion complex that is as a whole incorporated in micelle that, by widening the distance between polar heads of surfactants and in turn enlarging the micelle surface area, leads to the reducement of charge density at the interface and of electrostatic repulsion between polar heads of surfactants, resulting in the enhancement of micelle formation.

CONCLUSIONS

Monitoring of the TICT dual fluorescence of SDMAB in β-CD solution as a function of the concentration of added CTAB showed that an 1:1 CTAB-β-CD inclusion complex is formed by an association constant much larger than that of the SDMAB-β-CD inclusion complex which is also in 1:1 stoichiomertry. It was determined that the CMC* of CTAB in the presence of increasing β-CD concentration is lower than the sum of the CMC in the absence of cyclodextrin and the β-CD concentration in solution, which is an evidence for the β-CD induced CTAB micelle formation. Decrease in the charge density at micelle interface is the reason for β-CD induced micellization of CTAB, and this decrease is realized by inserting the 1:1 CTAB-β-CD inclusion complex into the micelle.

Acknowledgments. This work has been funded by the National Natural Science Foundation of China (to YBJ). We are grateful to Prof.Xiao-Ru Wang for her support.

REFERENCES

1. S.Hashimoto and J.K.Thomas, J.Am.Chem.Soc.,1985,107,4655.
2. R.A.Femia and L.J.Cline-Love, J.Colloid Interface Sci., 1985,108,271.
3. Y.Kusumoto,M.Shizuka and I.Satake, Chem. Phys. Lett., 1986,125,64.
4. X.-K.Jiang, J.-H.Gu, X.-E.Cheng and Y.-Z.Hui, Acta Chim.Sinica 1987,45,159.
5. R.Palepu and V.C. Reinsborough, Can J. Chem., 1988,66,325.

6. D.J.Jobe, R.E.Verral, R.Palepu and V.C.Reinsboyough, J. Phys. Chem.,1988,92 3582.

7. E.Junquera, E.Aicart and G.Tardajos, J.Phys. Chem.,1992,96,4533.

8. W.M.Z.WanYuns, J.Taylor, D.M.Bloor, D.G.Hall and E.Wyn-Jones, J. phys. Chem., 1992,96,8979.

9. E. Junquera, G.Tardajos and E.Aicart, Langmuir, 1993,9,1213.

10 D.J.Jobe and R.E.Verrall, J. Phys. Chem., 1993,97,1243.

11.E.A.Cummings, T.T.Ndou, V.K.Smith and I.M.Warner, Appl. Spectrosc., 1993,47,2129.

12.D.J.Jobe, C.Vincent, V.C.Reinsborough and S. D. Wetmore, Langmuir, 1995,11,2476.

13.Y.-B.Jiang and J.-S. Hu, Chem.J. Chinese Univ., 1993,14,1068.

14.Y.-B.Jiang and X.-J.Wang, Acta Physico-Chimica Sinica, 1994,10,716.

15.Y.-B.Jiang and X.-J.Wang, Appl. Spectrosc.,1994,48,1428.

16.(a) Z.R.Grabowski, K.Rotkiewicz, A.Siemiarczuk, D.J.Cowley and W.Baumann, Nouv. J. Chim., 1979,3,443. (b)W.Rettig, Angew.Chem.Int.Ed.Engl., 1986,25,971. (c)K.Bhattacharyya and M.Chowdhury, Chem.Rev., 1993,93,507. (d)K.A.Zachariasse, Th.von der Haar, A.Hebecker, U.Leinhos and W.Kuehnle, Pure & App. Chem., 1993,65,1745. (e)Th. Von der Haar, A.Hebecker, Yu.Il'ichev, Y.-B.Jiang, W.Kuehnle and K.A.Zachariasse, Recl.Trav.Chim. Pays-Bas, 1995,114,430.

17.(a) V.Ramamurthy, D.R.Sanderson and D.F.Eaton, Photochem. Photobiol., 1992,56,297. (b) V.Ramamurthy, D.F.Eaton and J.Caspar, Acc. Chem. Res., 1992,25,299.

18.Y.-B.Jiang, M.-G.Jin and J.-G.Xu, Spectroscopy Lett., 1996,29,751.

19.Y.-B.Jiang, Chinese Science Bulletin, 1994,39,1179.

20.G.C.Catena and F.V.Bright, Anal.Chem.,1989,61,905.

21.T.Okubo, H.Kitano and N.Ise, J.Phys.Chem., 1976,80,2661.

22.Y.-B.Jiang, J.-G.Xu and X.-Z.Huang, Chem.J.Chinese Univ., 1994,15,552.

23.(a)J.H.Fendler,Membrane Mimetic Cnemistry, John Wiley & Sons, NewYork,1982. (b)G.-X.Zhao, Physical Chemistry of Surfactants, Revised Ed., Peking University Press, Beijing, 1991.

24.Y.-B.Jiang and X.-J.Wang, Chinese Sci.Bull., 1994,39,1528.

25.I.Satake, T.Ikenoue, T.Takeshita, K.Hayakawa and T.Maeda, Bull. Chem.Soc.Jpn., 1985,58,2746.

26.L.-R.Lin, Y.-B.Jiang, X.-Z.Du, X.-Z.Huang and G.-Z.Chen, Chem.Phys.Lett., 1997,266,358.

27.D.K.Lee, Y.S.Kang and L.Kevan, J. Phys. Chem., 1997,101,519.

Date Received:May 5, 1997
Date Accepted:June 18, 1997