



Organization of amphiphiles, part XIV: Studies on the interaction of a novel organic molecule with surfactant in solution and at air–water interface[☆]



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ABSTRACT

The interaction between a novel organic molecule (3E, 5E)-bis(4-butyloxy)benzylidene-8-(4-butyloxy)phenylidicyclopentano[2,3-b:3,2-e]pyridine(BP₄) independently with a cationic surfactant, cetyltrimethylammonium bromide (CTAB) as well as with a nonionic surfactant, Triton-X-100 (TX-100) has been investigated through a number of analytical techniques such as conductivity, spectral analyses (fluorescence, UV–visible absorbance) and area/molecule measurements (Langmuir–Blodgett film method) in solution and at air–water interface. Both CTAB and TX-100 aggregate at lower concentration in the presence of BP₄ compared to the absence of later, indicating the generation of synergism in the solution mixture. The hydrocarbon chain of BP₄ interacts with the cetyl chain of CTAB or 1,1,3,3-teramethyl butyl chain of TX-100 through hydrophobic interaction thereby enhancing the surface activity of the mixture. Subsequently, CMC decreases. On the contrary, CMC of BP₄ increases upon addition of both CTAB and TX-100 due to the inefficiency of BP₄ to interact aptly with the CTAB/TX-100 to form hydrophobic complex (U. Dash, P. K. Misra, JClS, 357(2011)407–418). But both the surfactants and BP₄ adsorb as monomer in the presence of each other and form a mixed monolayer at the air–water interface by associating through lateral interaction of their hydrocarbon chain. This leads to an increase of the cooperative effect as evidenced by the decrease in area per molecule at the air–water interface.

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1. Introduction

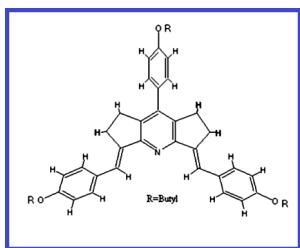
The presence of both lyophobic as well as lyophilic groups in the same molecular skeleton urges surfactant molecules to behave abnormally at higher concentrations leading to clustering phenomena such as micellization and adsorption. These clustering phenomena of surfactants in solution and at the interfaces have received considerable attentions because of their significant applications in industrial as well as in domestic sectors [1–3]. The applications are, however, recognized only at some threshold concentrations (called as critical micellar concentration or hemimicellar concentration, [4,5]) beyond which the clustering phenomenon occurs. A large number of factors such as, surfactant structure [6–9], solvent behaviour [10–12], presence of additives like electrolytes [13–15], hydrophobic solute

[16,17] and others [18–21], temperature of the systems [22–25] etc. depict the extent and spontaneity of the clustering phenomena. The primary drive of these factors is to minimize the distortion of the solvent structure and to diminish the increase in the free energy of the system arising out of the contact of lyophobic groups of the surfactant molecules with the solvent molecules, subsequently resulting in the transfer of the lyophobic groups from solvent to the clusters. The role of additives, in particular, is astounding since depending on their structure they can either promote or demote the clustering effect and hence the desired applications can be tuned [26,27]. Largely, the additives which break the solvent structure, promote the clustering effect whereas vice versa occurs when a structure making additive is added [28,29]. In water, the hydrophobic solutes add to the clustering effects (like micellization of surfactants) by enhancing the nonpolarity of the systems whereas phenomenon overturns when a hydrophilic solute is added. More interesting observations are experienced when the additives have both polar and nonpolar moieties because in such cases in addition to the effect of additives on clustering phenomena, the self-aggregation of the additives may occur. And hence, to understand these twin effects, a large number of molecules with dual character

[☆] Dedicated to Prof. B.K.Mishra, Sambalpur University, India on his sixtieth birthday.

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(Molecular structure **1**) (3E, 5E)-Bis(4-butyloxy)benzylidene-8-(4-butyloxy)phenyldicyclopentano[2,3-b:3,2-e]pyridine

have been synthesized and their effects on micellization have been investigated [30].

Our long term objective has been to analyze the organization of amphiphiles in solution and at interfaces and to explore the impact of this organization on different applications [31–35]. Herein, we have made an attempt to elucidate the complex interactions between a novel organic molecule (3E,5E)-bis(4-butyloxy)benzylidene-8-(4-butyloxy) phenyldicyclopentano[2,3-b:3,2-e]pyridine (BP₄) (Molecular structure **1**) with ionic surfactant, cetyltrimethylammonium bromide (CTAB) and TX-100 in solution and at air–water interface. The goal has been achieved through measurement of conductivity, absorbance, area/molecule and fluorescence intensity of the mixture.

2. Experimental

2.1. Material

The organic molecule (3E, 5E)-bis(4-butyloxy)benzylidene-8-(4-butyloxy)phenyldicyclopentano[2,3-b:3,2-e]pyridine was a gift from Dr. S. Thennerasu, Organic division, CLRI, Chennai (Molecular structure-**1**). The compound is pure to the extent of 99.9%. The surfactants, CTAB and cetyltrimethyl pyridinium chloride (CPC) were Sigma make (USA) and were used without purification. TX-100 of Loba was used without further purification. The absence of minimum in the surface tension–concentration curve of the surfactants confirmed the high purity [$>99\%$] of the surfactant [36–39]. White crystals of pyrene (Aldrich, USA) re-crystallized from ethanol were used throughout the fluorescence experiments. Chloroform of SRL and methanol of Anal R grade, Sisco-chem, India products were distilled before use.

2.2. Conductivity studies

Specific conductivities of the surfactants solutions of various concentrations in chloroform were measured by Systronic direct reading conductivity meter (D. D. R. conductivity meter type 303) in micro range. A dip type cell with cell constant 1 cm^{-1} was used. The reproducibility of the conductance value was within experimental error (± 0.2). The concentration in the plot of specific conductivities versus concentration of the surfactant at which sudden rise in conductivity occurred was considered to be the CMC of the surfactant.

2.3. Studies on the UV–visible spectra of the materials

The absorbance of the organic molecule BP₄ at its λ_{max} was measured using UV–visible double beam spectrophotometer, Lambda 35 UV–visible spectrophotometer (Made in Japan) in the absence and presence of CTAB/TX-100. The appearance of the break point in the plot of absorbance versus concentration of the CTAB/TX-100 indicated aggregate formation.

2.4. Studies on fluorescence behaviour of the organic molecule and the mixed system

Fluorescence spectra measurements were made on a fluorescence spectrophotometer (Hitachi F-4500, Japan). The required volume from a stock solution of pyrene in methanol was added to the sample bottle containing different concentrations of CTAB/TX-100 (with or without BP₄) to maintain a low concentration of pyrene ($= 5 \times 10^{-6}\text{ M}$) in order to avoid the formation of excimer or any kind of perturbation to the organization [39]. The emission spectra of pyrene was recorded by exciting at λ_{max} ($= 335\text{ nm}$) within the range of 350–600 nm. The CMC was determined from the plot of the I_3/I_1 ratio of pyrene versus surfactant concentration [37]. The fluorescence spectra of BP₄ alone in chloroform medium were obtained by exciting the molecule at its λ_{max} ($= 316\text{ nm}$) and emission spectra were recorded in the range of 400–600 nm.

2.5. Determination of area per molecule

The area/molecule was determined from surface pressure (π) versus area isotherms (π -A isotherms) using Langmuir–Blodgett film model 611 single barrier supplied by Nima Technology Limited, United Kingdom. For this purpose appropriate volume of the sample in the μL range from desired concentrations of the sample in chloroform were spilled on the trough using a syringe and the organic solvent was evaporated. On application of pressure the surface area of the molecule went on decreasing till a monolayer was formed which collapsed finally on application of further pressure. The area at the break of surface pressure versus area per molecule plot indicated the area occupied by single molecule. The limiting surface areas per molecule were thus measured for BP₄, CTAB/TX-100 in the presence of the other by plotting surface pressure versus area per molecule.

3. Results and discussion

3.1. Conductivities studies

Fig. 1 illustrates the plot of specific conductance of different concentrations of CTAB in chloroform. The chloroform being a non-polar solvent (dielectric constant 4.8) rarely assists the ionization of polar ionizable solute like CTAB. Cetyltrimethylammonium ion and bromide ion therefore, club together and cannot move in chloroform when electricity is passed through a solution of CTAB in chloroform

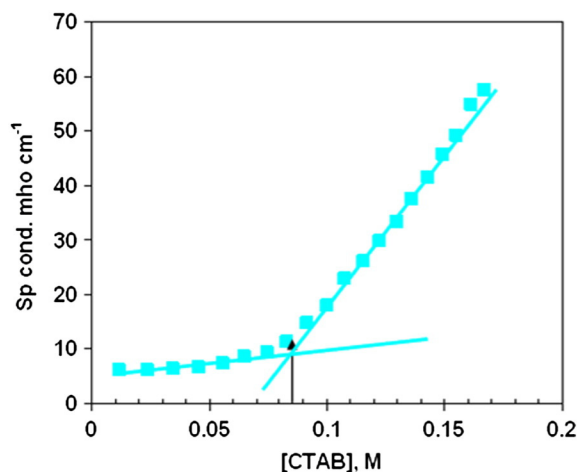


Fig. 1. Plot of specific conductance versus concentration of CTAB in chloroform at 20 °C.

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