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Micellar behavior of aqueous solutions of dodecyldimethylethylammonium bromide, dodecyltrimethylammonium chloride and tetradecyltrimethylammonium chloride in the presence of α-, β-, HPβ- and γ-cyclodextrins

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Abstract

Conductivity, static fluorescence and ^{1}H NMR measurements have been carried out to study the micellar behavior of aqueous solutions of dodecyldimethylethylammonium bromide (DDAB), dodecyltrimethylammonium chloride (DTAC) and tetradecyltrimethylammonium chloride (TDAC) in absence and presence of α-cyclodextrin (α-CD), β-cyclodextrin (β-CD), hydroxypropyl-β-cyclodextrin (HPβ-CD) and γ-cyclodextrin (γ-CD). The conductivity measurements were carried out at 298.15 K. The influence of cyclodextrins on the micellar parameters, such as cmc* (apparent critical micellar concentration), β (degree of ionization) have been analyzed. Thermodynamics of the systems was discussed in terms of the change in standard free energy of micellization, ΔG_m^0. Micellization was found to be less spontaneous in presence of cyclodextrins. The fluorescence intensity of the surfactant solutions is enhanced by the addition of cyclodextrins. The association constants obtained from conductivity and fluorescence data suggest the binding of γ-CD with the surfactants to be strongest among all the cyclodextrins used. ^{1}H NMR chemical shift changes provide powerful means for probing the cyclodextrin–micellar interactions and inclusion of surfactant is shown by the change in the chemical shift of some of the guest and host protons in comparison with the chemical shifts of the same protons in the free compounds.

Keywords: DDAB; DTAC; TDAC; Cyclodextrin; Conductivity; Fluorescence; ^{1}H NMR

1. Introduction

Cyclodextrins (CDs) are cyclic oligoglycosides made up of six to eight ($\alpha = 6$, $\beta = 7$, $\gamma = 8$) D-glucose monomers linked covalently at 1 and 4 carbon atoms. The internal cavities are relatively hydrophobic which gives CDs ability to form inclusion complexes with a variety of organic and inorganic molecules in aqueous solution. Accommodation of the guest molecule depends on its size and polarity and on the size of the particular cyclodextrin. CDs, as a result of their complexation ability and other versatile characteristics, are continuing to have different applications in different areas of drug delivery and pharmaceutical industry [1–13].

Surfactant molecules, [S], which have an ionic head group as well as a large hydrocarbon chain of varying hydrophobicity, are expected to form complex with cyclodextrins by the inclusion of the hydrophobic chain of the surfactant into the apolar cavity of the cyclodextrin, affecting the micellization process of the surfactant itself [14–20]. Inclusion complexes, formed between surfactants and cyclodextrins have been a subject of interest for further exploration by scientists since these systems can be used to mimic the effect of cyclodextrins on phospholipids (a major constituent of cell membrane) [21]. The importance of these inclusion complexes has been well appreciated and established from biophysical point of view, therefore,

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efforts are required to study the physicochemical properties and behavior of surfactants and cyclodextrins in solution and at interfaces to further improve our understanding of the CD/S interactions. A number of studies are focused on interaction between surfactant with β-CD and its derivatives only. However, much work has not been done on interactions of other forms of cyclodextrins (α- and γ-CD) with surfactants. Therefore, association between surfactants and cyclodextrins requires further investigations and explorations using all the different forms of cyclodextrins.

The objective of the present study is to study the encapsulation processes of cationic dodecyldimethylethylammonium bromide, dodecyltrimethylammonium chloride, tetradecyltrimethylammonium chloride (quaternary ammonium compounds) into the cavity of α-, β-, HPβ- and γ-cyclodextrins and its effect in the micellization process of the surfactant itself. Conductometric measurements and spectroscopic studies were done to predict the thermodynamics and to understand the type of interactions existing in the system respectively. In all, the influence of the presence of the inclusion complex on the micellization process of the surfactant has been focused in detail.

2. Materials and methods

2.1. Materials

Dodecyldimethylethylammonium bromide (DDAB) (purity >98%), dodecyltrimethylammonium chloride (DTAC) (purity >99%), tetradecyltrimethylammonium chloride (TDAC) (purity >98%), β-cyclodextrin (purity >99%), HPβ-cyclodextrin (purity >98%), γ-cyclodextrin (purity >98%) and pyrene (purity $\geqslant$97%) were purchased from Fluka while α-cyclodextrin (purity >98%) and hexadecylpyridinium chloride (purity $\geqslant$97%) were from HIMEDIA. Potassium chloride (purity >99%) and D_2O (99.9% atom D) was purchased from Merck and Aldrich, respectively. All the chemicals were used without further purification. Water used for the preparation of samples was deionized and triply distilled (conductivity lower than 3 μS).

2.2. Methods

2.2.1. Conductivity studies

The conductivity of mixtures was measured in a thermostatic glass cell with two platinum electrodes and Pico conductivity meter from Lab India. The conductivity meter was calibrated by measuring the conductivity of the solutions of potassium chloride of different concentrations (0.001, 0.01 and 0.1 M). Electrodes were inserted in a double walled glass cell containing the solution. The glass cell was connected to the thermostat controlled to better than ±0.01 K temperature variation. The cell constant of the cell used was 1.01 cm^{-1}. The measurement of conductivity was carried out with an absolute accuracy up to ±3%. The solutions were prepared by weight using an electronic balance with an accuracy of $\pm 1 \times 10^{-4}$ g.

2.2.2. Fluorescence spectroscopy

Fluorescence measurements were carried out with VARIAN spectrophotometer. A 1 cm rectangular silica cell was placed in a multicell holder whose temperature was kept constant at 298.15 K with a recirculating water circuit. Pyrene was used as luminescence probe and its concentration was kept constant at 10^{-3} M. Both excitation and emission band slits were fixed at 5 nm, and the scan rate was selected at 500 nm/min. The excitation wavelength was selected at 340 nm, while the emission spectra were collected from 350 to 450 nm. In the determination of aggregation numbers, the concentration of the quencher, hexadecylpyridinium chloride, was held low enough so as not to interfere with the assembly of the micelle. The ratio of the fluorescence intensity of the highest energy vibrational band (I_I) to the fluorescence intensity of the third highest energy vibrational band (I_{III}) has been utilized to investigate the formation of surfactant micelle.

2.2.3. ^1H NMR spectroscopy

^1H NMR for the binary and ternary systems of the surfactant was recorded in deuterated water (D_2O) using BRUKER AVANCE II (400 MHz) spectrometer. Chemical shifts are represented in ppm relative to tetramethylsilane as an internal standard ($\delta = 0$ ppm).

3. Results and discussion

Aqueous solutions of the ternary systems of dodecyldimethylethylammonium bromide, dodecyltrimethylammonium chloride, tetradecyltrimethylammonium chloride and various cyclodextrins (see Fig. I in Supplementary material) have been characterized through conductivity, fluorescence and NMR spectroscopy measurements.

3.1. Conductivity measurements

Figs. 1–3 show the plots of the specific conductivity κ vs [S] for solutions of DDAB, DTAC and TDAC, containing various constant concentrations of α-, β-, HPβ-, and γ-cyclodextrins. The inflection observed in all curves at a certain concentration of surfactant is considered to be the cmc of the micelles. In the presence of different cyclodextrin at different concentrations, here it is termed as apparent cmc or cmc*.

The lower curve in all the above graphs (Figs. 1–3) shows the behavior of binary S/W system. Before the cmc* is reached, another phenomenon occurs when the surfactant is added to the CD solution, i.e., the formation of the inclusion complex:

$$CD + S \leftrightarrow CDS.$$

The association between the CD and the surfactant is stronger in comparison with the micelle formation and thus the addition of surfactant shifts the above equilibrium toward the complex formation. When all the CD molecules present in the solution are complexed, the addition of more surfactant leads to the formation of micelles:

$$nS \leftrightarrow S_n.$$