Journal of Molecular Liquids 163 (2011) 93–98

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Study of surface and solution properties of gemini-conventional surfactant mixtures and their effects on solubilization of polycyclic aromatic hydrocarbons

Manorama Panda, Kabir-ud-Din *

Department of Chemistry, Aligarh Muslim University, Aligarh-202 002, India

A R T I C L E I N F O

Article history:
Received 19 April 2011
Received in revised form 22 July 2011
Accepted 3 August 2011
Available online 17 August 2011

Keywords:
Gemini surfactant
Polycyclic aromatic hydrocarbon
Synergism
Mixed micelle
Solubilization

A B S T R A C T

The aqueous solubility enhancement of the polycyclic aromatic hydrocarbons (PAHs) naphthalene, anthracene and pyrene by micellar solutions of single gemini surfactant hexanediyl-1,6-bis(dimethylcetylammonium bromide) (G6) and its mixtures with cationic cetyltrimethylammonium bromide (CTAB), anionic sodium bis(2-ethylhexyl)sulfosuccinate (AOT) and nonioinic polyoxyethylene (20) cetyl ether (Brij 58) have been investigated. Above the *cmc*, maximum solubilization occurs in the Brij 58 surfactant micelles whereas the solubilization is least in presence of AOT. The PAHs are solubilized synergistically in mixed gemini-conventional surfactant solutions, which is attributed to the formation of mixed micelles, their lower *cmc* values, and the increase of the solvents' molar solubilization ratios or micellar partition coefficients because of the lower polarity of the mixed micelles.

1. Introduction

Organic pollutants like polycyclic aromatic hydrocarbons (PAHs) are hydrophobic and can be removed from the contaminated soils and ground water by surfactants mainly due to the solubilization or mobilization of the pollutants inside micelles [1–5]. Solubility enhancements are, however, closely related to the properties of organic compounds and surfactants. The micelle-solubilization effects for various organic chemicals have been investigated by many workers to quantify the efficiency of surfactant-enhanced remediation (SER). In the remediation of hydrophobic organic polluted environment with high surfactant concentrations, the surfactants applied to remediate a site could again contaminate the soil and ground water significantly. To get a better system, mixed micellar systems have already been used for the significant enhancement of water solubility of poorly soluble organic compounds [6–8]. Mixed surfactants improve the performance of surfactant-enhanced remediation of soils and sediments by decreasing the applied surfactant level and thus the remediation cost [8–12].

Gemini surfactants are better solubilizers as they have better surface-active properties than the corresponding conventional surfactants of equal chain length. Differently from conventional surfactants, gemini surfactants consist of two hydrophobic groups, two hydrophilic groups and a spacer linked at or near head groups [13,14]. As a result, gemini surfactants form larger micelles than the conventional surfactants [15] and thus should have a better solubilizing capacity. In their study of the solubilization of pyrene in the micellar solutions of gemini surfactants of different spacer length, Zheng and Zhao [16] have shown that such micelles show stronger ability for pyrene solubilization than the conventional surfactant micelles. Although the gemini-conventional mixed micellar systems can increase the water-solubility of PAHs and other organic compounds significantly, those have not been explored extensively. To our knowledge, only limited reports of solubilization of PAHs in gemini-conventional mixed surfactant systems are available [17,18].

The objectives of the present study are: (i) to evaluate and compare the efficiency of some gemini-conventional mixed surfactants in enhancing the water solubility of PAHs, and (ii) to have a clear idea about the synergistic solubilization of PAHs by mixed surfactant systems. The experiments are aimed to ascertain if a mixed surfactant solution with a lesser total surfactant amount for reducing the surfactant quantities may be used in the SER of organic contaminants. In this study, we have examined mixed micellar systems of gemini-cationic, gemini-anionic, and gemini-nonionic conventional surfactants and intercomparison has been made for their abilities to solubilize the PAHs.

2. Experimental section

2.1. Chemicals

Anthracene (99.5%) was purchased from Koch-Light Laboratories Ltd., England. Naphthalene (99.7%) and pyrene (99%) were obtained from Fluka, Switzerland. The amphiphile AOT was procured from S. D. Fine, India with a purity of 98.5%. CTAB (99%) and Brij 58 were purchased from Merck, Germany. All the chemicals were used without further purification. Freshly prepared distilled water was used throughout. The PAHs have two or more benzene rings in their

---

* Corresponding author. Tel.: +91 571 2700920x3353.
E-mail address: kabir7@rediffmail.com (Kabir-ud-Din).

0167-7322/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.molliq.2011.08.002

structures (their properties and structures along with the structure of the surfactants are given in Scheme 1).

2.2. Synthesis of gemini surfactant

The dimeric gemini hexanediyl-*1*,*6*-bis(dimethylcetylammonium bromide) $C_{16}H_{33}(CH_3)_2$–N^+-$(CH_2)_6$–$N^+(CH_3)_2C_{16}H_{33}$,$2Br^-$ surfactant (16-6-16, G6) was synthesized in the laboratory by refluxing *1*,*6*-dibromohexane with *N*, *N*-dimethylcetylamine (molar ratio 1:2.1) in dry ethanol with continuous stirring at 80 °C for 48 h to ensure as much as possible a complete bisquaternization.

$$Br(CH_2)_6Br + 2CH_3-(CH_2)_{15}-N(CH_3)_2 \xrightarrow[48h,\ 80\ ^\circ C]{\text{Reflux, dry ethanol}} C_{16}H_{33}(CH_3)_2N^+-(CH_2)_6-N^+(CH_3)_2C_{16}H_{33}.\ 2Br^-$$

The progress of the reaction was monitored by using TLC technique. After the completion of the reaction the solvent was removed under vacuum. After crystallization, the surfactant was characterized by ^1H NMR and FT-IR [19]. All the values obtained were satisfying, which indicated that the surfactant was well purified.

2.3. cmc determination by surface tension measurements

Tensiometric experiments were performed using a platinum ring by the ring detachment method with a Kruss (Germany, Model K11) tensiometer equipped with a constant temperature water circulating device. The surfactant concentration was varied by adding concentrated surfactant solution in small installments, and the readings were noted after thorough mixing and temperature equilibration.

2.4. Solubilization experiments

The solubility of naphthalene, anthracene and pyrene were measured in different surfactant solutions between ranges of concentration above the *cmc*. Excess PAH was added to screw-capped vials containing a fixed volume of micellar solution to ensure maximum solubility. This mixture was stirred using a magnetic stirring bar for 24 h at 30 °C. An aliquot of the sample was collected and then centrifuged at 12,000 rpm to remove the undissolved PAH. The concentration of the solubilized PAH was determined spectrophotometrically with a Shimadzu spectrophotometer (Model UV mini–1240) following appropriate dilution of an aliquot of the supernatant with the corresponding surfactant solution. The surfactant concentration was kept the same in both the reference and the measurement cells to eliminate its effect on the UV-absorbance.

3. Results and discussions

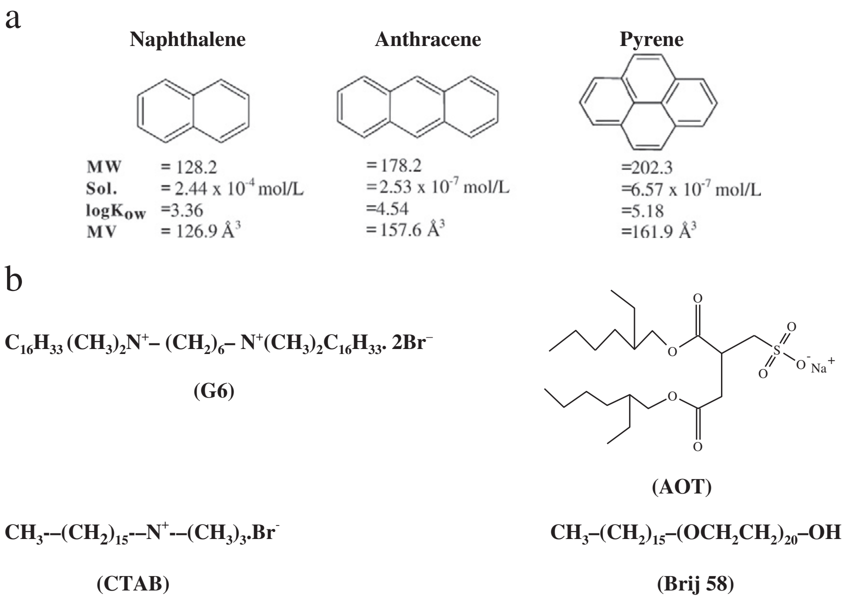
3.1. Surface and micellar properties

3.1.1. cmc

The concentration of surfactants in aqueous medium above which the surfactant monomers start assembling together to form the micelles is known as critical micelle concentration (*cmc*). The *cmc* values of pure as well as of binary surfactant mixtures (cmc_{exp}) were evaluated on the basis of tensiometric measurements. Surface tension decreases as the concentration of the surfactant increases. Surfactant molecules at low concentrations adsorb at the liquid/air interface until the surface of the solution is completely occupied. Then the excess molecules tend to self-associate in the solution to form micelles, and surface tension becomes constant. Two opposite effects control micellization: the effect of the hydrophobic group is an important driving force in micellization and the effect of the hydrophilic group opposing it. The *cmc* values were determined by noting inflections in the surface tension (γ) versus logarithm of surfactant concentration isotherms and are given in Table 1. The gemini surfactant has remarkably low *cmc* value as compared to the conventional surfactants because of its two polar head groups and two hydrophobic chains which transfer at the same time from the aqueous phase to micellar phase.

3.1.2. Γ_{max} and A_{min}

The liquid/air interface of a surfactant solution is well populated by the adsorbed molecules. The surfactant concentration is always more



Scheme 1. (a) Structures and physicochemical properties, viz., molecular weight (*MW*), aqueous solubility (sol.), log K_{OW} (K_{OW} = octanol − water partition coefficient), and molecular volume (*MV*) of the polycyclic aromatic hydrocarbons used in this study. (b) Structures of surfactant molecules used in this study: hexanediyl-1,6-bis (dimethylcetylammonium bromide) (G6), cetyltrimethylammonium bromide (CTAB), sodium bis(2-ethylhexyl) sulfosuccinate (AOT), and polyoxyethylene (20) cetyl ether (Brij 58).