Solubilization efficiency of mixed cationic aggregates towards aromatic compounds

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ABSTRACT

The present work deals with the aggregation behaviour and structure transitions of mixed system of dioctadecyldimethylammonium chloride (DODAC) and dodecylethyldimethylammonium bromide (DDAB) in order to further evaluate its solubilization efficiency of aromatic compounds. Structure transitions and stability of the prepared formulations have been assessed by differential scanning calorimetric (DSC), zeta potential and fluorescence spectroscopy. The vesicle–micelle transition has been analyzed by fluorescence anisotropy measurement at various pH (3.2, 7.2 and 11.2). The mixed surfactant system has further been utilized to enhance the solubility of a hydrophobic moiety i.e. pyrene. Various parameters such as molar solubilization ratio (MSR), partition coefficient (K_m), association constant (K_1) and average number of pyrene molecule associated with aggregate (S^M) have been estimated. Present work provides information about the precise vesicle–micelle transition point in a mixed micellar system and takes into account the solubilization selectivity, where vesicles show higher solubilization efficiency as compared to micelles.

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1. Introduction

There are reports [1–4] where surfactant mixtures have effectively resulted in spontaneous vesicle formation. The major thrust has been given to mixed aqueous systems based on two co-solutes of colloidal size. This results in varied pattern of phase behaviour and aggregation equilibrium [5–8]. The domain of vesicle concentration is constrained by critical vesicle concentration (cvc) towards the monomer-mixed vesicle transition and thereafter by the concentration at which the mixed vesicles are disrupted and dissolved due to the formation of mixed micelles, specified as critical mixed micelle concentration (cmc). Lichtenberg [9] suggested that equilibrated transitional phases are present where vesicles, micelles and intermediate mixed micelles coexist with mixed vesicles. The physico-chemical parameters of any micelle-vesicle formulations i.e. type, characteristics and stability are governed by several factors such as respective concentration of the two surfactants, counter ions and their molecular properties [10].

As far as the interactions between a single and the double chained surfactants are considered, lower concentrations play an important role where the single-chain surfactant is incorporated into the vesicle membrane (without vesicle breakdown), depending on the partition equilibrium between the vesicle bilayer and the aqueous phase. This feature largely affects the vesicle behaviour in terms of size, flexibility and solubility potential and offers variety of practical applications such as drug delivery, gene transport and solubilization etc. However, at concentration higher than cmc, the solubilization of vesicles are much pronounced, therefore vesicle–micelle transition is expected to take place [11]. The mixed surfactant micelle/vesicle formulations have emerged as prime systems to explore the interactions between the amphiphilic molecules and vesicular bilayers [12]. Feitosa et al. [13] have spontaneously obtained unilamellar supramolecular aggregates of dioctadecyldimethylammonium X (DODAX, X = Cl$^-$, Br$^-$) surfactant by simply mixing with water. The addition of a single-chain surfactant to a double-chain surfactant/water system drives to the formation of a mixed system especially vesicle aggregates [14–16]. Safran et al. [17] have analyzed the stability of such spontaneously formed vesicles in the mixed surfactant system where the curvature of outer and inner monolayer of the vesicular membrane plays a role.

Referring to simplicity in structural association and to enhance its water solubility, the aggregation properties of double chained dioctadecyldimethylammonium chloride (DODAC) in mixed surfactant system are important. Colloidal properties of DODAX (DODAX, X = Cl$^-$, Br$^-$) in single as well as in mixed states have been

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analyzed either keeping the same chain length or counter ion [18]. However, most of the experiments have been performed at low total concentration of mixed micelles.

Knowledge of solution behaviour of mixed surfactant can efficiently serve as remediation for different problems like solubilization of industrial pollutants (namely organic compounds), dye encapsulation and water contamination, etc. Almost all of the organic compounds are insoluble in aqueous media. Polycyclic aromatic hydrocarbons (PAH) are one such class of pollutants [19,20]. Owing to low aqueous solubility and vapor pressure [21], their removal from environment still presents a considerable challenge to the researchers. Therefore, the utility of surfactant assembly in solubilizing organic solutes is explored, where the central core of the micelle constituting a hydrophobic pseudophase is expected to accommodate a negligible water soluble entity [22,23]. In recent years, a considerable amount of work has been conducted on the surfactant aided remediation of PAHs, which focused on the use of single non-ionic, anionic and cationic surfactants [24–26]. In contrast, only limited numbers of investigations reported the solubilization of PAHs in mixed ionic surfactant systems [27].

The aim of the present study is to enhance the solubility of DODAC and for that the choice of surfactant has been made in such a way that aggregation concentration can be enhanced. Therefore, dodecylethyldimethylammonium bromide (DDAB) with cmc ~15 mM has been selected [28]. The analyses have been made keeping in mind parameters like different chain length and counter ion. Fluorescence, differential scanning calorimetric (DSC) and zeta potential measurements have been utilized to access the solution behaviour, structure transformation and stability of mixed system with increasing mole fraction of single chain DDAB. Further, the aggregation concentration of mixed system at each mole fraction has been estimated by fluorescence technique using anilinonaphthaline-8-sulfonate (ANS) as probe. An effort has also been made to estimate the enhanced aqueous solubility of pyrene in a cationic–cationic (DDAB + DODAC) mixed surfactant system as a function of mole fractions using UV–vis spectroscopy technique.

2. Materials

Dioctadecyldimethylammonium chloride (DODAC) (purity > 98%), dodecylethyldimethylammonium bromide (DDAB) (purity > 98%), pyrene (purity > 97%), cetylpyridium chloride (CPC), sodium acetate (purity> 99%), acetic acid (purity > 99%) and 1-anilinonaphthaline-8-sulfonic acid (ANS) were purchased from Sigma Aldrich. Potassium dihydrogen phosphate (KH_2PO_4) (purity 98%) and disodium hydrogen phosphate (Na_2HPO_4) (99%) were purchased from Merck. Sodium hydroxide (purity 97%) was purchased from Qualigens. Water used for the preparation of samples was de-ionized and double distilled (conductivity $\leq 3\,\mu S$ at 298.15 K).

3. Methods

To observe the critical aggregation concentration (cac) at each mole fraction ANS was used as a probe with excitation at 330 nm and emission collection range of 340–650 nm Excitation and emission slits were fixed at 5 nm (scan rate 1200 nm/min). Vesicle to micelle transition *via* anisotropy measurements of mixed surfactants in terms of mole fractions have been determined using fluorescence (Hitachi-F7000) with quartz cells. Pyrene was used as luminescence probe (because it shows better anisotropic properties in aggregate media) and its concentration was kept constant at 10^{-3} mM. Both excitation and emission band slits were fixed at 5 nm and scan rate 1200 nm/min was selected. The excitation wavelength was selected at 330 nm, while the emission spectra were

collected in the range 350–500 nm Aggregation number has also been determined by fluorescence quenching technique at all mole fractions. Instrument settings were same as used in anisotropy measurement using same stock solution of pyrene. Cetyl pyridium chloride (CPC) as quencher with concentration range of 70–700 μM was used. The transitions in mixed micellar structure have been confirmed by Differential Scanning Calorimetry (DSC Q-20) using 10 °C/min heating rate. The aluminium pan was filled with 5–10 mg of solution and the reference vessel with the same amount of deionized water. Stability of the formed assemblies has been assessed by zeta potential measurement (Microtrac nanotrac wave). For solubility studies, UV–vis spectra were collected in the range of 200–400 nm using quartz cells in Thermo Scientific Evolution 160 UV-vis spectrophotometer. All the experiments were performed in duplicate to assess the reproducibility.

4. Sample preparation

Batch tests for solubilization of pyrene in surfactant solutions were performed at various mole fractions using mixed cationic surfactants, DDAB having 12 carbon alkyl chains as hydrophobic group and DODAC with di-18 carbon alkyl chain as hydrophobic groups. 3 ml of five concentrations of mixed surfactants above the cmc values (at different mole fractions) were prepared. Pyrene was separately added to each vial in amounts slightly more than required to saturate the solution. The sample vials after sealing with screw caps were then agitated for a period of 24 h on a magnetic stirrer maintained at 298.15 K. The vials were left for sedimentation for a period of 2–3 h and then decanted. The decanted samples were subjected to centrifugation for 15 min to remove the undissolved solid pyrene. Further, the samples were filtered through 0.45 μm membrane. The concentration of dissolved pyrene was determined spectrophotometrically following appropriate dilution of an aliquot of the supernatant at respective concentrations of mixed surfactants. The surfactant concentrations were kept same in both reference and measurement cells.

5. Results and discussion

5.1. Aggregation of mixed surfactant system

An effort has been made to observe the critical aggregation concentration (cac) of mixed surfactant system using fluorescence spectroscopy with ANS as a probe. ANS is highly sensitive to polarity of the media, it has been found that ANS emit very weakly in water (polar) and strongly emitted in hydrophobic (nonpolar) media [29]. The experiment was designed by keeping DODAC constant (1 mM) and increasing DDAB mole fraction. The variation of fluorescence intensity of ANS for each mole fraction of DDAB in DODAB surfactant was measured with increasing total mixed surfactant concentration. At lower mole fraction of DDAB when DODAC is in excess and above its critical vesicle concentration (1 nM), only mixed vesicles are formed which can be seen in Fig. 1a–c, at low mole fraction of DDAB only a single transition appears which is due to mixed vesicles. While as DDAB mole faction is increased (X = 0.285) two significant transitions has been appeared, initially due to mixed vesicle formulation and later due to vesicle–micelle transitions. Micelles formation has been supported by decrease in intensity of ANS emission peak after second transition (Fig. 1c and d) due to less compactly bonded surfactant in micelles as compare to vesicles. However, mixed vesicle formulation concentration increases with mole fraction of DDAB (Table 1).

Further, vesicle–micelle transition has been confirmed by DSC. At lower mole fraction of DDAB (much lower than the cmc of DDAB), main peak transition is observed at $T_m \approx 408.15$ K (135 °C) (Fig. 2).