Aggregation behavior of Dioctadecyldimethylammonium chloride in mixed cationic surfactant system

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ABSTRACT

The spontaneous formation of mixed vesicles, their coexistence and solubilization due to formation of mixed micelles were investigated for the double chain Dioctadecyldimethylammonium chloride (DODAC) and a single chain Dodecylethyldimethylammonium bromide (DDAB), mixed cationic surfactants. Various analytical techniques viz., conductivity, surface tension, fluorescence and absorption spectroscopy were utilized. To gain an insight into the mixed aggregate formed, thermodynamic free energy, molecular interaction parameter, the total critical micelle concentration and degree of ionization of the mixed micelle (α) as a function of molar ratio were assessed. Acoustic properties of the mixed surfactant system as functions of temperature were also calculated. Interaction of pyrene with mixed aggregates in the present system was assessed through fluorescence spectroscopy (at cvc as well as cmc) at 298.15 K and atmospheric pressure.

1. Introduction

Vesicles are double-chain surfactant aggregates consisting of one or more surfactant bilayers that separate an inner region of water from a continuous phase of the same fluid. It is understood that non-equilibrium methods such as dialysis, extrusion of lamellar suspension, and reverse phase evaporation are required to obtain vesicles from open lamellar surfactant bilayers because the inner and outer mono-layers have an opposite sign of curvature [1–8].

Single-chain surfactant in aqueous medium forms micelles and their addition to the double chain surfactant system drives to the formation of mixed vesicle aggregates [3–5]. Safran et al. [9] successfully analyzed the stability of vesicles in the mixed surfactant system where the extent of curvature plays an important role. There are a number of reports on mixed surfactant vesicles, which formed spontaneously [10–13]. The major thrust has been given to mixed aqueous systems based on two co-solutes of colloidal size. This results in varied patterns of phase behavior and aggregation equilibrium [14–17]. This largely affects the vesicle behavior in terms of flexibility and solubility potential and offers a variety of practical applications such as drug delivery, and gene transport. The physico-chemical parameters of any micell–vesicle formulation are governed by several factors such as concentration of the two surfactants, counter ions and their molecular properties [18].

If interactions between a single and double chained surfactants are considered, at lower concentrations, single-chain surfactant merged

into the vesicle membrane (without vesicle breakdown) to form mixed vesicles. However, at concentration higher than the cmc of a single chain surfactant, it shows its character predominantly and therefore, vesicle–micelle transition is expected to take place [19–21]. Lichtenberg [20] suggested the coexistence of equilibrated transitional phases of vesicles, micellar and intermediate mixed micelles. DODAC vesicles (a cationic liposome) have been reported to be of profound use, both in fundamental studies on interfacial phenomena and in practical applications [22]. DODAC is a long double chained [$(C_{18})_2$] cationic surfactant. In aqueous media, it easily self-assembles as large unilamellar vesicles (LUV) above its phase transition (gel to liquid crystalline) temperature [23,24]. However, low water solubility restricts the utility of DODAC. Referring to simplicity in structural association and to enhance its water solubility, the present work is aimed at investigating the aggregation properties of double chained Dioctadecyldimethylammonium chloride (DODAC) (Fig. 1) in a mixed surfactant system. Analytical methods viz. surface tension, fluorescence spectroscopy, absorbance spectroscopy, density and conductivity have been utilized to access the solution behavior of the studied surfactant in the presence of a single chain Dodecylethyldimethylammonium bromide (DDAB) (Fig. 1) at increasing molar ratio. The analysis has been carried out between the critical micellization concentration (cmc) region of both the surfactants i.e. 15 mM for DDAB and 3.9 nM for DODAC [23,25]. The behavior of the DODAC/DDAB/H_2O mixed system has also been analyzed in terms of interaction (β^m) parameter, thermodynamic feasibility of the aggregation value (ΔG) and acoustical properties. Knowledge of solution behavior of DODAC (mixed form) can efficiently serve as remediation for different problems like solubilization of biomolecules, dye encapsulation and water

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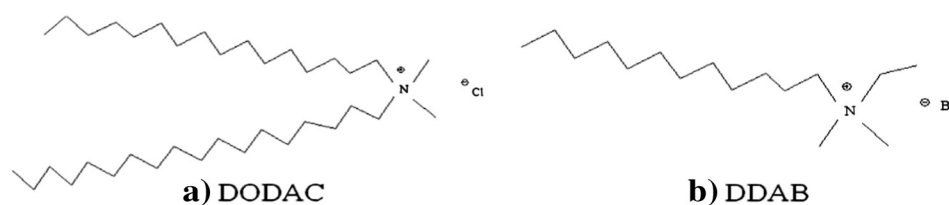E-mail address: skmehta@pu.ac.in (S.K. Mehta).

Fig. 1. Chemical structure of (a) DODAC and (b) DDAB.

contamination. The site of interaction of water contaminant (pyrene) with mixed vesicles and mixed micelles membrane has also been studied.

2. Experimental

2.1. Material

Table 1 shows the materials used in this study.

2.2. Methods

2.2.1. Conductivity measurements

The conductivity of mixture was measured in a thermostatic glass cell with two platinum electrodes and a Pico conductivity meter from LABINDIA. The glass cell was connected to the RE320 Ecoline thermostat controlled to better than ± 0.01 K temperature variations. The cell constant of the cell used was 1.11 cm^{-1}. The measurement of conductivity was carried out with absolute accuracy up to $\pm 3\%$. The solutions were prepared by weight using an analytical balance with an accuracy of $\pm 1 \times 10^{-4}$ g. The conductivity measurements were made at different molar ratios for the mixed surfactant system as a function of surfactant concentration.

2.2.2. UV–vis. spectroscopy

UV–vis. spectra were recorded with a Thermo Scientific Evolution 160 UV–vis. spectrophotometer using quartz cells. In the experiment for the DODAC/H$_2$O binary system, the concentration of surfactant was varied from 0 μM to 1 mM while for the DODAC/DDAB/H$_2$O ternary system concentration varies from 0 to 15 mM.

2.2.3. Fluorescence spectral studies

Fluorescence measurements were carried out with a Perkin Elmer-L55 spectrophotometer. A 1 cm rectangular silica cell was placed in a multicell holder at room temperature. Pyrene was used as a luminescence probe as it is highly polarity sensitive and its concentration was kept constant at 1 μM as it is poorly soluble in water [26]. Both excitation and emission band slits were fixed at 10 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 in the range 350–490 nm.

2.2.4. Surface tension measurements

The surface tension measurements (γ) of DDAB and DODAC aqueous solutions were made by the ring method using the Krüss K20

tensiometer, under controlled temperature using a thermostat having a temperature precision of ± 0.05 K. The platinum ring was cleaned and a flame dried before each measurement. Next it was dipped into the solution to measure its surface tension. Measurements of the surface tension of pure water at 298.15 K were performed to calibrate the tensiometer and to check the cleanliness of the ring and glassware. The measurements were conducted until equilibrium. Standard deviation did not exceed ± 0.2 mN/m. The observed surface tension for solvent used in this study i.e. water is comparable with the literature value indexes in Table 2.

2.2.5. Density and speed of sound analyzer

The thermodynamic properties viz. density (d) and speed of sound/ultrasonic velocity (u) of mixed surfactant at different temperatures (288.15–308.15 K) were measured using a commercial density and speed of sound measurement apparatus (Anton Paar DSA 5000 densimeter and speed of sound analyzer) which is controlled to better than $\pm 1 \times 10^{-3}$ K temperature by a built-in solid state thermostat. The reproducibility of density and speed of sound measurements is $\pm 1 \times 10^{-6}$g/cm^3 and $\pm 1 \times 10^{-2}$m/s, respectively. The uncertainties of density and speed of sound measurements are less than 5×10^{-6}g/cm^3 and 5×10^{-2}m/s, respectively. All measurements were done at least three times at constant temperature and average was recorded. Density and speed of sound values of water are listed in Table 2 and show a good agreement with literature values [27-32].

3. Results and discussion

3.1. Mixed surfactant formulations

Conductivity studies have been carried out for the mixed binary cationic surfactant system in complete concentration range (up to 15 mM) at different molar ratios (X_1) at 298.15 K. Fig. 2a shows a decrease in the conductivity of the mixed system with an increase in the molar ratio of DODAC. High conductivity of the system is mainly due to free ions which are governed by the precipitation of the mixed surfactant system. However, with an increase in the molar ratio of DODAC precipitation decreases and hence the conductivity also decreases. Two transition states appeared with the first break at very low concentration (Fig. 2b) which indicates the critical vesicle concentration (cvc) of the mixed system, since the concentration of DODAC is large enough to form the vesicle at whole molar ratio. The second break indicates the micellar formation by mixed surfactant formulation that is much lower than the critical micelle concentration (cmc) of pure DDAB and is caused by DODAC in the media.

Table 1
Specifications of chemicals used.

Compound name	CAS number	Molar mass (g/mol)	Supplier	Purity
Dioctadecyldimethylammonium chloride (DODAC)	107-64-2	586.5	Fluka	≥97%
Dodecylethyldimethylammonium bromide (DDAB)	68207-00-1	322.38	Sigma Aldrich	≥98%
Pyrene	129-00-00	202.25	Fluka	≥97%
Water	Triply distilled (conductivity ≤ 3 μS at 298.15 K)			