Journal of Molecular Liquids 258 (2018) 163–171

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Temperature controlled comparative physico-chemical studies of DTAB and 12-2-12 Gemini surfactants in aqueous solutions of fructose, maltose and raffinose

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ARTICLE INFO

Article history:
Received 22 December 2017
Received in revised form 20 February 2018
Accepted 28 February 2018
Available online 01 March 2018

Keywords:
Micellar behaviour
Critical micelle concentration
Standard Gibbs free energy
Surface excess concentration
Surface film pressure

ABSTRACT

The Micellar behaviour of synthesised cationic Gemini surfactant ethanediyl-1,2-bis (dimethyldodecylammonium bromide) and its single-chain counter-part i.e., Dodecyltrimethylammonium bromide (DTAB) in absence and presence of carbohydrates (fructose, maltose and raffinose) has been investigated. The conventional technique viz. surface tension measurements over a wide range of temperature, (293.15–313.15 K with an interval of 5 K) and spectroscopic method i.e. fluorescence probe at room temperature have been employed to determine critical micelle concentrations (*CMC*'s) of both the surfactants. The decrease in *CMC* have been found for both the studied surfactants; however the effect being more prominent in case of Gemini surfactant (GS). From surface tension data, various interfacial parameters have been evaluated that reflects the presence of stronger electrostatic attractions between carbohydrates and the micelle of surfactants. The *CMC* values calculated using both the studies have been found to be in good agreement and corroborate each other's observations.

1. Introduction

Several different experimental techniques have been explored by researchers to get insight of the molecular interactions between the surfactant-carbohydrate systems. Both surfactant and carbohydrates are widely used in chemical engineering, medicine, biology, cosmetics, food and life systems [1–3]. Surfactants can be assembled to form small organized aggregates such as micelles, micro–emulsions, vesicles and liquid crystals, used as models to simulate life systems and to prepare functional materials which occur at a concentration known as critical micelle concentration (*CMC*). Micelles can mimic biological cells to study the essentials and functions of bioactive substances in life system [4,5]. However, in recent years these surfactants have been replaced by the new class of amphiphilic molecules i.e., Gemini surfactant (GS) which emerged as better substitutes and attracted the attention of various individuals and academic research groups [6–8].

In comparison with corresponding single chain surfactants, these surfactants are more efficient in lowering surface tension and have much lower *CMC* values [9,10]. These kinds of surfactants have many unique properties that are superior to their single-chain counterparts, such as remarkably low *CMC*, much higher surface activity, unusual aggregation morphologies, better wetting, solubilizing and foaming properties. It has been established that the spacer plays a major role in the aggregation properties of these surfactants, which has been attributed to the variation in the confirmation of the surfactant molecule and to the change of the spacer location in the micelles [6,9–11].

Surfactant/Gemini surfactant in the presence of additives like electrolyte, drug, co-surfactant, bio-molecules (e.g. carbohydrate and amino acids) etc. have the ability to change their conformation in aqueous solutions which can lead to changes in the appearance, stability or rheology of the solution as is shown by recent studies on surfactant–carbohydrate–water systems [12–14]. Owing to the special architectures and properties of Gemini surfactants, it is interesting to compare the stabilizations of Gemini and single-chain surfactant micelles with additives such as carbohydrates, which can promote our understanding in respect of interaction mechanism of Gemini surfactant micelles in the presence of carbohydrates and further help to design the most effective encapsulation carrier of their hydrophobic part.

Although, the effect of these additives on the *CMC* of DTAB and 12-2-12 Gemini surfactant in aqueous systems has been well documented in literature by using different experimental techniques [15–18], but, the effect of carbohydrates like fructose, maltose, raffinose etc. on the micellization behavior of surfactants still have not been investigated,

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https://doi.org/10.1016/j.molliq.2018.02.129
0167-7322/

especially by using surface tension, viscometric, conductance, fluorescence and ultraviolet studies, respectively.

Keeping the above cited facts in mind, in the present paper, the *CMC* of synthesised 12-2-12 Gemini surfactant (GS), ethanediyl-1,2-bis (dimethyldodecylammonium bromide) and single-chain surfactant Dodecyltrimethylam-ammonium bromide (DTAB) have been determined in aqueous solutions of carbohydrates and critically compared at different temperatures.

2. Materials and methods

2.1. Materials

Carbohydrates, D (−) fructose, D (+) maltose monohydrate and D (+) raffinose pentahydrate of high purity were purchased from SD–fine Chem. Ltd. All Carbohydrates were re-crystallized twice in distilled water and dried in vacuum oven for 24 h at ~50–60 °C. Surfactant, Dodecyltrimethylammonium bromide (DTAB), obtained from SD–fine Chem. Ltd. has been used for the studies after re-crystallizing twice in A.R. grade ethanol. The final product was dried in vacuum oven for 24 h at ~50–60 °C. However, the 12-2-12 Gemini surfactant, namely ethanediyl-1,2-bis (dimethyldodecylammonium bromide) was synthesised from chemicals i.e., 1-Bromo dodecane and *N*,*N*,*N*,*N*-tetramethylethylenediamine purchased from SISCO research laboratory Pvt. Ltd. and HIMEDIA Laboratories Pvt. Ltd. respectively. The prepared Gemini surfactant was re-crystallized in the presence of acetone (A.R. grade). Distilled water being the main solvent in the present study for all experiments and also required to calibrate the apparatus, was obtained from a Millipore – Elix system; the conductivity, κ and the pH of the water collected water sample were ($1–2 \times 10^{-7}$ S cm^{-1}) and (6.8–7.0), respectively. The specification and mass fraction purity of the material used have been reported in Table 1.

2.2. Methods

2.2.1. Synthesis of 12-2-12 Gemini surfactant

12-2-12 Gemini surfactant referred to as m–n–m, where m = 12 and $n = 2$,was synthesised as reported in the literature [19–21]. Mixture of 1-Bromo Dodecane and *N*,*N*,*N*,*N*-tetramethylethylenediamine (TEMED) in a molar ratio of 2:1 in dry acetone (30 mL) was refluxed (approx. 48 h) at 343.15–353.15 K until the entire volume of diamine was consumed. After removal of the solvent by evaporation, the crude surfactants were re-crystallized twice in dry acetone. The resulting product was dissolved in the minimum volume of absolute ethanol and subsequent extractions with hexane/ethyl acetate (50/50) to eliminate the excess of alkyl bromide. A white product was finally obtained by filtration under vacuum pressure. The product was dried and stored in desiccators to prevent moisture absorption. A systematic scheme for the synthesis of 12-2-12 Gemini Surfactant is shown in Fig. 1:

The synthesised 12-2-12 Gemini surfactant has been characterised ^{1}H NMR, ^{13}C NMR and FTIR spectroscopic techniques using JNM–ECS400 spectrometer and RZX (Perkin Elmer) Fourier Transform Spectrometer, respectively. The spectrum present in our earlier publication [22] confirms the purity of the product.

2.2.2. Surface tension measurements

The surface tension of these surfactants solutions in water and aqueous solutions of carbohydrates have been determined by drop number method using Man Singh Survismeter supplied by Spectro Lab Equipment's Pvt. Ltd. [22,23], which is an inexpensive device for measuring surface tension and viscosity of the solution, simultaneously (calibration No. 06070582/1.01/C-0395, NPL, Govt. of India). The Survismeter was periodically cleaned by treating with chromic acid and distilled water and finally washed with acetone and dried in oven for sufficient time. Then it was filled with known volume of the test solution and was suspended in a high precision thermostated water bath supplied by Narang Scientific Works Pvt. Ltd., New Delhi, India which was maintained at a desired temperature ±0.01 K for about 30 min prior to recording the number of drops of solution at each temperature of study. The average deviation for two–three concordant measurements of a single concentration of the solution did not exceed ± 1 drop. The calibration of the Survismeter was done using DMSO and methanol at 298.15 K. The γ values of DMSO and methanol (43.33 and 22.41 mN m^{-1}) were found to be in reasonable agreement with those reported in literature [24,25]. The reproducibility for the surface tension measurements comes out to be 0.10 mN·m^{-1}.

However, the solutions for the study were prepared by making stock solutions of carbohydrates (fructose, maltose and raffinose) (0.01 and 0.10) mol kg^{-1} in distilled water and used as solvents for the preparation of surfactant solutions. The required concentrations of DTAB (3.0–-30 mmol kg^{-1}) and 12-2-12 Gemini surfactants (0.2–2.0 mmol kg^{-1}) have been obtained by adding small aliquots of a concentrated surfactant solution to 20 mL of carbohydrate stock solution. The solutions so prepared have been gently stirred on a magnetic stirrer before being subjected to measurements.

2.2.3. Fluorescence probe studies

Fluorescence probe analysis is an important technique in biophysical studies of multimolecular aggregates such as micelles. Various spectral methods using dye and other compounds as probes, and self–absorption of amphiphiles in solution are used for the evaluation of critical micelle concentration (*CMC*) [27,28]. In addition, fluorescence of probe molecules has been successfully employed for the above purpose [29]. Among the fluorescent probes, pyrene has been extensively used who's emission characteristics are very often considered to estimate the polarity level of its environment (say micelles) as well as *CMC* of amphiphiles [30]. Studies with pyrene as a fluorescence probe have received special consideration [31] due to its several interesting photo–physical properties which make it suitable for use as an effective probe, especially the long life–time of pyrene monomers and efficient formation of excimers. Further, pyrene is a strongly hydrophobic probe and its solubility in water is very low. In the presence of micelles and other macromolecular systems, pyrene is preferentially solubilized in the interior hydrophobic regions of these aggregates. It clearly shows that the pyrene senses the polar environment of solvent system

Table 1
Specification and mass fraction purity of chemical samples used in the experiment.

Chemical name	Source	Purification method	Mass fraction purity
Carbohydrates	SD–fine Chem. Ltd. (India)	Re-crystallized	0.98
Dodecyltrimethylammonium bromide (DTAB)	SD-fine Chem. Ltd. (India)	Re-crystallized	0.98
Ethanol, AR	MERCK (Germany)	none	0.99[a]
Acetone, AR	HIMEDIA (India)	none	0.99[a]
1-Bromo dodecane	SISCO Research Lab. Pvt. Ltd. (India)	none	0.99[a]
N,*N*,*N*,*N*-Tetramethylethylenediamine	HIMEDIA (India)	none	0.99[a]
Gemini surfactant	Synthesised in our laboratory	Re-crystallized	0.98
Pyrene	MERCK (Germany)	None	0.99[a]

[a] Declared by supplier.