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Influence of lactose on the micellar behaviour and surface activity of bile salts as revealed through fluorescence and surface tension studies at varying temperatures

S. Chauhan *, Vivek Sharma, Kuldeep Singh, M.S.Chauhan, Kailash Singh

Department of chemistry, Himachal Pradesh University, Shima-5, India

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ABSTRACT

In this paper, an attempt has been made to explore some information about the effect of disaccharide (lactose) on the micellization mechanism of bile salts namely sodium cholate (NaC) and sodium deoxycholate (NaDC) by applying surface tension and fluorescence probe techniques for ternary (water + lactose + NaC/NaDC) system. The critical micelle (aggregation) concentration (*CM(A)C*) values for NaC (4 to 22 mmol·dm^{-3}) and sodium NaDC (1 to 10 mmol·dm^{-3}) in aqueous solutions of lactose (0.0, 0.5, 1.0, and 1.5) % w/v in the temperature range 293.15 to 313.15 K at an interval of 5 K, has been determined from both the studies. Fluorescence probe study has also been applied in order to determine *CM(A)C* for the studied system, which endorses the results drawn from surface tension studies. Different interfacial and thermodynamic parameters derived from surface tension (γ) values and their variations have been explained in terms of modification in surface activity and micellar behaviour of these bile salts. The *CM(A)C* values determined from these measurements are found to be in excellent agreement with each other.

1. Introduction

Bile salts especially known as bio-surfactants are synthesized from cholesterol (bile acids) in the liver and stored in the gallbladder. Chemically, they are amphipathic molecules having large non-polar hydrophobic moiety of a steroid nucleus and polar hydrophilic head groups which cause them to manifest characteristic behaviour in aqueous solution: surface activity and self aggregation (micelle formation). Bile salts act as emulsifying or solubilizing agents for hydrophobic dietary lipid molecules and amphipathic bio-molecules such as glycerides, fatty acids, cholesterol, lipids etc. [1–6]. The amphipathic nature of bile salts helps in lipid transportation by solubilization and also controls bio-synthesis of bile acids and cholesterol by negative feedback mechanism [7]. However, bile salts differ from classical surfactants in the sense that instead of long flexible hydrocarbon tail, they possess rigid steroid backbone and the hydrophilic —OH/—COOH groups lying at the other face. So in aqueous solution, bile salts by virtue of their structure form aggregates with small aggregation numbers (4–6 for NaC and 7–12 for NaDC) at a particular concentration known as critical micelle concentration (*CMC*), which is dependent upon number of —OH groups and their orientation as well as length and polarity of side chain [8–13].

Saccharides (carbohydrates) are essential bio-molecules that are bountifully found in nature. They are the structural components of DNA and RNA and play key role in energy transportation in living organism. They are also used in food, pharmaceutical and cosmetic industries [14–17]. They consist of polyhydroxy aldehydic/ketonic groups with well-defined orientation and show peculiar hydration behaviour in aqueous solution which is responsible for thermodynamic stabilization of bio-molecules such as proteins. [18]. Lactose (Scheme 1) is a disaccharide formed by the combination of glucose and galactose which are joined by β (1 → 4) glycosidic linkage. It is found in milk and extracted from sweet and sour whey. Moreover, multiple polar groups (hydroxyl/carbonyl) present on saccharide (lactose) may co-operatively interact with water and different bio-molecules such as proteins, bile salts etc., and can affect their aggregation/micellar behaviour [19,20]. Thus, it is interesting to study the systems containing bio-molecules such as bile salts, proteins in the presence of saccharides in order to explore our knowledge about the interactions and their effect on micellar/aggregation behaviour of these bio-molecules.

Although, micellar properties of the bile salts viz. sodium cholate (NaC) and sodium deoxycholate (NaDC) (Scheme 2) have been extensively studied by surface tension, electrical conductivity, osmometry, density, speed of sound and spectroscopic techniques such as fluorescence, UV/ visible, NMR, FTIR etc. [21–25]. But to the best of our knowledge, none of the author has studied the micellar properties of these bile

* Corresponding author.
E-mail address: scschauhan19@gmail.com (S. Chauhan).

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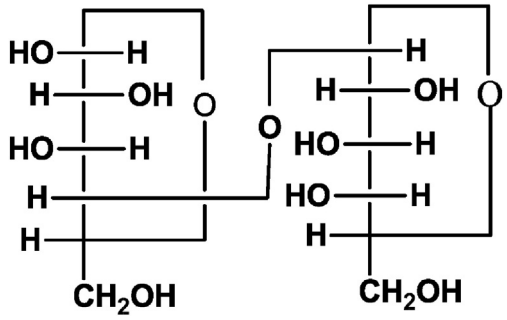


Scheme 1. Chemical structures of lactose.

salts in the presence of lactose. Keeping these points in mind and our own interest in such systems [26–28], in this paper our aim is to understand the effect of added different percentages of lactose (disaccharide) on micellar behaviour NaC and NaDC at the temperature range 293.15 to 313.15 K at an interval of 5 K.

2. Experimental

2.1. Materials

Sodium Cholate, sodium deoxycholate and lactose all were obtained from S.D. Fine-Chem limited and used after re-crystallization from ethanol following the similar procedure as reported in literature [29]. Doubly distilled water having conductivity (κ) in the range 2–3 × 10^{-6} S·cm^{-1}, surface tension ~72.14 mN m^{-1}, and pH 6.8–7.0 at 298.15 K, has been collected for use from Millipore-Elix distillation unit. Pyrene of A.R. grade with purity 96%, which is used as probe for the fluorescence studies, has been supplied by Merck, and is used without further purification. A summary of provenance and purity of chemicals used have also been provided in Table 1.

2.2. Methods

2.2.1. Fluorescence measurements

The fluorescence probe study has been carried out with LS 55 Perkins Elmer Fluorescence Spectrophotometer using a 10 mm path length quartz cuvette keeping excitation wavelengths at 334 nm and recording emission at 373 and 384 nm over the spectral range of 350–450 nm. The ratio of the intensities of the first and the third vibronic peaks in the fluorescence spectrum of pyrene (I_1/I_3) has been used to estimate the micropolarity sensed by pyrene in its solubilization site [22,30]. The excitation and emission slits have been kept at 8.0 and 2.5 nm, respectively. The accuracy and reproducibility in wavelength have been estimated to 0.1 nm and 0.5 nm respectively. However, the experimental solution of pyrene (2×10^{-6} mol·kg^{-1}) has been prepared according to the procedure reported in literature [31].

2.2.2. Surface tension measurements

The surface tension of bile salts solution in water and aqueous solutions of lactose has been measured by drop weight method using Man Singh Survismeter supplied by Spectro Lab Equipments Pvt. Ltd. [32]. The survismeter has been periodically washed with chromic acid, water and then with ethanol and dried for 3–4 h in oven. Then, survismeter is filled with experimental solution which is clamped in a high precision water thermostat (0.01 K) supplied by Narang Scientific Works Pvt. Ltd., New Delhi, India. The survismeter was subjected to calibration before use at 298.15 K by DMSO, MeOH, and 1,4-dioxane and surface tension (γ) values 43.33, 22.41 and 32.83 mN·m^{-1} are obtained which have been found reasonably in good agreement with those reported in literature [33,34]. The reproducibility for the surface tension measurements comes out to be in the range 0.10 mN·m^{-1}.

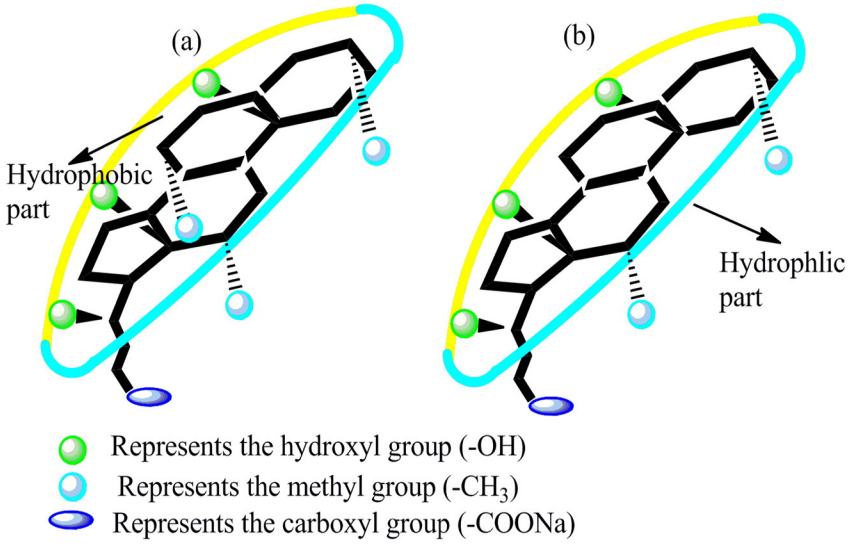
3. Results and discussion

3.1. Surface tension studies

Surface tension is a popular means for determining and understanding surface and bulk properties of the solution. In this paper, influence of lactose on the micellization behaviour and interfacial properties of NaC and NaDC have been examined by measuring surface tension of these bile salts in aqueous solution of lactose. The interfacial properties are useful in extracting valuable information about solute–solute and solute–solvent interactions in addition to micellar behaviour of bio-surfactants [35]. The surface tension, γ is calculated by using the relation [36]

$$\gamma = \gamma_0 \frac{n_0 \rho}{n \rho_0} \tag{1}$$

where γ_0, n_0, and ρ_0 are the surface tension, number of drops and density of solvent respectively and γ, n, and ρ are the surface tension,



Scheme 2. Hypothetical structural formula of (a) sodium cholate and (b) sodium deoxycholate.