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Probing effect of maltodextrin on micellar properties of bile salts at varying temperatures: A physico-chemical approach

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ABSTRACT

Surfactant micelles have a profound advantage to be used as an effective vehicle for the transport phenomenon and subsequently drug delivery purposes. In this context, density (ρ), speed of sound (μ), surface tension and viscosity techniques are employed in order to evaluate the type of interactions and micellar behaviour of bile salts i.e. sodium cholate (NaC) (4 to 22 $10^{-3}\cdot mol\cdot kg^{-1}$) and sodium deoxycholate (NaDC) (1 to 10 $10^{-3}\cdot mol\cdot kg^{-1}$) in aqueous solutions of maltodextrin (0.5, 1.0, and 1.5% *w/v*) over wide temperature range 293.15 to 313.15 K with interval of 5 K. The volumetric parameters have been calculated in order to explain bile salt-saccharide interactions through co-sphere overlap model. The surface tension data has been prudently analyzed in terms of interfacial parameters which assist to procure competing pattern of various intermolecular interactions, modification in surface activity and micellar behaviour existing in ternary (saccharide + water + surfactant) system. The surface tension values of *NaC* are found to be greater than *NaDC* in all the studied solvent systems, which clearly reflect the greater hydrophobic nature of *NaDC*. The viscometric parameters corroborate well with the finding of other techniques with respect to interaction. In conclusion, the results give an indication to assess and develop surfactant immobilized maltodextrin for better biological action.

1. Introduction

Bile salts, which are the biological surfactants, are important primarily for life of living organism. They are synthesized from cholesterol in the liver of vertebrates and stored in the gallbladder involved in the metabolism and excretion of cholesterol in mammals [1]. Bile salts have a crucial role in hepatobiliary and intestinal homeostasis and digestion. In addition, they play important biological roles in the absorption and transport of dietary lipids and fat soluble vitamins, as potent signalling molecules in both the liver and intestine through micelle formation [2]. Bile acids are tetracyclic steroid ring biplanar compounds whose molecules have two functionally different areas, the hydrophilic groups i.e. —OH/—COOH are oriented to the concave side of the rigid steroid ring system, while the convex side is hydrophobic i.e. hydrophobic ring [3–5]. By virtue of their structure, simultaneous presence of polar and non-polar areas in bile acid molecules yields their self-association as well as modification of a number of physico-chemical properties at the boundary surfaces. Because of their interesting physiological and physicochemical functions, these compounds are responsible for their unique properties, such as adsorption at interfaces, self-association, and solubilization of hydrophobic molecules [6–8]. In practical applications, reduction of the interfacial tension ensuring amphiphile usefulness in a given process is very often demanded underlying their wide use in the pharmaceutical, cosmetic, food, agrochemical, textile, paint, and coating industries as emulsifying, wetting and (anti)foaming agents, solubilizers, and suspension stabilizers. The unicity of the physico-chemical nature of such class of compounds can be invoked to explain this extraordinary interest. Due to their structure difference bile salts have also been studied in recent years as alternatives to conventional detergents for chemical analysis [9–10].

Saccharides are poly-hydroxy compounds typically non-electrolytes with several hydrophilic hydroxyl groups with complex three-dimensional arrays of functionality to their surroundings which are responsible for their peculiar hydration properties. The atypical nature of carbohydrates i.e. their pronouncedly hydrophilic character containing multiple hydroxyl groups with well-defined orientations are logical choices in stereoselective reactions for the synthesis of biologically active target molecules [11]. They not only are basic materials for energy metabolism in organisms but also play a significant role in the configuration of biological molecules. So the role of saccharides in biological regulation has attracted a great deal of attention in recent years [12–14]. In this paper, the saccharide used is maltodextrin which is derived from corn, rice, or potato starch. It is made of long chains of monosaccharides that are joined together by α-(1–4) glycosidic bonds. However upon hydrolysis maltodextrin is rapidly broken into simpler sugars i.e. glucose. The interactions of carbohydrates with food surfactants are extremely important in many food industries including chemical feed stocks, food production, preservation of processed foods, and so on [15–16].

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Saccharides have well defined orientation, show peculiar hydration behaviour in aqueous solution and by virtue of presence of various groups, they can interact well with bile salts, proteins etc. and may affect their aggregation process. This fact, together with the hydrophobic interactions between long hydrocarbon chains of bio-surfactants and saccharides lead to spontaneous association in water to form micelles. However, further aggregation and stabilization of these micelles in aqueous solution occurs through attractive forces such as intermolecular forces of attraction through hydrogen bonding between hydrophilic groups [17–19].

Thus, it is interesting to study the effect of saccharides on micellization behaviour and their interactions with these bio-surfactants. The micellar properties of bile salts have been extensively studied by surface tension, electrical conductivity, osmometry, speed of sound and some spectroscopic techniques such as fluorescence, UV/visible, NMR, FTIR etc. [20–23]. These experimental techniques are useful and provide sensitive information about ion-solvent interaction, ion-ion association and solvent structure. The aim of present work is to clarify the interactions and micellization of sodium cholate and sodium deoxycholate (Scheme 1) with the effects of different percentages of aqueous maltodextrin and temperature by using different techniques.

2. Experimental

2.1. Materials

Sodium cholate and sodium deoxycholate were obtained from s.d. fine-chem limited and used after re-crystallization from ethanol following the similar procedure as reported in literature [24]. Maltodextrin of high purity was purchased from Loba Chemie Pvt. Ltd. Doubly distilled water having conductivity (κ) in the range 2–3$\times$ 10^{-6} $S\cdot cm^{-1}$, surface tension ~72.14 $mN\cdot m^{-1}$, and pH 6.8–7.0 at 298.15 K, has been collected for use from Millipore-Elix distillation unit. A summary of provenance and purity of chemicals used have also been provided in Table 1.

2.2. Methods

2.2.1. Density and speed of sound measurements

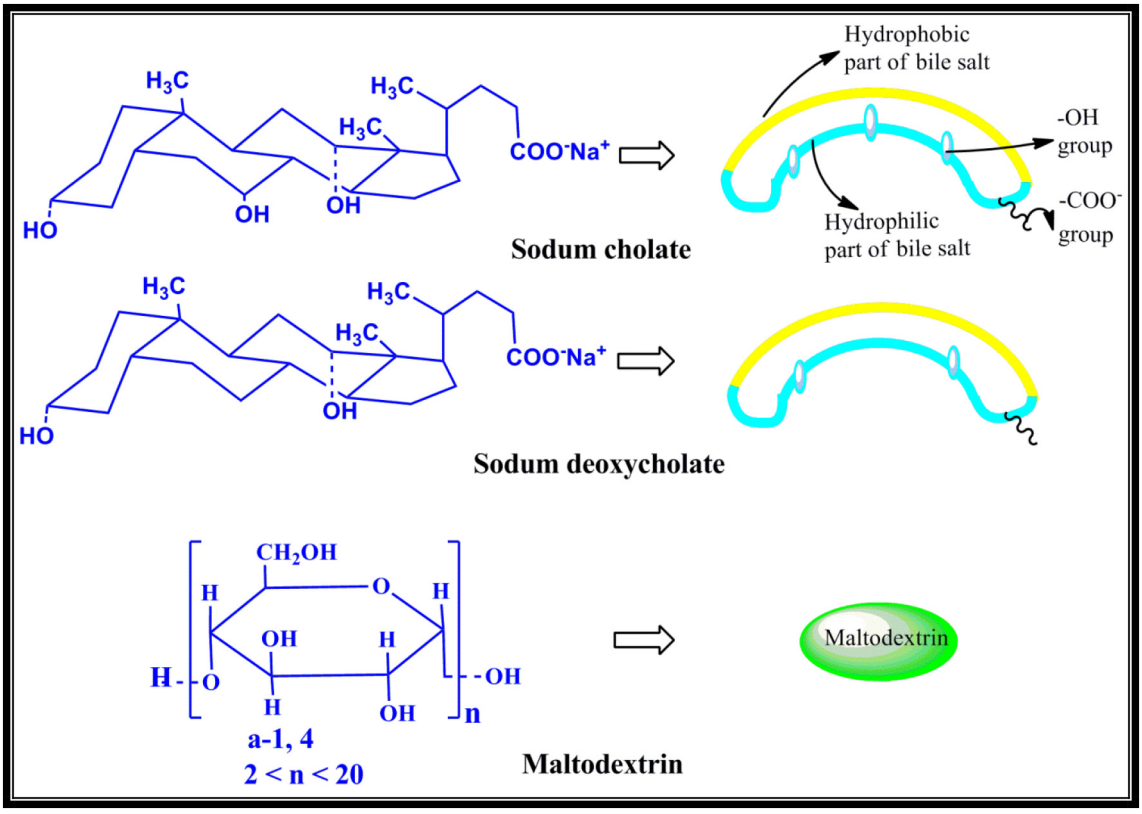
Density and speed of sound measurements have been performed with a high–precision digital Density and Sound Velocity Analyzer-5000 (DSA-5000) supplied by Anton Paar Gmbh, Austria. The instrument has been calibrated periodically with two fluids i.e. dry air and distilled water over a temperature range (293.15–313.15) K. This two-in-one instrument has been equipped with a density cell and a speed of sound cell; both the cells are thermally controlled by intrinsic Peltier thermostat. The sample is injected into a U- shaped glass tube that is electronically excited to vibrate at its characteristic frequency. This characteristic frequency depends upon the density of the sample. The working frequency for the measurement of speed of sound is ~3 MHz [25]. The uncertainties in the density measurements were found to lie well within 0.15 $kg\cdot m^{-3}$ while those in speed of sound data were found to be better than 0.5 $m\cdot s^{-1}$. The precision in temperature of the DSA-5000 was $\pm$0.001 K.

2.3. Viscosity measurements

A high precision water bath fitted with a digital temperature controlled device used for viscosity measurement supplied by Narang Scientific Works (NSW) Pvt. Ltd. New Delhi. Viscosity measurements have been carried out by using jacketed Ostwald viscometer having flow time 348 s for distilled water at 298.15 K. The viscometer was subjected to calibration before use at 298.15 K using water (η = 0.891 cP), Dioxane (η = 1.19 cP) and DMSO (η = 2.01 cP) as solvents. These values agreed reasonably well with the literature values [26,27]. The reproducibility of the measurements of viscosity was within $\pm$0.02 cP.

2.3.1. Surface tension measurements

The surface tension of bile salts solution in aqueous solutions of maltodextrin has been measured by drop weight method using Man



Scheme 1. Systematical representation of chemical as well as hypothetical structures of Sodium cholate and Sodium deoxycholate showing the hydrophobic surface (indicated yellow) and hydrophilic portion (indicated in blue) of the molecule.