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Ultrasonic relaxation studies on micelle formation in aqueous solutions of some bile salts

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ABSTRACT

Ultrasonic relaxation studies have been carried out in aqueous solutions of biological surfactants namely bile salts (sodium cholate and sodium deoxy cholate) at 303.15 K in the concentration range 1 to 14 mM and in the frequency range 2–30 MHz. The ultrasonic velocity is determined at 2 MHz using a Digital Ultrasonic velocity meter. The ultrasonic absorption is measured in the frequency range 2–30 MHz using Fallen Instruments and Pulsed Power Oscillator systems. The variation in the ultrasonic absorption is explained on the basis of exchange of a surfactant monomer between the micelles and the surrounding bulk solution. An attempt has also been made to extend the application of Aniansson and Wall and Teubner models to explain the micellar kinetics of biological surfactants which is otherwise applied to explain the kinetics of ordinary surfactants only. Various kinetic parameters such as associative rate constant (k_{+1}), dissociative rate constant (k_{-1}) and the volume change (ΔV) for the monomer–micelle exchange are estimated and reported in this paper.

1. Introduction

Bile salts are naturally occurring biological surfactants. The molecular structure of bile salts exhibits hydrophobic nature due to the steroid ring and hydrophilic nature due to the presence of hydroxyl and carboxylic groups. This combined nature of hydrophobicity and hydrophilicity of bile salts provides them the aggregating ability. The aggregation behaviour of bile salts is responsible for their important physiological functions such as solubilisation, transport of fats and lipids, assistance to hydrolysis of triglycerides by pancreatic enzymes along their transport, cholesterol homeostasis and in the formulation of food, cosmetics and several other chemicals [1–3]. In addition, bile salts have also been tried as drug delivery media for the transport of some drugs through the intestine mucus membrane [4–6]. Moreover, it is believed that the micelles formed by bile salts play a vital role in the early crystallisation which in turn leads to gall stone formation in human beings. Owing to these widespread applications and unique facial amphiphilic structure, many researchers carried out investigations on different aspects of aggregation process and physicochemical properties of bile salts using various experimental methods [7–14].

Among the bile salts, sodium cholate and sodium deoxy cholate represent a special class of potential biosurfactants which act differently from simple aliphatic surfactant molecules with regard to aggregation behaviour. Due to the unusual aggregation behaviour of bile salts, their critical micelle concentration (CMC) is considerably lower, and the micelles formed just above the CMC are characterised by much smaller aggregation number than that of simple aliphatic surfactants [15]. The most accepted primary–secondary micelle model for bile salts aggregation is the model proposed by Small. This model proposes a two-step aggregation process of bile salts in which small or primary aggregates with up to 10 monomers are formed above CMC by hydrophobic interactions and then secondary micelles are formed by hydrogen bonding between the primary micelles [16]. The micellar kinetics of bile salts is not thoroughly studied as that of simple aliphatic surfactants. Our earlier ultrasonic relaxation studies on aqueous solutions of sodium taurocholate revealed interesting results [17]. In continuation of our earlier studies on aqueous solutions of sodium taurocholate, the present study has been undertaken to understand the micellar kinetics of aqueous solutions of other bile salts namely, sodium cholate and sodium deoxy cholate. The absorption data obtained from the present study are discussed on the basis of a general kinetic model on micelle formation developed by Aniansson and Wall [18,19] and then modified by Teubner [20]. In the present study, an attempt has also been made to explain the micellar kinetics of aqueous solutions of biological surfactants using the above model which is generally applied for the study of micellar kinetics of simple aliphatic surfactants.

2. Materials and method

The bile salts (sodium cholate and sodium deoxy cholate) used in the present study are of AR/BDH grade purchased from SD-fine chemicals Ltd., India. The purity of the bile salts is checked using TLC method.

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Both the bile salts produced a single spot in TLC indicating that the purity is greater than 99%. Aqueous solutions of bile salts namely sodium cholate and sodium deoxy cholate are prepared by dissolving known amount of bile salts in Millipore water having a specific conductance of 4.52×10^{-6} Sm^{-1}. The ultrasonic velocity [21] and absorption measurements are carried out in various solute concentrations ranging from 0.001 to 0.014 M at a fixed temperature of 303.15 K. The ultrasonic velocity is measured at a fixed RF frequency of 2 MHz using a Digital Ultrasonic velocity meter (Model VCT-70A, Vi-Microsystems Private Ltd., Chennai, India). The ultrasonic absorption is measured in the frequency range 2–30 MHz using Fallen Instruments (Mark IV system) and Pulsed Power Oscillator system (DUCOM EL-550). The ultrasonic absorption is measured using pulse echo technique. The echo pattern obtained is fitted to an exponentially decaying curve ($Y = Ae^{-\alpha x}$) in order to determine the absorption coefficient (α). The temperature of the solutions is maintained constant within ± 0.01 K using a thermostatically controlled water bath. The accuracy in the measurement of velocity and absorption is ± 2 parts in 10^5 and 3% respectively. The density of aqueous bile salt solutions is determined using a graduated dilatometer [21]. The accuracy in the measurement of density is ± 2 parts in 10^5. The measured ultrasonic absorption in the concentration and in the frequency range studied is fitted to a suitable relaxation equation in order to estimate various relaxation parameters such as relaxation frequency (f_r), relaxation time (τ) and relaxation amplitudes (A and B). In addition, various kinetic parameters namely associative rate constant (k_{+1}), dissociative rate constant (k_{-1}) and the volume change (ΔV) for the proposed fast relaxation process are also estimated and reported.

3. Theory of micellar kinetics

3.1. Estimation of kinetic parameters for the fast relaxation process in surfactants

The kinetic parameters for the fast relaxation process can be estimated by applying the equations derived from a general kinetic model on micelle formation developed by Aniansson and Wall [18,19] and then modified by Teubner [20]. Aniansson and Wall derived an expression for the relaxation time (τ) of fast exchange process as

$$\left(\frac{1}{\tau}\right) = 2\pi f = \left(\frac{k_{-1}}{\sigma^2}\right) + \left[\left(\frac{k_{-1}}{m}\right)\left(\frac{c}{c_1} - 1\right)\right] \quad (1)$$

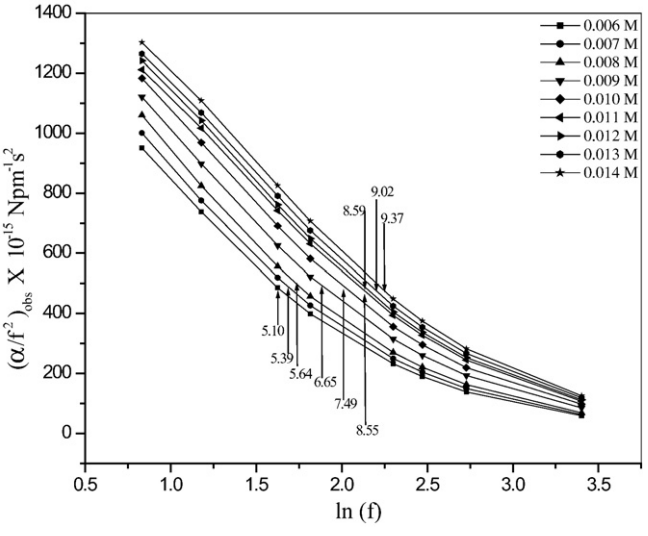

Fig. 1. Variation of observed absorption with frequency for aqueous sodium cholate in the different concentration range of 0.006 to 0.014 M at 303.15 K. 0.006 M (—■—), 0.007 M (—●—), 0.008 M (—▲—), 0.009 M (—▼—), 0.010 M (—◆—), 0.011 M (—◀—), 0.012 M (—▶—), 0.013 M (—⬢—), 0.014 M (—★—). The arrows indicate the location of relaxation frequency.

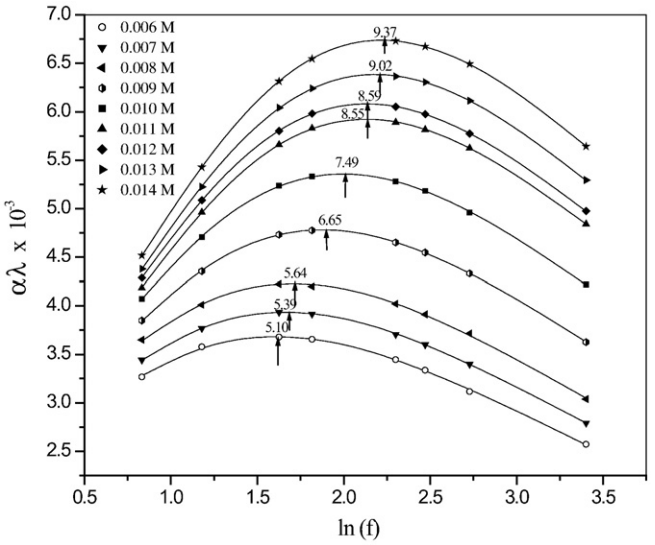

Fig. 2. Variation of absorption per wavelength with frequency for aqueous sodium cholate in the different concentration range of 0.006 to 0.014 M at 303.15 K. 0.006 M (◌), 0.007 M (▼), 0.008 M (◀), 0.009 M (◑), 0.010 M (■), 0.011 M (▲), 0.012 M (◆), 0.013 M (▶), 0.014 M (★). The arrows indicate the location of relaxation frequency. The different symbols represent the experimental values and solid lines represent the calculated values.

where c and c_1 are total and monomer concentrations of the surfactant respectively. Usually c_1 is assumed to be equal to critical micelle concentration. m, σ^2, and k_{-1} represent the mean aggregation number, the variance of size distribution on proper micelles and the mean dissociative rate constant, respectively. The following equation (Eq. (2)) for maximum absorption per wavelength $(\alpha\lambda)_{max}$, has been derived by Teubner [20] on the basis of the kinetic model proposed by Aniansson and Wall.

$$(\alpha\lambda)_{max} = \frac{\pi\rho u^2 (\Delta V)^2 c_1 \left(\frac{\sigma^2}{m}\right)\left(\frac{c}{c_1} - 1\right)}{2RT\left[1 + \frac{\sigma^2}{m\left(\frac{c}{c_1} - 1\right)}\right]}. \quad (2)$$

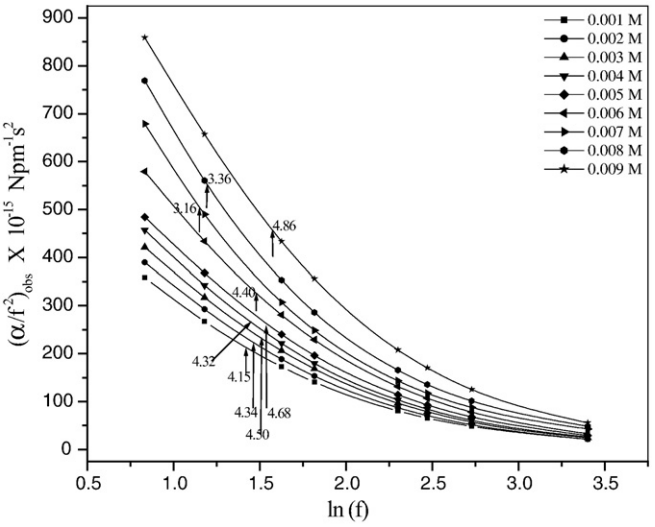

Fig. 3. Variation of observed absorption with frequency for aqueous sodium deoxy cholate in the different concentration range of 0.001 to 0.009 M at 303.15 K. 0.001 M (—■—), 0.002 M (—●—), 0.003 M (—▲—), 0.004 M (—▼—), 0.005 M (—◆—), 0.006 M (—◀—), 0.007 M (—▶—), 0.008 M (—⬢—), 0.009 M (—★—). The arrows indicate the location of relaxation frequency.