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Volumetric, compressibility and viscometric studies on sodium cholate/sodium deoxycholate–amino acid interactions in aqueous medium

Kuldeep Kumar, Suvarcha Chauhan *

Department of Chemistry, Himachal Pradesh University, Summer Hill, Shimla 171005, India

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ABSTRACT

This paper reports density, speed of sound, and viscosity data for the bile salts: sodium cholate (1–30 mmol kg^{-1}) and sodium deoxycholate (1–17 mmol kg^{-1}) in 0.1 mol kg^{-1} aqueous solution of amino acids viz. glycine, leucine, methionine, and histidine at different temperatures (293.15–318.15 K) under atmospheric pressure. From the experimental density and speed of sound data, the apparent molar volume (ϕ_v), isentropic compressibility (κ_s), and apparent molar isentropic compression (ϕ_κ) have been calculated, and the results have been interpreted in terms of different hydrophobic and electrostatic interactions pertaining in the bile salt–amino acid–water ternary system. Based on experimental viscosity data, the relative viscosity (η_r) and viscous relaxation time (τ) have been calculated and their dependence on concentration of bile salts and temperature has confirmed the existence of significant amount of bile salt–amino acid interactions.

1. Introduction

The physiological actions of biological important molecules like proteins, saccharides, bio-surfactants, etc., are made possible due to various kinds of interactions which they undergo with the different metabolites present in the living body. In order to understand these interactions, a systematic knowledge of solution behavior of such compounds may prove to be highly beneficial. Also there are evidences in literature that interactions of surface active agents with macromolecules like proteins, drugs, etc., have developed a great deal of interest in various aspects of researches due to their important functions in the fields related to biology, medicine, cosmetics, catalysis, etc. [1–5]. In addition, the aggregates of different types of surfactants have also been investigated for their potential food and agricultural applications as they are capable of solubilizing a large range of hydrophilic and hydrophobic substances. In this context, Cid et al. [6,7] have explored considerably the uses of sodium dodecylsulphate + salicylic acid/ascorbic acid mixed micellar systems for fruits postharvest and antioxidant actions. Arias et al. [8] have highlighted the agricultural importance of micelles in terms of the inhibitory effects of micelles of anionic/non-ionic surfactants for the persistence of the carbofuran pesticide.

Moreover, surfactant–protein interactions may result in the stabilization or destabilization of the protein structure depending upon the type of surfactants [9,10]. Ionic surfactants are known for their binding ability to proteins by virtue of strong electrostatic interactions, which induce the unfolding, i.e., destabilization of proteins beyond a saturation point [11]. However, in contrast, non-ionic surfactants bind weakly to proteins, probably due to the absence of the electrostatic interactions [12] and therefore, non-ionic surfactants are often added to prevent or minimize protein aggregation under different stresses and other processes [13]. However, owing to complexities of proteins, amino acids have been used in the recent past as models to investigate different surfactant–protein interactions in aqueous solutions [14–16]. In our earlier communications, we have studied the effect of amino acids on the micellization of different surfactants by volumetric and compressibility measurements [17–20] in order to explore different surfactant–amino acid interactions.

Although extensive data for surfactants are available in aqueous solutions of amino acids, there have been relatively fewer investigations on the solution behavior of bile salts in aqueous amino acids solutions [21], and moreover, volumetric and compressibility studies for bile salts in aqueous solutions are rare [22,23]. Further, the structure of bile salts modulates the bile salt–protein interactions, for instance, the stability constant of the

* Corresponding author. Tel.: +91 177 2830803; fax: +91 177 2830775.
E-mail address: chauhansuvarcha@rediffmail.com (S. Chauhan).

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adducts formed by albumin with bile salts is, at least, two orders of magnitude lower than *n*-alkyl chain surfactants, fatty acids and soaps [24]. In this context, a detailed knowledge of physico-chemical properties of bile salts in aqueous amino acid solutions may be proved convenient to get reasonable hypothesis on bile salt–protein interactions, as these interactions are expected to accompany by significant changes in physico-chemical properties.

Therefore, in the present study, we have chosen two bile salts, i.e., sodium cholate (NaC) and sodium deoxycholate (NaDC) (Fig. 1) to under seek the bile salt–protein interactions in aqueous solution of amino acids (Fig. 2) by using density, speed of sound, and viscosity techniques at different temperatures.

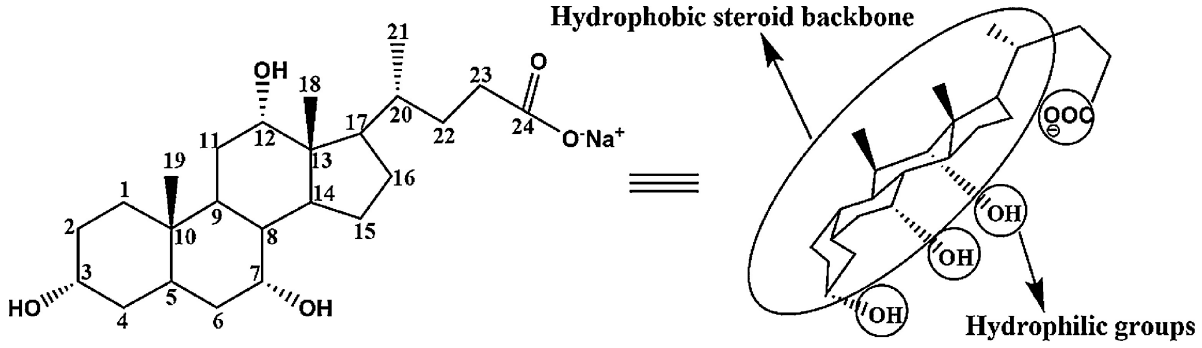
2. Experimental

2.1. Materials

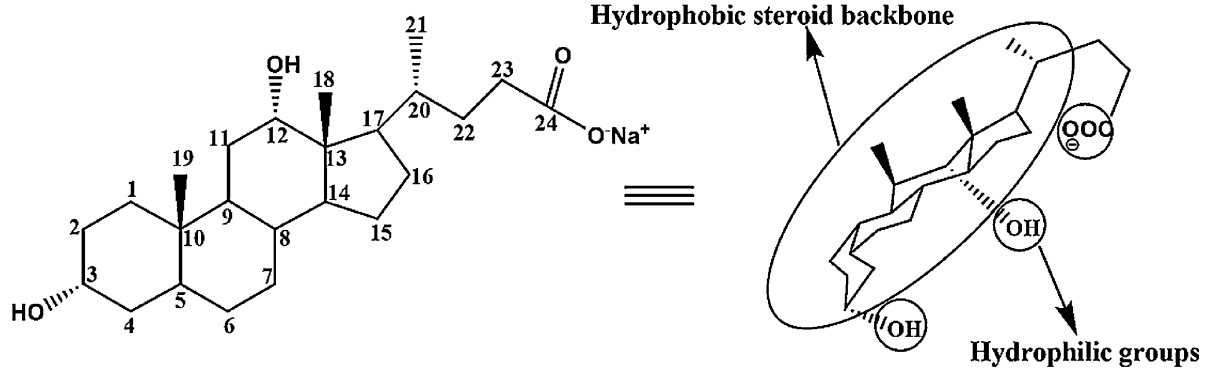
The deionized distilled water (Millipore-Elix) having conductivity (2–3) $\mu S\,cm^{-1}$ and pH 6.8–7.0 at $T = 298.15$ K has been used for all experiments. Sodium cholate and sodium deoxycholate both of A.R. grade have been procured from S.D. Fine-Chem Ltd., India and used after recrystallized from ethanol in the same manner as reported in literature [25]. Amino acids glycine (Calbiochem, U.S. and Canada), leucine (S.D. Fine-Chem Ltd., India), methionine (S.D. Fine-Chem Ltd., India), and histidine (Merck, Germany) all of A.R. grade have been recrystallized from distilled water before use [26]. After this all chemicals have been dried in vacuum oven and kept in a vacuum desiccator over anhydrous calcium chloride at room temperature. The provenance and purity of chemicals used have also been provided in Table 1.

2.2. Methods

Stock solution of amino acids (0.1 mol kg^{-1}) has been prepared in distilled water and used as solvent for the preparation of different bile salts concentrations. All solutions have been prepared by using Shimadzu balance with a precision of ±0.0001 g. Density (d) and speed of sound (u) values of aqueous NaC and NaDC solutions in absence and presence of amino acids have been measured simultaneously using Anton Paar DSA-5000 instrument. The instrument has been calibrated before use as reported in our previous study [26]. The uncertainty in density and speed of sound measurements has been estimated as $\pm 2 \times 10^{-6}\,g\,cm^{-3}$ and $\pm 0.2\,m\,s^{-1}$, respectively. The two in one instrument is equipped with a density cell and a speed of sound cell, which are temperature controlled by a built-in Peltier thermostat [27]. For measuring density, the U-shaped sample tube completely filled with the sample is excited to a continuous oscillation at its natural frequency by means of magneto-electrical excitation system. The oscillation frequency of the tube changes as the density of the sample changes. Thus, the density of the sample is calculated from the quotient of the period of oscillations of the U-tube and reference oscillator by using Eq. (1) [28].



Sodium-3-alpha, 7-alpha, 12-alpha-trihydroxy-5-beta-cholan-24-oate (Sodium cholate)



Sodium-3-alpha, 12-alpha-dihydroxy-5-beta-cholan-24-oate (Sodium deoxycholate)

Fig. 1. Molecular structures of sodium cholate and sodium deoxycholate.