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# pH and surface tension dependence of mixed sodium deoxycholate–sodium dehydrocholate pre-micellar aggregation in aqueous solution

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ABSTRACT

Bile salts are biologically important amphiphiles whose micellar behavior is considerably different from that of ordinary surfactants. In this work pre-micellar sodium dehydrocholate (NaDHC)–sodium deoxycholate (NaDC) mixed aqueous solutions composition is determined and their surface tension behavior is interpreted based on the information about the bulk solution composition which was obtained from the analysis of pH data. We used the pH of carboxylate soap solutions theory developed by Lucassen and generalized by Kralchevsky et al.

In general it was found that the NaDHC:NaDC mixture pre-micellar solutions were mostly composed by acid soaps like complexes with different compositions and no presence of neutral soap was identified. The equilibrium solubility ($S_{HZ}$) and dissociation constant of acid ($\tilde{K}_A$) values found for pure NaDC and NaDHC were $6.081 \times 10^{-7}$ and 0.0797, respectively, similar results were obtained from literature.

Surface tension isotherms were interpreted from the pH data. It can be seen that the presence of precipitates notably affected the surface tension behavior of rich NaDHC solutions but this conduct decreased as the content of $DC^-$ ion in the mixture augmented. This fact is probably due to the formation of H-bonds between $DC^-$ and water molecules and the consequent monolayer saturation.

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## 1. Introduction

Bile salts are biologically important amphiphiles whose micellar behavior is considerably different from that of ordinary surfactants (having a long alkyl chain and a hydrophilic head group) [1–3].

The bile salts possess a rigid steroid backbone having polar hydroxyl groups on the concave α-face and methyl groups on the convex β-face. Because of their particular structure and their rigidity, the aggregation properties in aqueous media are completely different from conventional detergents. Bile salt micelles have much smaller aggregation numbers [4–6]. Furthermore, the aggregation process seems to proceed stepwise over a broad concentration range [7]. Small and co-workers [8–10] suggested a two-step model for the aggregation of bile salts. Initially, small aggregates (where the hydrophobic surface of the molecules is shielded towards water) with an aggregation number less than 10 are formed. In the second step, at higher concentration, secondary aggregates are formed by interaction of the primary aggregates via formation of hydrogen bonds. This sequential model was extended by Kawamura et al. [11] who suggested a back-to-back association mechanism of bile salt entities with an alternating up and down orientation of the molecules, the hydrophobic surfaces thus shielded from water. An alternative model was suggested by Giglio and co-workers [12,13]. In this model, association of the molecules proceeds by polar interaction leading to a helical association of the monomers in the aggregate with their hydrophobic surfaces exposed to water. A whole range of different experimental methods have been applied to decide which of these models is correct [9–17] but a definite consensus on the structure of the aggregates still does not exist [18]. Several studies were performed on bile salts and bile salts mixtures with emphasis in their micelle or monolayer formation and the solubilization of biological lipids such as cholesterol and glycerides [19–23]. In particular for sodium deoxycholate (NaDC) several investigations were performed to evaluate two of its most unique properties: its specific hydrolysis and its polymer-like aggregation [24–27].

The dissolution of such alkanoates (carboxilates) in water is accompanied by an increase of pH, which is due to the protonation (hydrolysis) of the alkanoate anion [28]. The alkanoic acids with 12 and more carbon atoms are weekly insoluble in water. So, their formation causes a typical turbidity of the soap solutions. Moreover, the hydrogen-bonding interactions between the alkanoic acid molecules and alkanoates ions lead to the formation of acid-soap complex [29–33]. Most bile salts precipitate as insoluble bile acids

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in stomach or colon. The reason is that values of precipitation pH (ppt pH) for bile salts are higher than the pH value in the intestine [34,35]. In general, if pH values of aqueous solutions of bile salts decrease until about p$K_a$ values of bile acids, the bile salts change to insoluble bile acids in the solutions, and then some bile acids are solubilized into micelles of bile salts. These facts are consistent with pre-micellar aggregation theories exposed above.

In a previous work we investigated the sodium dehydrocholate (NaDHC)–NaDC mixed system behavior in aqueous solution [36]. These two bile salts are very similar to each other except for the presence of hydroxyl groups, i.e., NaDC has two hydroxyl groups (3 and 12 α-OH) while NaDHC has three carbonyl groups at positions 3, 7 and 12 of the steroid backbone. This difference leads to a great divergence in interfacial [37] and solution properties [36].

Our first purpose in the present paper was, by analysis of pH isotherms, to determine the composition of the pre-micellar NaDHC–NaDC mixed aqueous solutions at various bile salt ratios and to identify (if there are) the type of precipitates (alkanoic acid, $j$:$n$ acid soap, neutral soap and two phase precipitates).

The simultaneous presence of anionic and non-ionic amphiphiles (despite the existence of precipitates) in solution leads to a complicated concentration dependence of its surface tension [38]. Our second goal was to interpret the surface tension isotherms of such mixtures based on the information about the composition of the bulk solution obtained from the analysis of the pH data.

The information derived from these measurements may be useful to complete the knowledge of the complex aggregation behavior of bile salts and related compounds, which are very important for the understanding of their interaction with biological membranes, billiary secretions or cholesterol solubilization. NaDHC is a scarcely studied bile salt derivative, which adds interest to this work.

## 2. Experimental

### 2.1. Materials

Dehydrocholic acid (HDHC) was obtained from Dr. Theodor Schuchardt (Munich) and was of analytical grade. NaDC was obtained from Aldrich, 99%, and used as purchased.

### 2.2. Solutions

NaDHC solution was prepared by weighing a quantity of HDHC and by dissolution in an appropriate amount of concentrated NaOH.

Stock NaDHC and NaDC solutions (0.1 mol dm$^{-3}$) were prepared and diluted as required for each experiment. The appropriated amount of NaDHC and NaDC stock solutions were mixed to obtain the different NaDHC–NaDC mixture solutions. Only double-distilled water was used.

### 2.3. Methods

pH determination were performed with a millivoltmeter and a pH-meter from CRIBABB with a Broade and James glass electrode. Surface tension was measured with a ring tensiometer from Krüss.

All determinations were performed by titration of 50 mL of a stock solution (0.1 mol dm$^{-3}$) of each pure surfactant and their mixtures with water at 25.0 ± 0.1 °C.

## 3. Theoretical section

We use the pH of carboxylate soap solutions theory developed by Lucassen [28] which is applicable at $c_T$ (total surfactant concentration) lower than critical micelle concentration (cmc), generalized to account for the presence of inorganic electrolytes, base and formation of acid soaps of arbitrary stoichiometry by Kralchevsky et al. [39].

Considering the followed equilibriums of alkanoate dissolution in water:

$$Z^- + H_2O \leftrightarrows HZ + OH^-$$

$$HZ + Z^- + M^+ \leftrightarrows MHZ_2 \leftrightarrow \text{precipitate}$$

where $Z^-$ is the alkanoate anion, $M^+$ the metal cation, HZ the alkanoic acid, MZ the neutral soap and $MHZ_2$ the acid soap. In our work $Z^-$ is the surfactant anion ($DC^-$, deoxycholate or $DHC^-$, dehydrocholate) and $M^+$ is $Na^+$.

Three of the basic equations express the dissociation equilibria and the solution electroneutrality.

$$c_H c_Z \gamma_\pm^2 = K_A c_{HZ} \tag{1}$$

$$c_M c_Z \gamma_\pm^2 = Q_{MZ} c_{MZ} \tag{2}$$

$$c_M + c_H = c_{OH} + c_{HCO_3} + c_Z \tag{3}$$

Here $c$ is the concentration of the component denoted by the respective subscript expressed in molarity (M), $K_A$ and $Q_{MZ}$ are the dissociation constants of HZ and MZ, respectively, and $\gamma_\pm$ is the activity coefficient, which can be calculated from the known semiempirical formula originating from Debye-Hückel theory [40]:

$$\log \gamma_\pm = \frac{-A\sqrt{I}}{1 + Bd_i\sqrt{I}} + bI \tag{4}$$

where $I$ (M) is the ionic strength of the solution; $d_i$ is the diameter of the ion; $A$, $B$ and $b$ are parameters which are tabulated [40]. For our experimental conditions we used $A = 0.5091\ M^{-1/2}$, $Bd_i = 1.316\ M^{-1/2}$ and $b = 0.155\ M^{-1}$. In the considered case (where there are no added salts or bases), the ionic strength can be estimated from $I \approx c_T$.

In the right hand side of the electroneutrality condition (Eq. (3)) we have taken into account the presence of hydroxyl, $OH^-$, and hydrocarbonate, $HCO_3{}^-$. From the equilibrium of the reactions $H^+ + OH^- \leftrightarrows H_2O$ and $H^+ + HCO_3{}^- \leftrightarrows CO_2 + H_2O$, it can be obtained:

$$c_H c_{OH} \gamma_\pm^2 = K_W \tag{5}$$

$$c_H c_{HCO_3} \gamma_\pm^2 = k_{CO_2} S_{CO_2} \equiv K_{CO_2} \tag{6}$$

Here, $K_W$ is the dissociation constant of water, $k_{CO_2}$ is an equilibrium constant, $S_{CO_2}$ is the concentration of dissolved $CO_2$ and $K_{CO_2}$ is defined by Eq. (6). From such equation, considering the pH of experimental pure water at 25 ± 0.1 °C equilibrated with the atmospheric air, with $c_{HCO_3} = c_H$ and $\gamma_\pm \approx 1$, $K_{CO_2}$ was estimated.

Substituting $c_{OH}$ and $c_{HCO_3}$ from Eqs. (5) and (6) into Eq. (3), it can be obtained that:

$$c_M + c_H = \frac{K_H}{c_H \gamma_\pm^2} + c_Z \tag{7}$$

$$K_H \equiv K_W + K_{CO_2} \tag{8}$$

The amount of component M and Z incorporated in the solid phase per unit of volume are given by equations [28]:

$$m_M = c_T - c_M - c_{MZ} \tag{9}$$

$$m_Z = c_T - c_Z - c_{HZ} - c_{MZ} \tag{10}$$

As before, $c_{HZ}$ and $c_{MZ}$ are the concentrations of dissolved (but none dissociated) HZ and MZ molecules. According with this, if

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