



The thermal signature of wormlike micelles



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ABSTRACT

The variations in enthalpy (ΔH_{WLM}) and critical concentrations associated with the formation of wormlike micelles (WLMs) from combinations of tetradecyltrimethylammonium bromide ($C_{14}TAB$) and various aromatic co-solutes were determined using isothermal titration calorimetry (ITC). Three groups of aromatic molecules were investigated: neutral (phenol), benzoate derivatives and cinnamate derivatives. In addition, the thermal stabilities of the WLMs (of hexadecyltrimethylammonium bromide, $C_{16}TAB$) and the aromatic co-solutes of the three groups were investigated by measuring the temperatures at which the WLMs break and lose their ability to produce hydrodynamic drag reduction. A comparison of the results was used to establish correlations between the spontaneity of WLMs formation, their thermal stability and the molecular structure of the aromatic co-solutes. A characteristic thermal pattern with four steps was observed when WLMs are formed, that depended on the co-solute structure. Micellar growth was found to be an exothermic process, related to the fusion of the end caps allied with the incorporation of more co-solutes. The co-solutes that had negative charge and were able to maintain planar configuration demonstrated stronger interactions and also showed higher thermal stability through drag reduction.

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1. Introduction

An interesting history of the discovery and study of the structure of wormlike micelles (WLMs) is succinctly presented in the introduction of the book “Giant Micelles”, which was edited by Zana and Kaler [1]. The first experimental description of such elongated structures was reported by Debye and Anacker [2] in 1951, when these structures were detected using light scattering. Subsequently, the long micellar chain model was demonstrated by visualization using Cryogenic-temperature Transmission Electron Microscopy (Cryo-TEM) [3]. The viscoelastic property of a WLM is probably the most fascinating characteristic of this system, and our current understanding of its rheological behavior is mainly based on the works of Pilpel [4] Cates [5] Hoffmann [6] Candau [7] and their collaborators. WLMs can reach microns in length and a few nanometers across and the long chains are dynamically breaking and reforming. WLMs are suitable for the rheological control of aqueous systems and are widely used in cosmetics [8,9] in drilling fluids [10] and as drag reducers [11].

The self-aggregation process that results in the formation of micelles can be understood by comparing two opposing forces: the hydrophobic forces that pull the surfactant molecules out of the aqueous phase into the micellar pseudo-phase (favouring the

aggregation), and the head group interactions, which work in the opposite way [11]. Based on such considerations, a model was proposed by Mitchel and Ninham [12] and Israelachvili [13]. According to their model, WLMs are formed when the packing parameter (p), which is related to the head group area, the extended length and the volume of the hydrophobic part of the surfactant molecule is $1/3 < p < 1/2$. Following the seminal work of Pilpel [4] the growth of the micelles formed with ionic surfactants can be driven by adding salt at high concentrations. Screening the head group charge of the surfactant molecules reduces its area, which affects p . WLMs containing cationic surfactants are formed even in dilute regimes in the presence of aromatic anions (strongly binding anions), such as salicylate [14] tosylate [15] chlorobenzoate [16] and naphthalene sulfonate [17]. In these cases, micelle growth is driven by inserting the co-solute into the palisade layer of the micelle [18]. However, the sphere-to-rod transition is sensitive to the chemical structure of the aromatic anion.

Important calorimetric data for the interactions between dodecyltrimethylammonium bromide (DTAB) and ortho-, meta- and para-hydroxybenzoate were obtained by Šarac *et al.* [19]. However, only recently were the profiles of the calorimetric signals interpreted by correlating them with static light scattering measurements (SLS) [20].

In this work, the calorimetric study was extended to other aromatic co-solutes, which are indicated in figure 1, to verify the existence of a universal component in the calorimetric signal when

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WLMs are formed. This study was complemented by measuring the thermal stability of WLMs based on the temperature range in which they were capable of maintaining a reduced hydrodynamic drag. The calorimetric and hydrodynamic drag reduction experiments allow the establishment of the strength of the interaction between co-solute and surfactant. The values for the variation of enthalpy of WLM formation for the several surfactant/aromatic co-solute systems are shown for the first time and contribute to the understanding of the driven thermodynamic forces that lead to WLM formation.

2. Experimental

2.1. Materials

Pure components (table 1) without further purification were used to prepare the solutions. The following co-solutes in their acidic forms: *o*-hydroxycinnamic acid (OHCA), *o*-methoxycinnamic acid (OMCA), cinnamic acid, 3-phenylpropanoic acid (3-PPA) and 3-(*o*-hydroxyphenyl)propanoic acid (OHPA), were converted into their carboxylate forms using a sodium hydroxide solution. Cinnamic acid and its isomers are in the *trans*, (*E*) form.

2.2. Methods

The calorimetric experiments were carried out in a VP-ITC MicroCal Inc. calorimeter by injecting between (3 and 10) μL of $14 \text{ mmol} \cdot \text{kg}^{-1}$ C_{14}TAB into the reaction vessel (with a volume of

TABLE 1
The reagents used in study, their purities and the suppliers.

Reagent	Purity in mass fraction, as stated by the supplier	Supplier
Tetradecyltrimethylammonium bromide, (C_{14}TAB)	≥ 0.99	Sigma Aldrich
Hexadecyltrimethylammonium bromide, (C_{16}TAB)	≥ 0.98	Sigma Aldrich
<i>o</i> -hydroxycinnamic acid, (OHCA)	0.97, predominantly <i>trans</i>	Sigma Aldrich
<i>o</i> -methoxycinnamic acid, (OMCA)	0.98, predominantly <i>trans</i>	Sigma Aldrich
<i>trans</i> -cinnamic acid	≥ 0.99	Sigma Aldrich
3-Phenylpropanoic acid, (3PPA)	0.99	Sigma Aldrich
3-Hydroxyphenylpropanoic acid, (OHPA)	0.99	Sigma Aldrich
2-methoxybenzoic acid, (OMBA)	0.99	Sigma Aldrich
Sodium hydroxide, NaOH	≥ 0.98	Sigma Aldrich
Sodium salicylate, NaSal	0.995	Sigma Aldrich
Phenol	0.9950	Merck
Sodium benzoate	0.99	Synth-Brazil

1.436 mL) containing $1.5 \text{ mmol} \cdot \text{kg}^{-1}$ of the co-solutes. The measurements were made at $(298.1 \pm 0.1) \text{ K}$ ($25.0 \pm 0.1 \text{ }^\circ\text{C}$). The interval between the additions was approximately 5 min so that the baseline could be reached at the end of the thermal process.

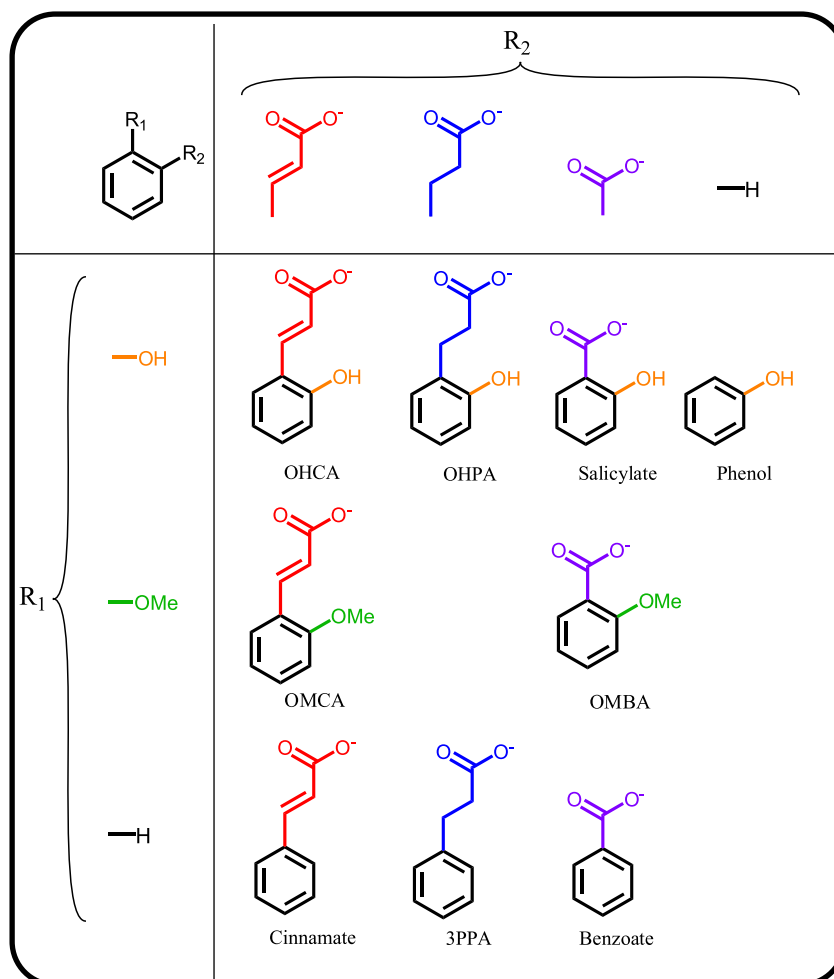


FIGURE 1. Structures of the aromatic co-solutes used in the investigation. The abbreviations are detailed on Section 2.1.

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