



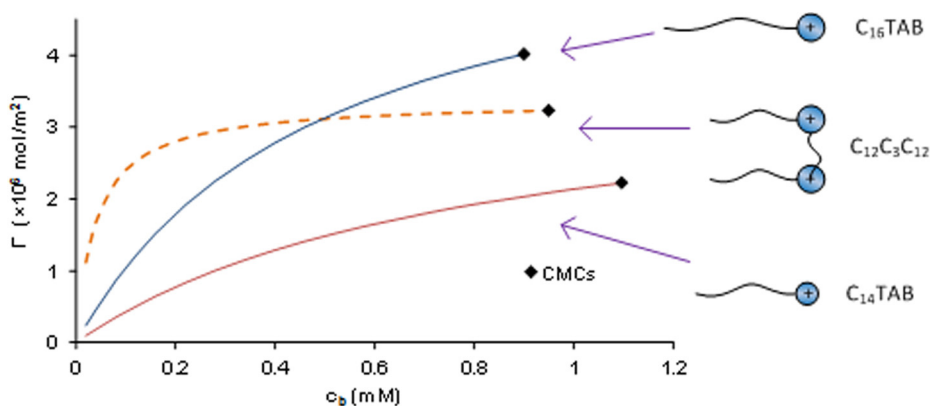
Dynamic adsorption of a gemini surfactant at the air/water interface

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HIGHLIGHTS

- A gemini surfactant, $C_{12}C_3C_{12}$, was synthesized.
- Surface tension of surfactant solution was measured and modelled by a new modelling framework.
- The new model does not require the Gibbs equation or the ionic binding constant.
- Consistent modelling results was obtained at 5 concentrations.

GRAPHICAL ABSTRACT



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ABSTRACT

The adsorption of a gemini surfactant, α, ω -bis(N-alkyl dimethylammonium) alkane dibromides, at the air/water interface was investigated by tensiometry. Equilibrium and dynamic surface tension were modelled by a new modelling framework, which is not based on Gibbs adsorption isotherm. The method consistently predicted the dynamic surface tension at five different concentrations and circumvented the uncertainties around the ionic state of the gemini surfactants. It was found that the gemini surfactant had much higher surface affinity, which arose from the double tails, than that of the normal cationic surfactants. The maximum surface excess was consistent with the proposed orientation of gemini surfactant at the air/water interface. The modelling framework provides an effective and consistent method to characterize the interfacial adsorption of gemini surfactants.

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1. Introduction

Gemini surfactants consist of two monomeric head groups that are connected by a spacer group [1]. In comparison with conventional surfactants, gemini surfactants have a number advantages,

including high capability, lower critical micelle concentrations (CMC) and low Kraft temperatures [2–4]. Amongst the gemini surfactants, the bis-quaternary ammonium bromide surfactants, $[C_mH_{2m+1}N(CH_3)_2-(CH_2)_s-N(CH_3)_2C_mH_{2m+1}]Br_2$, are the most popular due to their simple synthesis [5,6]. This group, labelled as $C_mC_sC_m$, is the focus of this paper.

In spite of many studies over the last two decades, including tensiometry [4,7] and neutron reflectometry (NR), [8,9] the interfacial adsorption is not well understood. Some deficits in the current

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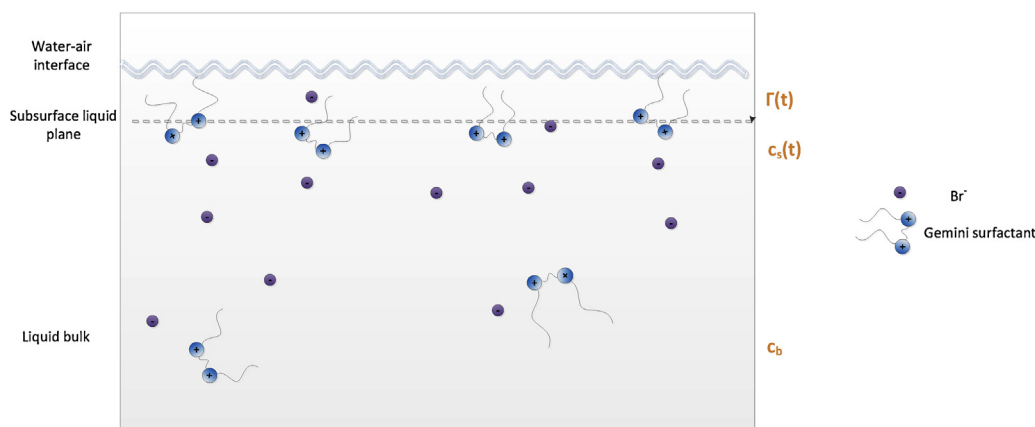


Fig. 1. Gemini surfactant and adsorption process.

understanding arose from the theoretical basis. For the interfacial adsorption, most studies in the literature relied on the Gibbs adsorption equation:

$$d\gamma_{eq} = -nRT(\Gamma d \ln c_b) \quad (1)$$

where γ_{eq} is the surface tension, c_b and Γ are the bulk concentration and surface concentrations, respectively, and n is the constant accounted for ionic state of the surfactant.

The value of n is well-accepted for common surfactants, $n = 1$ for non-ionic and 2 for cationic/anionic surfactants [10]. For gemini surfactants, however, the value of n remains questionable due to its ionic nature (Fig. 1). The contrasting hypotheses in the literature have been reviewed by Zana [5]. Given that each gemini surfactant has two counter-ions, some researchers selected $n = 3$ [11]. In contrast, other authors argued $n = 2$, implying that the gemini surfactants behave as normal ionic surfactants. The underlying argument was that one of the counter anions was ionically bound to the surfactant [12]. Neutron reflectometry, [9] in combination with slope of γ_{eq} vs. c_b , showed inconclusive answers: n is not constant for $C_{12}C_5C_{12}$, with $s = 2, 3, 6$ and 12. The results indicated that n was equal to 2 for $C_{12}C_5C_{12}$ near the CMC only. For $C_{12}C_6C_{12}$, which is the only case with a clear trend, n monotonically increased from 2 at CMC to 3 at 10% CMC [9]. For the other three gemini surfactants, the relationship was reportedly neither constant nor monotonic. The results from this method indicated the ionic binding of gemini surfactants varies with concentrations.

On the other hand, the conductivity data over the same concentration range showed a linear relationship between conductivity and c_b [12], which evidently means that the ionic binding is independent on concentration. From these two contrasting results, one may infer a compromising picture that the ionic binding of gemini surfactant is constant in the bulk and concentration-dependent at the interface. The uncertainties can be also related to the formation of second layer structure [8] or pre-micellar aggregation [1]. A key advantage of Eq. (1) in modelling surfactant adsorption is that it can be integrated with an adsorption equation to produce the equation of state [10]. If n is a function of c_b or Γ , integrating Eq. (1) would be tedious with many additional parameters.

It should be noted that conventional method, i.e. combination of Eq. (1) and γ_{eq} vs. c_b plot, has been questioned in the literature [13]. The usage of the slope in γ_{eq} vs. c_b plot may produce unreliable results, especially in case of cationic surfactants [14]. Recently, a detailed NR analysis has found that the conventional method failed to predict the cationic surfactant adsorption near the CMC [15]. These latest development may undermine the previous NR interpretation of gemini surfactants.

Moreover, we have demonstrated a fundamental failure of Eq. (1) in synergistic adsorption [16]. A critical comparison between six different variations [17] of the adsorption models, which are based on Eq. (1) with different adsorption equations, has showed that all models gave good fittings for ionic surfactants. In summary, the usage of Eq. (1) produces non-consistent results for gemini surfactants. The ionic nature of adsorbed gemini surfactants cannot be addressed with the current method.

The above uncertainties can be overcome by circumventing Eq. (1). Recently, we developed a new model for dynamic surface tension without using Eq. (1) [18]. The model was successfully applied to two cationic surfactants myristyltrimethylammonium bromide ($C_{14}TAB$) and cetyltrimethylammonium bromide ($C_{16}TAB$). The result quantified the influence of the length of the hydrocarbon chain on the adsorption of surfactant at air/water interface. In this study, a gemini surfactant, $[C_{12}H_{25}N(CH_3)_2-(CH_2)_3-N(CH_3)_2C_{12}H_{25}]Br_2$ or $C_{12}C_3C_{12}$, was synthesized and investigated using tensiometry. The dynamic model was employed to generate adsorption parameters of this gemini surfactant.

2. Theoretical model

In our modelling framework, the equilibrium surface tension was used to determine the direct relationship between γ_{eq} and c_b . Consequently, the relationship is applied to the dynamic adsorption at different concentration. For 2-nanonol [19] and alkyl trimethylammonium bromide [18], the relation between interfacial tension and concentration is given by:

$$\gamma_{eq} = \gamma_0 e^{-\chi c_b} \quad (2)$$

$$\gamma(t) = \gamma_0 e^{-\chi c_s(t)} \quad (3)$$

where γ_0 is the surface tension of pure water and χ is an adsorption constant (M^{-1}), $c_s(t)$ and $\gamma(t)$ are transient sub-surface concentration (Fig. 1) and dynamic surface tension, respectively.

The above equations provide a direct relationship between two measurable quantities. The critical advantage of the method is the uniqueness of the solution. The disadvantage of the method is its reliance on the dynamic data and a complicated numerical framework [20]. However, the dynamic data can be obtained at different concentrations, and provide independent verifications for

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