



Dynamic adsorption of cetyl trimethyl ammonium bromide at decane/water interface



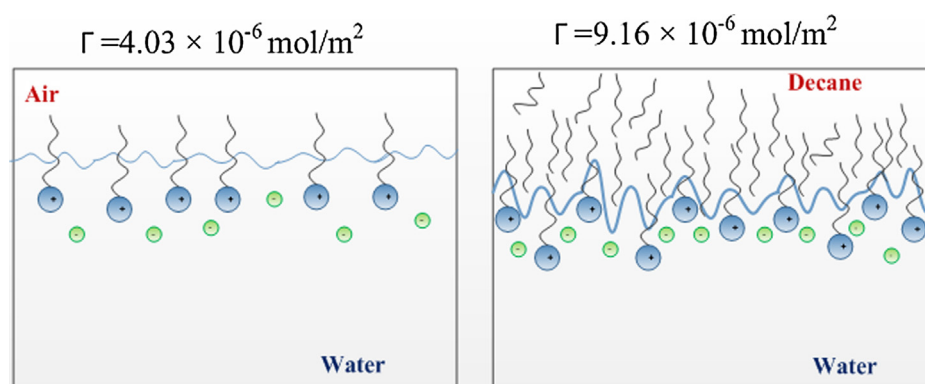
Abdulsalam Salamah, Chi M. Phan*, Hung G. Pham

Department of Chemical Engineering, Curtin University, 6102 Bentley, Australia

HIGHLIGHTS

- Dynamic adsorption of CTAB at decane/water interface was measured.
- The surface tension was modelled by a new modelling framework.
- The new model does not require the Gibbs equation and produce a unique solution.
- The obtained data indicated that CTA⁺ are moved away from monolayer arrangement due to interaction with decane in the interface.

GRAPHICAL ABSTRACT



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ABSTRACT

The dynamic adsorption of cetyl trimethyl ammonium bromide (CTAB) was investigated at decane/water interface by pendant drop technique. The images were analysed using Axisymmetric Drop Shape Analysis software and then were modelled using a new model. The model provided a unique solution for equilibrium adsorption. Consequently, dynamic data at two different concentrations were fitted simultaneously to determine the adsorption parameters. Good fittings have been achieved and then applied to predict dynamic tension at other concentrations. The outcomes revealed a significant increment in term of interfacial adsorption in comparison with adsorption at the air/water interface. The nature of this increment can be explained by considering the impacts of hydrophobic oil molecules and interfacial layer arrangements of alkane/water interfaces. The results can be used to quantify the interaction between alkane and the hydrocarbon tail of ionic surfactants at the oil/water interface.

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1. Introduction

Adsorption of surfactants at oil/water interfaces has many important applications, which has been investigated both theoretically and experimentally [1–6]. These applications are widely

used in different processes such as: enhanced oil recovery [7,8], pharmaceutical industry [9] biological and biochemical processes [10,11]. While there have been many studies on air/water interface [12–16], the number of studies on surfactant adsorption at oil/water interface is limited. This deficit was due to difficulties in experimental work at oil/water interface, including contaminations from the surfactants and oils, and purification procedures [17].

For most studies in the literature, the oil/water interfacial adsorption is modelled from the Gibbs adsorption equation with

* Corresponding author. Fax: +61 892662681.

E-mail address: c.phan@curtin.edu.au (C.M. Phan).

Table 1
Adsorption parameters of C₁₆TAB at hexane/water interface.

Γ_m (mol/m ²)	K (M ⁻¹)	Model	Reference
2.38×10^{-6}	1.5×10^7	FC	[2]
2.63×10^{-6}	2.2×10^4	FIC	[2]
3.13×10^{-6}	120×10^5	Binary model	[23]
2.38×10^{-6}	1.6×10^7	LC	[20]
2.61×10^{-6}	2.2×10^4	FIC	[20]

some variations in the adsorption isotherm. The general theory is briefly summarized below. The quantities of surfactant adsorbed at surface can be correlated to the surface tension and bulk concentration [18]:

$$\Gamma = -\frac{1}{2R_gT} \frac{d\gamma}{d \ln c} \quad (1)$$

where γ is surface tension, R_g is the ideal gas constant, T absolute temperature, Γ is the surface excess and c is the bulk concentration.

Integrating Gibbs equation with Langmuir isotherm yields Szyszkowski equation [18]:

$$\gamma_0 - \gamma_{eq} = -2R_gT\Gamma_m \ln(1 + Kc_b) \quad (2)$$

where γ_0 and γ_{eq} is the pure solvent and equilibrium surface tension, respectively, c_b is the surfactant concentration, K and Γ_m are the two adsorption parameters: surface affinity and surface saturated excess [19].

In case of using Szyszkowski equation, one will have to find two parameters to solve the equation. Other example is Frumkin equation, where the model has three parameters: with A is an additional parameter [18]. It also can be extended to include compressibility, Langmuir Compressibility (LC), Frumkin Compressibility (FC) and Frumkin Ionic Compressibility (FIC) [2]. However, the extension requires more parameters. For instance, the Frumkin ionic compressibility model required up to 6 independent parameters [20].

The above theoretical frameworks are applicable to both air/water and oil/water interfaces [3,20]. By applying the same model to the surfactant adsorption at both air/water and oil/water interfaces [2,20,21], the influences of oil/surfactant interaction can be quantified. In the literature, the interaction of the oil and surfactants is described by the values of adsorption parameters, especially Γ_m . On contrast, experimental studies on oil/water interfaces have highlighted the distinguishing role of the oil molecules on the adsorption process. Experimental data with a variation in surfactant molecules or oil molecules have demonstrated the molecular origins of the interaction within the interface. For instance, results from a series of alkyltrimethyl ammonium bromide at hexane/water interface has demonstrated a competitive adsorption between short alkyl surfactants and hexane molecules [2]. Study of C₁₀TAB and C₁₂TAB with different alkanes (from octane to tetradecane) also demonstrated the distinguishable impact of the oil molecules on interfacial adsorption [22]. Similarly, study on C_nTAB with hydrocarbons of same length indicated a strong dispersive force between surfactant and oil molecules [12]. Consequently, Fainerman et al. [23] proposed a new “binary” model, which included a new term accounting for the competitive adsorption between oil and surfactants molecules. The model has more fitting parameters than air/water interfacial model. However, the proposed model had the same quality of agreement with experimental data and thus cannot be justified from such data. The variations in adsorption parameters for a common cationic surfactant, C₁₆TAB or cetyl trimethyl ammonium bromide, are presented in Table 1.

In spite of different parameters, all models provided a good fit to equilibrium data. A comparative study on different models have found that most models can fit the equilibrium data well [24] and

good fitting cannot justify the underlying mechanism of the models. In summary, the available experimental data demonstrate a strong interaction between oil and surfactant at the oil/water interface. The non-unique values of the adsorption parameters render the procedure ineffective, especially for oil/surfactant interaction. The main deficit arose from the fact that the equilibrium data is too rudimentary to distinguish the multiple effects on oil/water interfacial adsorption. The current fitting procedure, which is based on the equilibrium data, is not sufficient to justify modelling assumptions.

Previously, we have developed a new modelling approach to obtain the adsorption parameters from the dynamic, instead of equilibrium, surface tension [25]. By fitting simultaneously to two dynamic curves, i.e. dynamic surface tension at different concentrations, we were able to obtain unique modelling solution. In present study, we aim to investigate the adsorption behaviour of CTAB at decane/water interface. The adsorption parameters were in comparison at two interfaces and provide new insights into the oil/surfactant interaction at the interface.

2. Experimental

2.1. Materials

Cetyl trimethyl ammonium bromide (CTAB) with purity up to 99% was supplied by Sigma–Aldrich. Subsequently, the surfactant was recrystallised twice using pure acetone. The 99% decane was purchased as well from Aldrich and purified by passing four times on silica gel column. The purified decane was immediately applied in the experiment as fresh compound. All CTAB aqueous concentrations were prepared at room temperature (25 °C) by deionized water at concentrations below CMC. For better mixing solution, the main stock solution was sonicated for 30 min just before the experiment. Deconex 15E 6% by volume was applied for cleaning the apparatus, glassware and tubes just before use.

2.2. Interfacial tension measurements

In this study, the dynamic interfacial tension of decane/water interface system was performed at room temperature (25 °C) and different molar concentrations of CTAB using pendant drop technique. The experiment was run under undisturbed surface area, and the configuration achieving by forming a drop of aqueous solution immersed in a cavetti containing purified oil. Syringe piston movement was carefully controlled to form CTAB droplet on 2 mm-diameter needle. The measurements were conducted at concentrations all much lower than critical micelles concentration CMC, ~0.9 mM. The surface tension of water was measured to record 71.79 mN/m. On the other hand, the surface tension of decane/water was obtained at 52.3 mN/m, which was compatible to the literature values [26,27].

2.3. Theoretical model

The modelling approach is based on a recent theoretical framework [25] to measure dynamic surface tension. The model has been applied successfully on C₁₄TAB and C₁₆TAB [28] as well as a gemini surfactant [29] at air/water interface. The model is based on the following relationship:

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

where χ is adsorption constant with similar unit to K , $\gamma(t)$ is the dynamic surface tension, $c_s(t)$ is the transient sub-surface concentration [25].

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