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Wetting in oil/water/surfactant systems

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ABSTRACT

The behaviour of oils at aqueous interfaces is ubiquitous to many industrially and biologically relevant processes. In this review we consider modifications to the wetting properties of oils at the air/water, oil/water and solid/liquid interfaces in the presence of surfactants. First-order wetting transitions can be induced in a wide range of oils by varying the aqueous surfactant concentration, leading to the formation of mixed monolayers at the interface. In certain cases, these mixed monolayers display novel surface freezing behaviour, including the formation of unusual bilayer structures, which further modifies the properties of the interface. The effects of surfactant on line tension at the three-phase contact line and differences between the air/liquid and liquid/liquid interfaces are discussed.

1. Introduction

Although oil and water do not mix, the appearance of interference colours on the surface of puddles is testament to the fact that complex oils will, in general, spread across a water surface. Indeed there are numerous historical accounts showing a fascination with the spreading of oil on water. The ancient Romans and Greeks were familiar with the smoothing of waves by oil poured from ships, a method revisited during the nineteenth century, and Benjamin Franklin took great delight in demonstrating the spreading of oil on water using a sample he carried in his cane. Franklin made the first quantitative observation of the extent of spreading of an oil when he reported that a teaspoon of oil on Clapham Pond spread to cover half an acre. Famously, and despite a belief in the particulate origin of the forces driving the spreading, Franklin never deduced the average film thickness and hence missed an opportunity to estimate the dimensions of the constituent particles in the oil. The calculation of film thickness was finally carried out over a hundred years later by Lord Rayleigh who deduced an average film thickness of 2 nm, although he inferred little from the magnitude of this dimension.

Everyday experience might suggest that the spreading of oil (wetting behaviour in modern terminology) on water is a ubiquitous phenomenon, yet the simplest oil molecules of all, the linear alkanes, do not spread on (pure) water, with the exception of the shortest liquid homologues.

In this review, we first summarise the interactions that determine the wetting of alkanes on water, and then describe recent work on the wetting behaviour of alkane/water systems in the presence of surfactant 'impurities' in the aqueous phase.

2. Equilibrium wetting behaviour

A liquid droplet placed at a planar surface displays one of three distinct wetting behaviours (Fig. 1). Conceptually the most obvious outcomes are that the droplet will either spread to form a uniform film that covers the whole surface or remain as a lens floating at the surface (in equilibrium with a dilute 2D gas as required thermodynamically). The former case is known as complete wetting and the latter, termed partial wetting, is the situation common to most linear alkanes on water; complete wetting is restricted to pentane–heptane, as described by Bonn et al. in the 1990s, and a number of papers and reviews have been published on this subject [1••,2–7•,8,9]. The third possibility describes an intermediate wetting state where the drop spreads to form a uniform microscopically thick film at the surface in equilibrium with a number of floating lenses of excess oil. This situation, dubbed 'pseudo-partial wetting' [10] or 'frustrated complete wetting' [3], is the one most commonly encountered for oil drops at the air/surfactant solution interface, and hence is of most relevance to this review.

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Chemical abbreviations

DTAB	dodecyl trimethylammonium bromide
TTAB	tetradecyl trimethylammonium bromide
CTAB	hexadecyl trimethylammonium bromide
STAB	octadecyl trimethylammonium bromide
C_nTAB	trimethylammonium bromide with alkyl tailgroup of length *n*
C_nE_m	non-ionic poly(ethylene glycol) alkyl ether
SDS	sodium dodecyl sulphate
AOT	sodium dioctyl sulphosuccinate
CPC	cetyl pyridinium chloride
PDMS	polydimethylsiloxane
TMADS	tetramethylammonium dodecyl sulphate
TWEEN 20	polyethylene glycol sorbitan monolaurate

Which of the three possibilities, illustrated in Fig. 1A, actually occurs is governed by competition between long- and short-range forces. The long-range forces are described by the variation in free energy, $F(D)$, with film thickness, D. For a sufficiently thick film the free energy is simply the sum of the interfacial tensions of the air/oil and oil/water interfaces. If the thickness of the film is similar to the range of long-range dispersion forces an additional contribution due to the interaction of water and air across the film must be included and $F(D)$ can be expressed as,

$$F(D) = \gamma_{ow} + \gamma_{ao} - \frac{A_{aow}}{12\pi D^2} \tag{1}$$

where γ_{ow} and γ_{ao} are the interfacial tensions of the oil/water and air/water interface, respectively, and the final term approximates the long-range van der Waals interaction across the film ($D >$ molecular dimension).

An important point regarding the effect of the long-range contribution in Eq. (1) relates to the sign of the Hamaker constant, A_{aow}. A negative Hamaker constant leads to a reduction in free energy as the film thickens (favouring complete wetting), whilst a positive Hamaker constant promotes thinning of the film. In the case of the short *n*-pentane, the Hamaker constant is negative (above a certain critical temperature, as discussed later) leading to a net repulsive van der Waals force and complete wetting behaviour. For the higher *n*-alkanes, the dispersion contribution to the Hamaker constant is large and dominant, leading to a net attractive force and the formation of lenses at the air/water interface.

Short-range contributions to the free energy can be considered from the behaviour of Eq. (1) as film thickness tends to zero. In this limit, the free energy of the system reduces to that of the neat air/water interface, leading to the initial spreading coefficient, S_i.

$$P(D \rightarrow 0) = \gamma_{aw} - (\gamma_{ow} + \gamma_{ao}) = S_i \tag{2}$$

Like the Hamaker constant, the sign of the initial spreading coefficient determines how the free energy of the system behaves in the presence of an oil film. If $S_i < 0$, the oil will not wet water, whereas if $S_i > 0$ spreading is favoured. In effect these two statements describe a net energy penalty (or gain) upon destruction of an air/water interface and subsequent replacement with air/oil and oil/water interfaces. The example of *n*-pentane can again be used as an illustration of the effect of short range forces on wetting. The relevant surface tensions, and therefore S_i, are temperature-dependent. Upon heating beyond 25 °C, S_i changes sign from negative to positive and a first-order wetting transition from partial to pseudo-partial wetting occurs [5].

Combining long- and short-range forces leads to four possible situations, shown schematically in Fig. 1B. Partial wetting is favoured when $S_i < 0$, regardless of the sign of the Hamaker constant. Complete wetting occurs when $S_i > 0$ and the Hamaker constant is negative (i.e. when both effects favour spreading/thickening of the film). Finally, when $S_i > 0$ (favouring spreading) and the Hamaker constant is also positive (promoting thinning of the film) the film is in the pseudo-partial wetting state. The minimum in $F(D)$ in this latter case occurs at some finite value of D (D_{eq} in Fig. 1B). In the presence of excess oil, therefore, the equilibrium state of the system is a film of thickness D_{eq} coexisting with a lens of oil ($D \rightarrow \infty$).

The wetting behaviour of *n*-pentane can be understood in terms of the possibilities in Fig. 2, as demonstrated by Bonn et al. [5]. At low temperatures, the initial spreading coefficient is negative and the Hamaker constant is positive leading to partial wetting. At 25 °C the initial spreading coefficient changes sign and there is a first-order transition from partial to pseudo-partial wetting. At 53 °C, the Hamaker constant changes sign and there is a second, continuous transition to complete wetting (it should be noted that the normal boiling point of pentane is 36 °C and these experiments were performed under pressure in the presence of a saturated vapour). The first-order nature of the lower temperature transition is in line with the theoretical predictions of Cahn [11]. Similar sequences of wetting transitions have been found

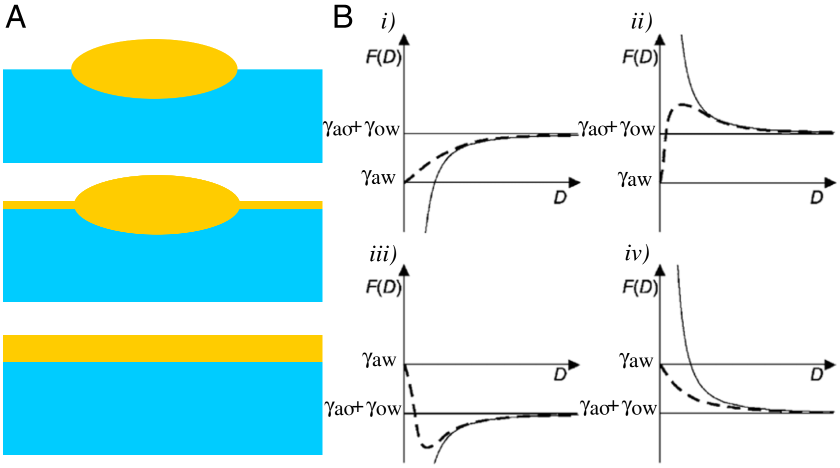

Fig. 1. (A) Wetting behaviour of an oil drop placed on an aqueous surface. Top, partial wetting. Middle, pseudo-partial wetting. Bottom, complete wetting. (B) Schematic representation of the effect of oil film thickness, D, on the free energy (dashed line), $F(D)$, of the air/water interface. Long-range van der Waals contribution shown as solid line. i) $S_i<0$ and $A>0$, ii) $S_i<0$ and $A<0$, iii) $S_i>0$ and $A>0$, iv) $S_i>0$ and $A<0$.
Reproduced with permission from Fig. 2 [15].