Colloids and Surfaces, 34 (1988/89) 389-398
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

Mechanisms of Oil Removal from a Solid Surface in the Presence of Anionic Micellar Solutions

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(Received 4 March 1988; accepted in final form 13 October 1988)

ABSTRACT

We use a differential interference microscope to observe the separation of crude oil droplets from a solid silica surface in the presence of a micellar solution. Surfactant adsorption lowers interfacial tension, resulting in a receding oil/water/solid contact line. Because water and surfactant molecules diffuse between the solid and oil phases, a process that occurs ahead of the (outer) moving contact line, the conventional three-phase contact line is preceded by a second contact line. The mechanism of oil droplet separation appears to be a combination of both a rolling-up mechanism and a diffusional mechanism.

INTRODUCTION

In the past two decades, many researchers have investigated oil/solid interactions in the presence of surfactant–micellar solutions. The rapid progression of these studies is represented by the works of Cutler and Davis [1–3], Cutler and Kissa [4], Lucassen-Reynders [5], Matijević [6], Schick [7,8], Lewin and Sello [9], Petrova et al. [10], de Gennes [11], and Churaev and Starov [12]. Despite these efforts, we do not yet fully understand the mechanisms by which an oil phase and solid surface interact in the presence of a micellar solution, specifically the mechanisms by which oil droplets are removed from a solid surface in the presence of the micellar solution. In this paper we explore the process of removing a crude oil droplet from a solid silica surface in the presence of a micellar solution. Previous investigations have demonstrated that the wettability properties of the solid and the properties of the pseudo-emulsion film (aqueous film formed between the solid and oil phases) are important features of the mechanism for oil droplet removal. Our observations regarding

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0166-6622/89/$03.50

these issues are particularly relevant for the enhanced oil recovery from within a porous sandstone core [13,14].

EXPERIMENTAL METHOD

We studied oil/solid interactions, both in the presence of air and in the presence of a micellar solution, using a reflected light differential interference microscope (Epival Interphako, Jena). A schematic of the experimental arrangement is given in Fig. 1. We used the differential interference method (DI) to determine the profile of the oil droplet at the solid/air surface, but the usual reflected light interferometry (UI) to determine the profile of the mobile oil droplet at the solid/micellar solution surface.

The basic principle of the differential interferometric method lies in the

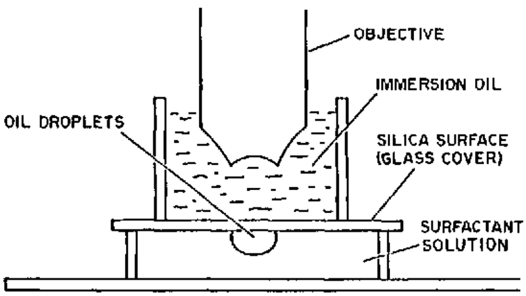

Fig. 1. Schematic diagram of experimental cell, single oil droplet.

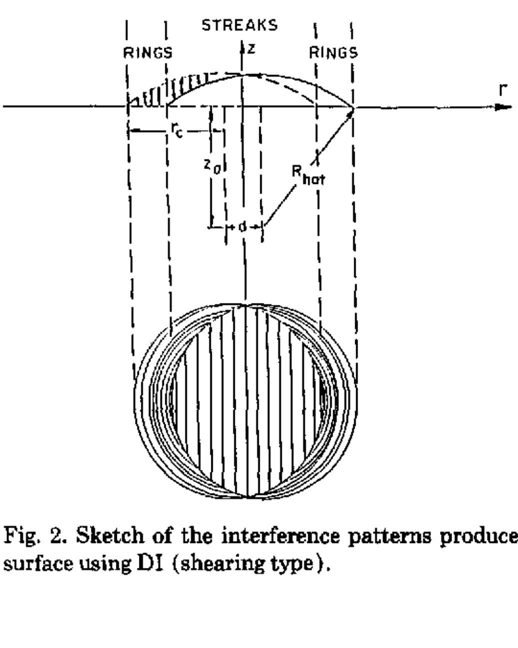

Fig. 2. Sketch of the interference patterns produced from a droplet at the plane parallel solid surface using DI (shearing type).

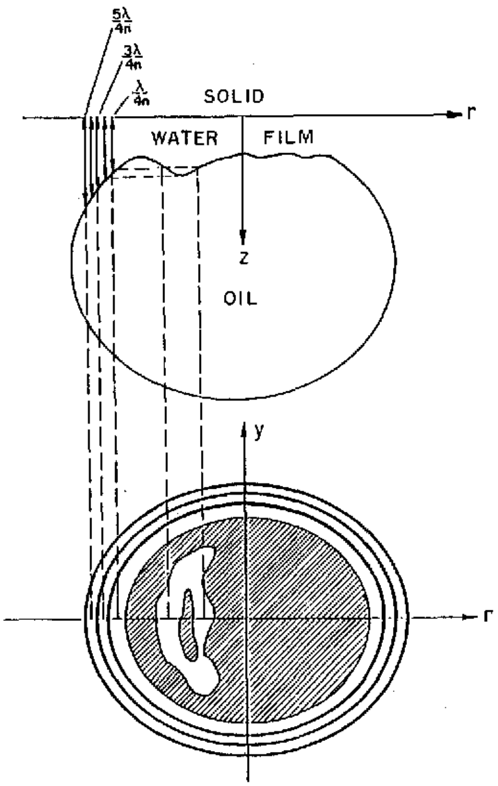

Fig. 3. Sketch of the interference patterns produced from an oil droplet interacting with plane parallel solid surface by using UI reflected light technique.

splitting of an original image into two images [15–17]. In the so-called "shearing" method, horizontal splitting is used so that the two images are shifted a distance d, which is called the shearing parameter. Figure 2 depicts a characteristic differential interferometric pattern. Each fringe is created by the interference due to the optical paths Δ of the two beams reflected by the surfaces $z(x,y)$ and $z'(x,y)$. (Here z, x, y are cartesian coordinates.) Then

$$\Delta = k\frac{\lambda}{2} \quad k=0, \pm 1, \pm 2, \ldots \tag{1}$$

and

$$\Delta = 2(z-z')n \tag{2}$$

where $\lambda = 546$ nm is the wavelength of the light, k is the order of interference (odd for the bright fringes and even for the dark fringes) and n is the refractive index of the continuous phase (e.g. in the case where splitting occurs in air, $n=1$). By measuring the distance between the fringes, we can determine the

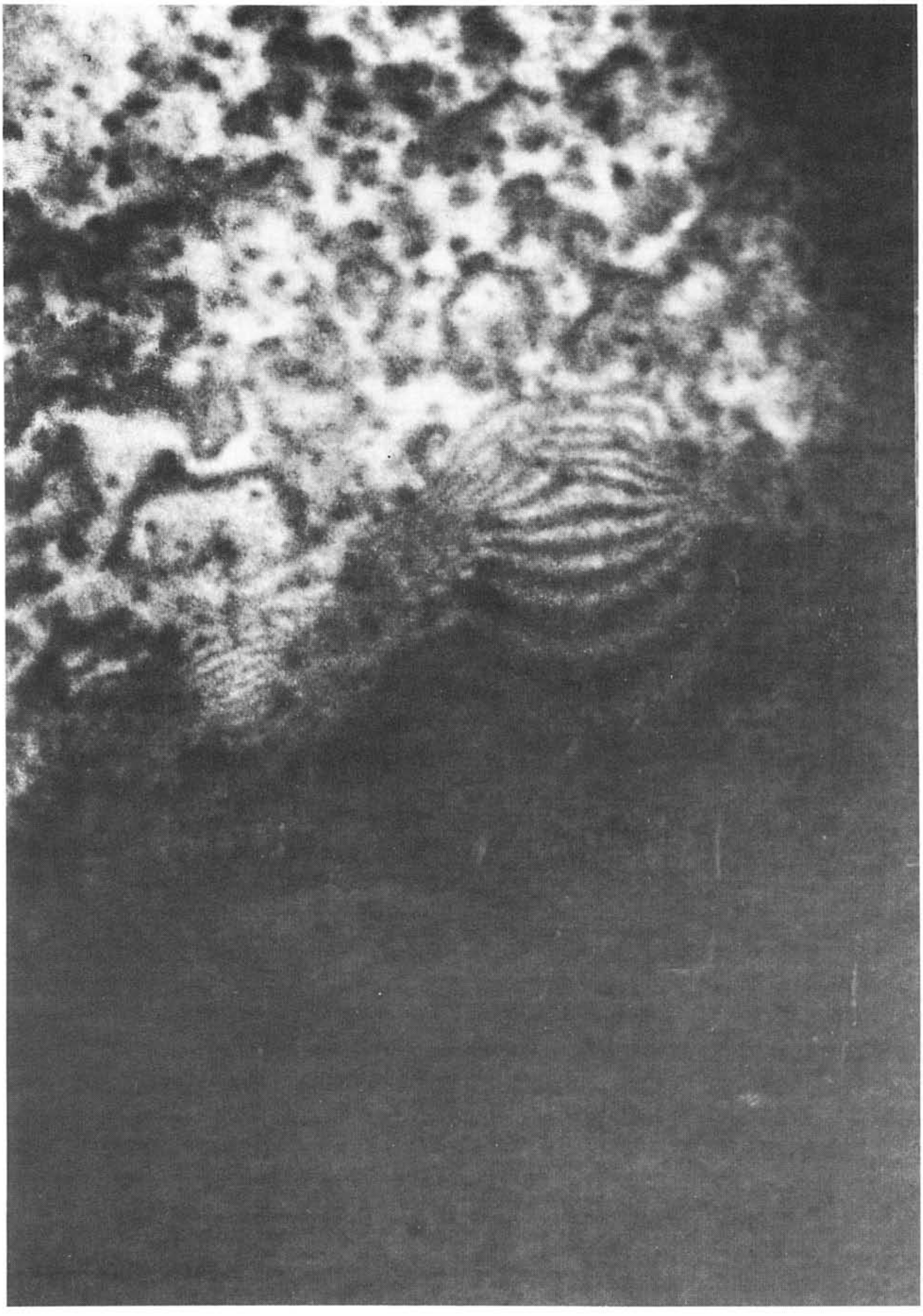

Fig. 4. Differential interference pattern of oil droplet–solid–air meniscus.

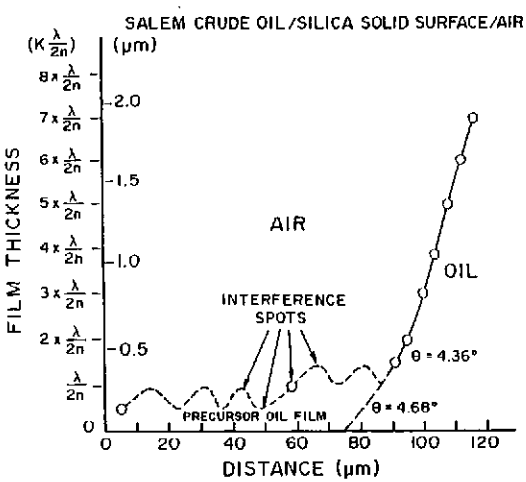

Fig. 5. Meniscus profile of oil droplet–solid–air.

shape of the oil droplet surface. However, as the "thinnest" fringe occurs at roughly 100 nm, before we can accurately determine the contact angle between the oil droplet and solid surface (or thin prewetting film), we must solve Laplace's equation to determine the shape in the film region where no optical information exists.

The more familiar UI method is illustrated in Fig. 3. Again, Eqns (1) and (2) are used, with n now denoting the refractive index of the aqueous solution.

EXPERIMENTAL OBSERVATIONS

Figure 4 shows a differential interference photograph of the three-phase contact region between a crude oil droplet (resting on the top of a horizontal glass silica surface), the solid silica surface, and air. The dark and bright "spots" are produced by the light interference from the surfaces of the precursor oil film. The meniscus profile is sketched in Fig. 5, revealing a contact angle of $4.68 \pm 0.05°$. The relative humidity in the experiment was 40%. The outer two fringes apparent in Fig. 4 and indicated in Fig. 5 by the arrows deviate noticeably from the meniscus line, suggesting the existence of a precursor oil film, (see Hardy [23], Fowkes [24] and Ghiralldella et al. [25]). A similar precursor film will be seen to play a major role in the separation of the oil droplet from the solid surface in the presence of the micellar solution.

In Fig. 6, microscopic photographs depict the initial stages of crude oil droplet separation from a silica solid surface in the presence of 1 wt% C_{16} alpha olefin sulfonate and 1 wt% NaCl (the droplet is attached below the horizontal glass slide in the aqueous micellar solution, with the photographs taken from above the glass surface). The speckled band between the dark and light areas

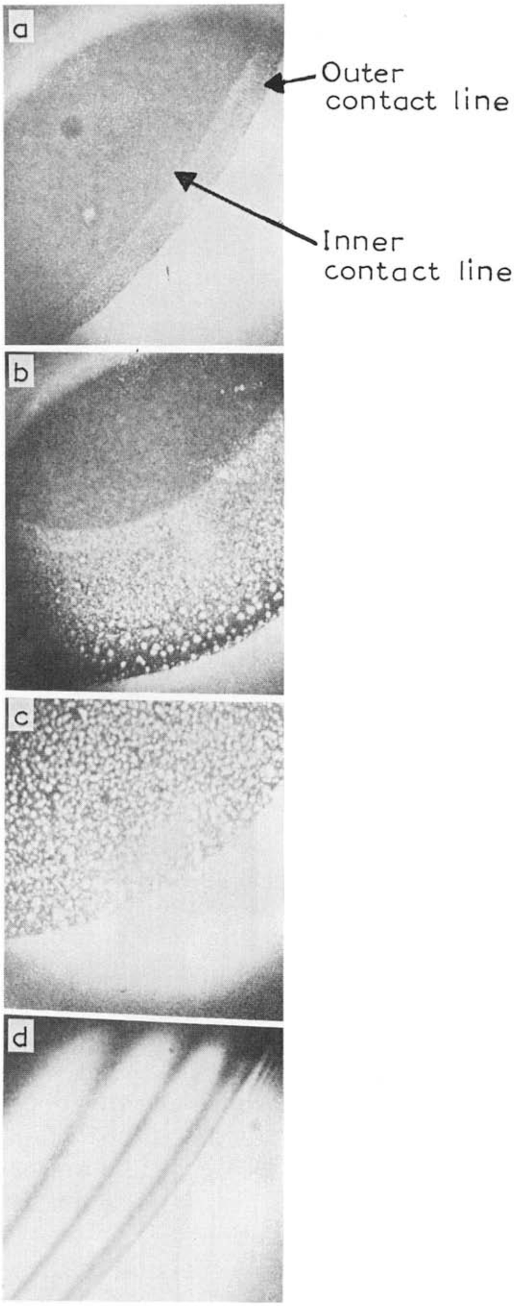

Fig. 6. UI photographs of separation of oil droplet from a solid silica surface in the presence of a micellar solution.

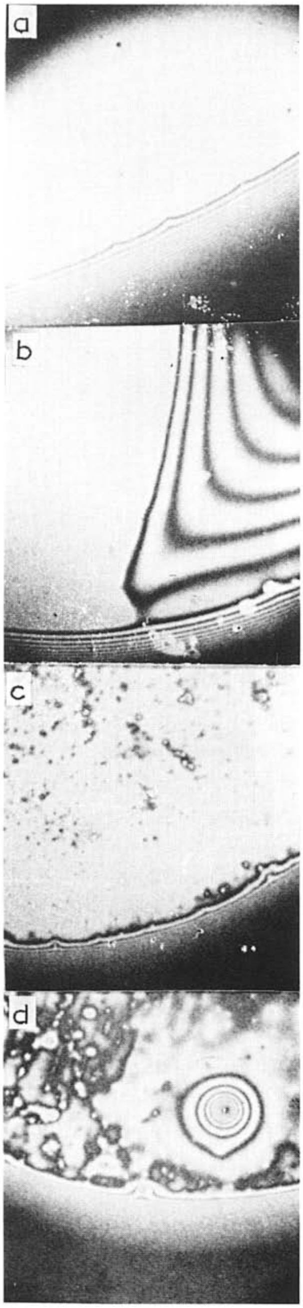

Fig. 7. UI photographs of thin film drainage on solid silica surface.

in Fig. 6a shows the formation of small water lenses (the white spots) between the oil and solid surfaces. In effect, two contact lines have been established: the first is between the oil droplet, solid surface and water film (outer line), and the second is between the oil droplet, solid surface and mixed oil/water film (inner line) (see Figs 6a and 6b).

In the subsequent photographs of Fig. 6, each representing a lapse of time, the thickness of the speckled band increases since the inner contact line recedes more rapidly than the outer contact line. Eventually the oil droplet is separated completely by the mixed oil/water film (Fig. 6c). The small water lenses (white spots) coalesce, drawing aqueous solution from the precursor film, and the oil droplet detaches from the solid surface. The final photograph in Fig. 6d shows the oil droplet rolling along the (slightly inclined) solid surface.

While somewhat distinct from the oil droplet removal mechanism, it is interesting to observe in Fig. 7 that when the oil droplet reaches the boundary of the measuring cell, it stops rolling and begins to drain. In Fig. 7a, the bright area denotes a thick water film (roughly 50 nm) and the circular bands (fringes) denote the droplet meniscus. In Fig. 7b a film thickness transition is occurring, with a thick film region apparent in the top right of the frame and a thin film region apparent in the top left of the frame. In Fig. 7c the entire film has accomplished the thickness transition and has achieved a thickness of roughly 5 nm. In the final frame, continued drainage results in a film thickness comparable to the roughness of the glass surface.

Two additional experiments were performed: in the first, we studied the separation of a crude oil droplet from silica in the presence of the C_{16} alpha olefin sulfonate solution without electrolyte, in this case the droplet separation process occurred much more rapidly. In the second additional experiment, we replaced the silica surface with a plastic surface; the oil droplet consequently did not detach from the solid surface.

DISCUSSION

Several investigators have studied the process of oil removal from a solid surface in the presence of micellar solutions [1–10]. Of the mechanisms suggested, the "rolling-up" mechanism of Adam [18] has gained the most accep-

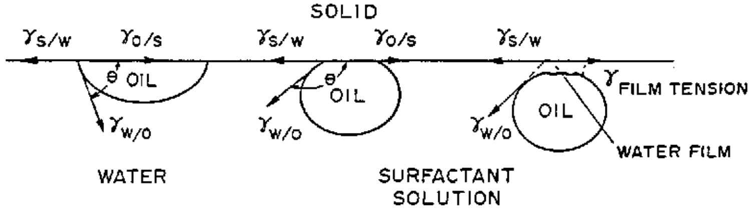

Fig. 8. Sketch of rolling-up mechanism.

tance. In this mechanism, the driving force causing the oil separation from the solid surface is an imbalance of interfacial tensions at the three-phase contact line (see Fig. 8). In the ideal case for oil separation, the apparent contact angle of the oil on the solid increases to almost 180° when the oil droplet rolls up. The "rolling-up" of the droplet occurs when

$$\gamma_{w/o} \cos\theta + \gamma_{o/s} - \gamma_{s/w} > 0 \tag{3}$$

where $\gamma_{w/o}$ is the water/oil interfacial tension, $\gamma_{o/s}$ is the oil/solid interfacial tension and $\gamma_{s/w}$ is the solid/water interfacial tension. Equation (3), known as Neuman's equation, suggests that the conditions for oil removal by the "rolling-up" mechanism are favorable when the interfacial tensions $\gamma_{s/w}$ and $\gamma_{w/o}$ are small and $\gamma_{o/s}$ is large. Surfactant adsorption at the water/oil and solid/water interfaces promotes "rolling-up" by lowering both $\gamma_{w/o}$ and $\gamma_{s/w}$.

Two additional mechanisms have been suggested as occurring in parallel with the "rolling-up" mechanism: the "necking and drawing" mechanism and the "diffusional" mechanism. In the "necking and drawing" mechanism [19], gravitational forces become significant with the diminishing capillary forces caused by the adsorption of surfactant, resulting in the drawing away of the oil droplet from a horizontal surface. In the "diffusional" mechanism, water and surfactant diffuses between the oil droplet and the solid phase [20–22]. In the present investigation, the "rolling-up" mechanism is evidenced by the receding oil/water/solid contact line, and the "diffusional" mechanism is evidenced by the small water lenses (white spots in Fig. 6) between the oil and the solid phases. The existence of the "diffusional" mechanism then gives rise to the presence of the second contact line apparent in Fig. 6.

The additional experiment performed using the plastic surface, in which the oil droplet was observed not to detach from the surface, indicates that short range hydration forces [26,27] between the water droplets and the solid surface are significant for the mechanism of diffusional oil separation. The experiment performed in the absence of electrolyte, in which oil removal was more rapid, may suggest that micellar interactions in the precursor water film are needed to establish a significant disjoining pressure in the film, thus promoting oil droplet separation. Decreasing the electrolyte increases the electrostatic repulsive environment surrounding the micelles, causing a more rapid detachment of oil droplets.

SUMMARY

Using a differential interference microscope, we have observed the separation of oil droplets from a solid surface in the presence of a micellar solution. The mechanism of oil droplet separation appears to be a combination of a "rolling-up" mechanism, in which surfactant-suppressed interfacial tensions provide the driving force for oil removal, and a "diffusional" mechanism, in

which water and surfactant molecules diffuse between the oil and solid surfaces ahead of the moving contact line. Considerably more evidence is required to elucidate the role of micelles in the oil separation process. For this purpose, similar experiments should be performed, investigating the efficiency of oil droplet removal in relation to micellar type and presence, solid surface type, oil type and salt concentration.

ACKNOWLEDGEMENTS

This work was supported by the U.S. Department of Energy and by the National Science Foundation.

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