A Study of Oil Displacement on Model Surfaces

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Experiments were performed to study bitumen film rupture and displacement on model surfaces. Bitumen film on a glass plate was found to thin down and rupture in the presence of water having a high pH; whereas on a polytetrafluoroethylene surface, film rupture did not take place. Experimental results on the rate of bitumen/water contact line displacement on a glass surface are also reported. A thin coating of bitumen on a glass surface retracted spontaneously in the inward radial direction upon exposure to an aqueous environment. The initially circular bitumen disk was reshaped into a spherical droplet. The time variation of the apparent dynamic contact angle of bitumen on the glass surface was measured at different pH and temperature. Finally the equilibrium contact angle of the bitumen on the glass surface was also measured. The bitumen displacement rate on the glass plate is higher at lower pH and the corresponding equilibrium contact angle is smaller. The rate of bitumen displacement increases with a decrease in the initial bitumen volume. The water temperature has minimal effect on the equilibrium contact angle; however, it has a significant influence on the bitumen displacement rate through changes in the bitumen viscosity. The displacement of a three-phase contact line is modeled using a simple force balance at the contact line. The experimentally measured dynamic contact angle is predicted well by the proposed model. The dynamic contact angle predictions by other contact line displacement models were compared with the experimental data. The practical implications of these results for bitumen extraction from oil sands are discussed.

Key Words: dynamic contact angles; equilibrium contact angles; oil displacement; film thinning; film rupture.

1. INTRODUCTION

Understanding the mechanisms of oil film rupture and the displacement of oil by water on sand grains is of importance in both in situ and mined oil recovery. For example, in the Clark (1) hot water extraction process, commonly used to extract bitumen from mined oil sands deposits, an aqueous phase under controlled temperature and pH is contacted with the oil sands in a digestor to facilitate the disengagement of bitumen from the sand grains. Although the process is proven, a desire to improve the performance of the process, resulting in decreased energy consumption and increased bitumen recovery, is the impetus for undertaking a systematic study of the mechanisms involved in oil–water displacement on a solid surface. Such mechanistic understanding can also help in other applications such as in situ recovery of petroleum using water flooding or enhanced-oil-recovery processes used to displace oil from the pores of a reservoir (2). The treatment of beaches exposed to oil spills entails the use of dispersants to produce a stable oil-in-water emulsion upon agitation with water (3). The use of sand for the sinking of oil slicks on the surface of sea water has also been reported. Here sand is dredged up from the sea bed and fluidized with water and additives to separate oils (4).

In each of the above situations, it is necessary to know (i) whether water can displace oil from the sand particles and (ii) how quickly the displacement process takes place. Preferential wetting by water occurs if the free energy per unit area of water/sand interface is less than the free energy per unit area of the oil/sand interface. If this occurs, oil is released from the sand surface and separation of oil and sand can take place. The rate of disengagement of the bitumen from the oil sands ore depends on the following sequential steps: (i) thinning and rupture of the bitumen film which is present as a coating on the sand surface in the presence of water, (ii) displacement of the bitumen/water interface and the formation of oil droplets on the sand surface, and (iii) detachment of adhered bitumen droplets from the sand surface.

Our objective is to present observations on a unique set of experiments dealing with the spontaneous displacement (dewetting) of bitumen by aqueous solution under different ambient conditions on both hydrophobic and hydrophilic solid surfaces. Qualitative observations are presented on the bitumen film thinning and film rupture processes on both hydrophilic and hydrophobic surfaces in the presence of water. The effect of pH on film thinning and film rupture process is investigated. Quantitative measurements are presented on the three-phase contact line displacement process; these include data on the rate of displacement, the dynamic, and the equilibrium contact angles. The effects of different pH and temperature on the displacement process are also investigated. We then examine various models proposed in the literature (5, 6, 7) to describe the motion of a three-
phase contact line with the objective of identifying a single model that would show quantitative agreement with our measured data. Our model is based on the approach of de Gennes (5) for describing the wetting dynamics. Such a model will then form the basis for developing an optimal route for processing the oil sands.

Brown et al. (8) present a similar study on the contact line displacement, in the context of crude oil recovery from oil reservoirs. In their work, water is forced to displace crude oil in a capillary tube, a condition similar to water flooding. They examine the dynamics of the displacement of crude oil from a glass surface under an externally applied force, whereas, in the present study, we focus on the spontaneous displacement of bitumen in the presence of water.

The process of film thinning and film rupture and the displacement of the fluid/fluid interface on a solid surface is also of importance in a number of other technologies such as film coating (pulp and paper, photographic emulsions, plastics, etc.). Hence a rich literature exists and several excellent reviews (Teletzki et al. (9), de Gennes (10), and Kistler (11)) are available on the current state of knowledge on the dynamics of thin films.

2. EXPERIMENTAL

2.1. Materials

The solid surfaces used are polytetrafluoroethylene plates (PTFE) and microscope glass plates. The PTFE surface is hydrophobic whereas the glass surface is hydrophilic. The surfaces of the plates were smooth and homogeneous down to the microscopic scale. The plates were cleaned with chromic acid and then with hot water to remove all impurities. The plates were also rinsed with ethanol and then with distilled water and dried before use. The bitumen is a coker feed bitumen supplied by Syncrude Canada Ltd. A notable difference between this bitumen and a conventional crude oil is the presence of higher molecular weight (low volatility) components in bitumen. About 50% is sufficiently volatile to vacuum distill without thermal cracking. A typical bitumen elemental analysis (wt%) is carbon 83%, hydrogen 10.6%, nitrogen 0.4%, sulphur 4.8%, Conradson carbon 1.2%, and carbon:hydrogen = 7:8 (12). Distilled water was used in all the experiments. HCl or NaOH were added to obtain the desired pH level.

2.2. Physical Properties of Bitumen

The pertinent physical properties of bitumen were measured under varying temperature and pH. The viscosity of bitumen was measured at different temperature using a viscometer (Contraves, rheomat 115). The change of viscosity with shear rate is presented in Fig. 1a at different temperatures. For a given temperature, the bitumen viscosity does not change with shear rate, indicating Newtonian behavior. The interfacial tension between bitumen and water changes with pH and temperature. The interfacial tension was measured using a ring tensiometer (Fisher surface tensiometer, Model 21). The effect of pH and temperature on the interfacial tension of bitumen/water is illustrated in Fig. 1b. The interfacial tension decreases with an increase in pH and temperature. The increase in pH (due to addition of NaOH), activates the surface-active agents (carboxylic type) present at the bitumen/water interface, leading to a decrease in the interfacial tension between bitumen and water (13).

The bitumen density, at different temperatures, was measured using a hydrometer and is shown in Fig. 1c. On the same figure, the variation of the water density with temperature is also plotted. It can be observed that there is little difference between the density of bitumen and water.

2.3. Film Thinning and Film Rupture Experiments

Experiments on film thinning and rupture were conducted with glass and PTFE plates in order to study the effects of
through which water was circulated to keep the temperature of the inner chamber constant. Small protrusions (E) on the middle part of the wall of the inner chamber held the test plate (F) on which test plates were placed. The top of the inner chamber was covered with a lid (G). A video Hi8 camcorder (ccd V101) with a macro lens was positioned on the side to record the displacement process. A high-resolution TV monitor was connected to the camcorder for display purposes.

2.4.2. Experimental method. Water from a constant-temperature circulating bath was maintained at the required temperature and circulated through the outer chamber. The inner chamber was half filled with water, having the same temperature as the bath and the desired pH. Bitumen was heated to the water temperature in a separate container and was used to coat a glass plate with a thin sheet of bitumen in the form of a disk (diameter, \( D = 9.0 \times 10^{-2} \text{ m} \)) at ambient temperature (23°C). The thickness of the bitumen sheet was \( 7.62 \times 10^{-4} \text{ m} \). The coating was made with the help of a circular template so that in each case the initial geometry of the bitumen sheet was the same. The test plates were placed side by side on a Plexiglas platform. The light sources were fixed at the bottom and the top of the platform for proper illumination. A camera (Nikon F4) with a macro lens was fixed to a stand to photograph the film thinning and rupture process.

A few drops of warm water at 50°C and known pH were placed on top of the bitumen film with the help of a glass tubing in such a way that they did not spill over to the bitumen/solid contact line. A schematic view of a bitumen-coated test plate with water placed on the bitumen sheet is shown in Fig. 2. Photographs were taken at various times to record the bitumen film thinning and rupture process. Bitumen film rupture led to bitumen/water interface movement on the glass surface until an equilibrium condition was reached.

Separate experiments were conducted to measure the rate of displacement of the bitumen/water contact line on the glass surface and the equilibrium contact angle. The measuring procedure is outlined below.

2.4. Dynamic and Equilibrium Contact Angle Measurements

2.4.1. Experimental setup. The experimental setup used to observe the rate of displacement of bitumen is shown in Fig. 3a while the schematic of the video recording setup is shown in Fig. 3b. A rectangular jacketed vessel (test chamber) made of Plexiglas was fabricated. The jacketed vessel consisted of an outer chamber (A) and an inner chamber (B). Tubes (C and D) were connected to the outer chamber through which water was circulated to keep the temperature of the inner chamber constant. Small protrusions (E) on the middle part of the wall of the inner chamber held the test plate (F) on which test plates were placed. The top of the inner chamber was covered with a lid (G). A video Hi8 camcorder (ccd V101) with a macro lens was positioned on the side to record the displacement process. A high-resolution TV monitor was connected to the camcorder for display purposes.

![FIG. 2. A schematic view of a bitumen-coated test plate with water placed on the bitumen sheet.](image)

![FIG. 3. Experimental setup for observation of bitumen displacement: (a) Detailed diagram of the jacketed vessel. (b) Schematic view of the experimental set-up: A, outer chamber; B, inner chamber; C, inlet tube; D, outlet tube; E, protrusion; F, test plate; G, lid.](image)
approached the equilibrium contact angle value. A typical sequence of three phase boundary (bitumen/water/glass) movement will be presented later. The initially thin, disk-shaped sheet of bitumen took the final shape of a droplet and the equilibrium condition (Young–Dupré equation) was reached. The bitumen droplet remained attached to the glass plate. The variation of the dynamic contact angle of the bitumen/water interface on the glass surface with time was measured\(^1\) by replaying the camcorder. Initially, the dynamic contact angle was measured with the help of a protractor from the enlarged photographic print. The interface was easily distinguishable between bitumen (black) and water. The dynamic contact angle was also estimated by measuring height, \(h\), and the instantaneous radius, \(R\), of the bitumen sheet from the following “spherical cap” expression (24):

\[
\cos \theta_d = \frac{1 - (h/R)^2}{1 + (h/R)^2}.
\]

The equilibrium contact angle of bitumen on the glass surface in the presence of water was measured when the equilibrium condition was reached (i.e., the contact angle did not change with time).

3. THEORETICAL MODELING

Many investigators have studied film thinning and rupture in the context of film stability on a solid surface (9, 14, 15, 16, 17). Under idealized conditions, the film thinning and rupture is viewed in the literature as a growing instability at the oil/water interface which thins the oil film sufficiently to trigger the action of molecular forces such as van der Waals forces leading to a rupture of the film and formation of a three-phase contact line. In this process, interesting events occur over a range of scales from the continuum scale down to molecular scales. The later effects are included as an effective body force through the use of potential functions to capture the molecular interactions. Experimental verification of nucleation and dewetting models is plagued with problems caused by heterogeneities and defects on the solid surface. Hence our efforts in film thinning and rupture studies remain qualitative in nature.

In the displacement tests, the bitumen, which was coated in the form of an initially circular sheet on the glass plate, was observed to recede in the presence of water to form a droplet which remained attached to the glass plate. The receding movement (dewetting) of the bitumen/water interface on the glass surface is similar to the three-phase contact point movement observed in the case of spreading (wetting) of a liquid drop on a solid surface. In the case of complete wetting (dewetting), the contact angle advances (recedes) toward 0° (180°). The dynamics of the wetting/dewetting phenomena is complicated, and despite increasing attention, the problem remains only partially resolved.

Nucleation and growth of dry patches, i.e., the dewetting process of unstable polymer films, were elaborately studied experimentally as well as theoretically by de Gennes (5), Brochard-Wyart et al. (18), Reiter (19, 20), Redon et al. (21, 22), and Shull et al. (23). After the creation of a hole on the thin film, the contact line is displaced through formation of a visible rim. The rim moves while the dewetting process continues and the native film outside the rim remains motionless. The velocity of the contact line is found to be constant except for in a few cases (22, 23). The dewetting of a metastable thin film of silicone on a low-energy silicon wafer surface was investigated by Redon et al. (21), Redon et al. (21), from their experimental findings, expressed the contact line velocity, \(v = k\sigma(\theta^2/\mu)\) where \(k\) is a constant, \(\theta\) is the equilibrium contact angle, \(\sigma\) is the surface energy of the liquid, and \(\mu\) is the viscosity of the liquid. The equilibrium contact angle was varied from 15° to 55°. De Gennes (5) and Bouchard-Wyart (18) arrived at a similar dependency of contact line velocity with \(\theta\), \(\sigma\), \(\mu\). Later, Shull et al. (23) obtained an expression \(v = k(\sigma/\mu)(1 + (\sigma_d - \sigma_s)/\sigma)\) for \(\theta = 180°\). Shull et al. (23) fixed an upper bound (145°) of the dynamic contact angle for \(\theta = 180°\) by using Hoffman’s (6) universal correlation for partial wetting systems. In the present investigation, the velocity of the bitumen/water contact line on the glass surface is not constant. In fact, the velocity of the contact line decreases as the dynamic contact angle value changes from a low value (18°) to high equilibrium contact angle values (106°, 168° at different water pH). There is no formation of a rim at the bitumen/water/glass contact line, and the dewetting process occurs exactly in the reversal form of the spreading of a liquid drop on a solid substrate. The spreading of a liquid drop in the presence of a second immiscible liquid on a smooth solid surface was studied experimentally by Foister (24). Foister (24) was not able to predict the dynamic contact angle for drop spreading using Hoffman’s (6) universal correlation. However, Cox’s (7) model fared much better for different viscosities of the spreading liquid drop (inner phase) in an immiscible liquid (outer phase). But a closer look at the graph in terms of Cox’s (7) model variables shows that there still exist discrepancies between experimentally measured dynamic contact angle values and Cox’s model predictions. Thus there remains uncertainty in the dynamic contact angle predictions.

3.1. Current Status

There are two approaches to model the three-phase contact line displacement on a solid surface. The first approach is based on the adsorption/desorption kinetics of a fluid/fluid
interface on the solid surface (25, 26), and the second approach is based on the triple-phase contact line hydrodynamics (6, 7, 10, 27–30). In the adsorption/desorption model, the number of adsorption sites involved per unit area is difficult to determine for different systems. In spite of this difficulty, the theory works quite well at low capillary numbers, i.e., when the viscosity of the liquids involved is low. Blake (26) suggested that when the viscous forces are comparable with the surface tension forces, deviation of the experimental data from the theory based on the adsorption/desorption model occurs. This would mean that the hydrodynamic forces play an important role in the three-phase contact line movement if the capillary number is high, i.e., when the viscosity of the liquids involved is low.

The relation between the contact line movement and the capillary number is given by

\[ \theta_d = f_{	ext{Ho}}(\lambda), \]  

where \( f_{	ext{Ho}} \) is a universal function, represents the data well for completely wetting systems; i.e., \( \theta_c \to 0 \). The capillary number is defined as, \( \lambda = \mu l / \sigma \), where \( v \) is the contact line velocity. Hoffman (6) deduced the universal function from a systematic experimental study of silicone oils displacing air in glass capillaries. Equation [2] reduces to \( \theta_d = 4.54 \text{ ca}^{0.353} \) when \( \lambda < O(0.1) \). Subsequently, Tanner (31) derived the \( \theta_d \sim \lambda^{1/3} \) power law from a simple hydrodynamic theory, which is known as Hoffman–Tanner law. Disregarding contact angle hysteresis, Hoffman’s universal law for a partially wetting system takes the form of

\[ \theta_s^* - \theta_d^* = C_T \lambda \text{ for } \theta_d < 135^\circ, \]  

where \( C_T \) is constant. The sign in Eq. [3] is reversed for the dewetting process and the capillary number is defined for the present case as \( \lambda = \mu_b v / \sigma_{bw} \), \( v \) is the contact line velocity, \( \mu_b \) is bitumen viscosity, and \( \sigma_{bw} \) is bitumen water interfacial tension.

Cox (7) presents a rigorous analysis of the flow structure near a dynamic contact line. Allowing a slip boundary at the contact line and defining a slip length, \( s \), Cox (7) constructed a solution to the Stokes equations in three parts using matched asymptotic expansion, which is valid for \( \epsilon \ll 1 \). The solution in terms of the present experimental fluids is given by

\[ g(\theta_d, \lambda) = g(\theta, \lambda) - \lambda \ln \epsilon_s^{-1} + O(\lambda) \]  

where,

\[ f(\beta, \lambda) = \frac{2 \sin \beta (\lambda^2 - \sin^2 \beta) + 2 \lambda^{1/3} (\beta - \sin \beta \cos \beta)}{\lambda (\beta^2 - \sin^2 \beta) (\pi - \beta)} \]

and

\[ \epsilon_s = \frac{s}{r}, \]

where \( s \) is the slip length which is on the order of microscopic length scale, \( r \) is on the order of macroscopic length scale, and \( \lambda \) is the ratio of viscosities.

In earlier studies, Hocking et al. (29) and Vionov (30) had arrived at similar expressions, correlating the apparent dynamic contact angle, the equilibrium contact angle, and capillary number through a hydrodynamic function. The forms of the hydrodynamic functions are different in each case, but the limiting form of the correlation becomes similar within a certain range of dynamic contact angle values. As Kistler (11) observes, these hydrodynamic theories predict apparent dynamic contact angles that agree remarkably well with experimental data when \( \epsilon_s \) is taken to be independent of \( v \) and adjusted empirically to optimize the fit between theory and experiment. However, a systematic deviation occurs for \( \lambda > 0.2 \). It can be noted that there is also a similarity between Cox’s expression and the Hoffman–Tanner law for a partially wetting system.

Many investigators (5, 30–34) used lubrication approximation to estimate the viscous dissipation in an advancing liquid front. In the lubrication approximation, the singularity at the three-phase contact line can be ignored, however there exists a shock-type discontinuity at the advancing liquid wedge or the liquid/liquid interface meets the solid at a 90° contact angle. Hocking’s (34) leading-order asymptotic solution of lubrication-flow approximation for thin, two-dimensional drop spreading under the action of capillarity has similar form to that of Cox (7) and Vionov’s (30) expression and the Hoffman–Tanner law. In order to describe polymer coating dynamics, de Gennes (5) used lubrication approximation, where a balance between viscous force and wetting
force determines the shape of the liquid wedge. De Gennes’ (5) result, in the limit of small angles, is given by

$$\theta_d (\theta_u^2 - \theta_d^2) = 6 \ln \varepsilon^{-1}, \tag{5}$$

and it has a different form than that of the generalized Hoffman–Tanner law, viz. $g(\theta_d) - g(\theta_u) = f(\varepsilon)$. It should be noted that other hydrodynamic theories (7, 28–31) substantiate the form of the generalized Hoffman–Tanner law. When $(\theta_u - \theta_d)/\theta_d \ll 1$, Eq. (5) closely approximates the Hoffman–Tanner law. Further, for a completely wetting system, $\theta_u = 0$, Eq. (5) reduces to the familiar form, $\theta_d \approx \varepsilon^{1/3}$, of the Hoffman–Tanner law even though de Gennes’ (5) derivation does not apply rigorously when the precursor film is present at the advancing liquid front. De Gennes’ theory is applicable only to a partially wetting system.

We will present a working model for the dewetting of bitumen in the presence of water on a glass surface where the basic framework of de Gennes’ (5) model is used. During the bitumen water contact line displacement no precursor film was observed. The dewetting models of Shull et al. (23), Redoen et al. (22), and Brochard-Wyart et al. (18) are not used here because the dynamics of contact line motion in their experimental studies is different from the present investigation. These differences are identified as: (i) the contact line velocity is not constant, rather the bitumen/water/glass contact line velocity decreases with time as the contact angle approaches the equilibrium contact angle value, and (ii) there is no formation of a liquid rim near the contact line while bitumen is displaced by water.

3.2. Present Model

3.2.1. Contact line dynamics. Bitumen can easily be spread on a glass surface in the presence of air and it is not observed to recede. Therefore, the interfacial forces are balanced at the triple-phase contact point and the angle of contact between bitumen and glass is at equilibrium. An imbalance in the interfacial forces occurs when water is added to the bitumen/air/glass contact line. This is due to the change in the interfacial tension. Consequently, the bitumen–water interface moves to a new equilibrium state such that an equilibrium contact angle of bitumen in the presence of water is reached and the interfacial forces are balanced. Figure 4 shows a schematic view of a bitumen droplet on a solid surface. The inequality in the equilibrium contact angle gives rise to a driving force to the relaxation process which can be called retracting force. The retracting force ($F_R$) at the three-phase contact line is expressed as

$$F_R = \sigma_{bw} (\cos \theta_e - \cos \theta_d), \tag{6}$$

where $\sigma_{bw}$ is the bitumen/water interfacial tension, $\theta_e$ is the equilibrium contact angle of bitumen on the glass surface in the presence of water, and $\theta_d$ is the dynamic contact angle of bitumen at time $t$.

During the relaxation period, viscous dissipation mostly takes place within the bitumen layer (not in water) close to the solid substrate, because the viscosity of bitumen is much higher than that of water. The viscous force per unit length of contact line ($F_v$) can be written (5, 11) as

$$F_v = \frac{3 \mu_b}{\theta_d} \frac{dR}{dt} \ln (\varepsilon^{-1}), \tag{7}$$

where $\mu_b$ is the viscosity of bitumen, $R$ is the radius of the circular shaped bitumen in contact with the surface at time $t$ and $\varepsilon = L_d/L$. $L_d$ is the microscopic scale cut-off region, and $L$ is the characteristic length of the macroscopic flow, i.e., the macroscopic scale cut off region. The expression for the viscous force is obtained from lubrication theory (5, 11), where the viscous effect at a smaller distance than $L_d$ (Fig. 4) from the putative contact line is ignored. The interface between bitumen and water is assumed as a flat liquid wedge with a dynamic contact angle $0 < \theta_d < \pi/2$. The condition for the lubrication approximation (35) to be valid, $\theta_d (\rho R / \mu_b) \ll 1$, is easily satisfied in this case because of the high bitumen viscosity. A typical value for $\theta_d (\rho R / \mu_b)$ is on the order of $10^{-5}$ for the upper bound of the $\theta_d$ value, i.e., 180°.

The viscous dissipation at the triple-phase contact line is equated to the retracting force. Thus equating Eqs. (6) and (7), the force balance equation can be written as

$$\frac{3 \mu_b}{\theta_d} \frac{dR}{dt} \ln (\varepsilon^{-1}) = \sigma_{bw} (\cos \theta_e - \cos \theta_d). \tag{8}$$

The gravitational and the inertial effects on the receding movement of bitumen are neglected since the Bond number ($\Delta \rho g R^2 / \sigma_{bw} \approx 10^{-5}$) and the Weber number ($\rho_b (dR/dt)^2 R / \sigma_{bw} \approx 10^{-5}$) are small within the range of experimental parameters of this study.

3.2.2. Bitumen shape. The contact angle of bitumen on the glass surface increases with time after the addition of
water. During this period, the shape of the bitumen sheet is assumed to be a segment of a sphere, i.e., a spherical cap as shown in Fig. 4. Different segments of a sphere form different contact angles with the plane on which they are attached. Thus, if the dynamic contact angle is 90°, the drop is assumed to be a hemisphere. The volumes of the different segments associated with the different dynamic contact angles are constant and equal to the initial volume of the bitumen coating. It is assumed that the volume of the bitumen is constant while the dynamic contact angle changes. This assumption is reasonable since there is no daughter droplet formation and the bitumen is immiscible in water. Therefore, the volume of the segment is given by

\[ V = \frac{1}{6} \pi h (3R^2 + h^2) = \frac{4}{3} \pi r^3, \]  

where \( r \) is the equivalent radius of the bitumen droplet and \( h \) is the height of the segment.

The height of the segment is a function of the dynamic contact angle \( \theta_d \) and the base radius \( R \) of the bitumen droplet. Thus, initially, as the dynamic contact angle of a droplet increases, the base radius of the droplet decreases and the height of a segment increases. From geometrical consideration, the height, \( h \), of the segment can be expressed as

\[ h = \frac{R}{\sin \theta_d} (1 - \cos \theta_d). \]  

Thus, the bitumen volume conservation gives,

\[ \frac{1}{6} \frac{\pi R}{\sin \theta_d} (1 - \cos \theta_d) \left[ 3R^2 + \frac{R^2}{\sin^2 \theta_d} (1 - \cos \theta_d)^2 \right] = \frac{4}{3} \pi r^3. \]  

\[ \]  

The validity of the above assumption (viz. the shape of the bitumen sheet is a segment of a sphere) has been tested for the current set of experiments.


\[ \frac{d\theta_d}{dt} = -\left( \frac{\theta_d \sin \theta_d}{3 \mu_b R} \right) \left[ 3 + \left( \frac{1 - \cos \theta_d}{\sin \theta_d} \right)^2 \right] \left( \frac{1}{\ln(\epsilon_d)} \right) \sigma_{bw} (\cos \theta_e - \cos \theta_d), \]  

where

\[ R = \left( \frac{4}{3} \right)^{1/3} \epsilon_d \left[ \frac{\left( 1 - \cos \theta_d \right)}{2 \sin \theta_d} + \frac{(1 - \cos \theta_d)^3}{6 \sin^3 \theta_d} \right]^{1/3}. \]  

[13]

Equation [12] can be expressed in terms of capillary number, \( ca \), as

\[ \frac{d\theta_d}{d(ca^{-1})} = -\left( \frac{1}{3} \right)(\theta_d \sin \theta_d) \times \left\{ \left[ 3 + \left( \frac{1 - \cos \theta_d}{\sin \theta_d} \right)^2 \right] / \left[ 1 + \left( \frac{1 - \cos \theta_d}{\sin \theta_d} \right)^2 \right] \right\} \times \left( \frac{1}{\ln(\epsilon_d)} \right)(\cos \theta_e - \cos \theta_d). \]  

[14]

where \( ca = \mu_b R / \sigma_{bw} t \). Equation [14] is solved numerically to determine the dynamic evolution of \( \theta_d \) with \( ca \) using an ODE integration package. The initial condition of \( \theta_d (t = 0) = \theta_i \) is the initial dynamic contact angle of the bitumen on the glass plate in the presence of water and it is assumed to be same as the equilibrium contact angle of bitumen on the glass plate in air. The value of \( \theta_i \) was observed to be 18°. The equilibrium contact angle, \( \theta_e \), of the bitumen on the glass plate in the presence of water at different \( pH \) and temperature was measured and it was used in the solution of Equation [14].

The parameter, \( \epsilon_d \) appearing in Equation [14] is varied as a fitted parameter to match the experimental data. The \( L_d \), the microscopic scale cut-off region, can be estimated from the \( \epsilon_d \) value when the \( L_d \), macroscopic length scale cut-off region, of, say, 1 mm is used.

The equivalent radius, \( r_e \), for different amounts of bitumen coated on the glass surface was measured experimentally. The volume of bitumen was measured using a photographic method. After reaching equilibrium, the bitumen droplet was made to detach from the glass plate when the surrounding liquid was slightly disturbed. The rising bitumen droplet was photographed and the radius, \( r_e \), of the drop was then measured. The photographic method was particularly convenient as no daughter droplets were formed during the displacement of bitumen or as during the detachment of the bitumen droplet from the glass plate. An indirect method of bitumen volume estimation was also performed by weighing the bitumen-coated glass plate. This procedure required bitumen density at different temperatures (Fig. 1c). The estimated bitumen volumes from both of these methods matched quite well (within 0.2%).

The bitumen viscosities at different temperatures and bitumen/water interfacial tensions for different \( pH \) and temperature, given, respectively, in Figs. 1a and 1b, were used.
experiment on a PTFE plate, which resulted in no appreciable thinning down of the bitumen film. With the passage of time, the bitumen film on a glass plate ruptured, as seen in Fig. 5c, thus exposing the glass surface. No rupture of bitumen films was observed on the PTFE surface (Fig. 5d).

The initial thickness \( W = 7.62 \times 10^{-4} \text{ m} \) of the bitumen film was large and hence the presence of the solid substrate is believed to have no effect on the thinning process during the initial stages. During this stage, the thickness of the bitumen layer just beneath the water phase decreases either due to gravity (weight of water) or thinning initiated by the interfacial tension gradient at the three-phase contact line (bitumen/water/air). The interfacial tension gradient occurs at the three-phase contact line when a water drop is added on the top of the bitumen surface. The addition of water with a high pH (presence of NaOH) on the bitumen sheet activates the alkyl carboxylic acid present in the bitumen due to the adsorption of Na\(^+\) ions at the bitumen/water interface. The activation of alkyl-carboxylic acid, which is a surfactant by nature, leads to a decrease in the bitumen/water interfacial tension (Fig. 1b), and thus the interfacial tension gradient develops at the three-phase contact line.

Once the thickness becomes sufficiently small (below a critical thickness), the thinning process of the bitumen film continues, aided by the intermolecular attractive forces (also known as conjoining pressure), resulting in the eventual rupture of the bitumen film, as seen in Fig. 5c. The PTFE surface, on the other hand, is preferentially wetted by the oil phase in the presence of both oil and water (36, 37). Thus, the thinning process in the case of the PTFE surface ceases when a critical thickness is reached, as seen in Fig. 5d.

The formation of a light brown ring was also observed on the bitumen-coated glass plate when water with a pH of 3 was used. However, the thinning process was observed to be much slower at this pH and the bitumen film did not rupture on the glass surface.

The above experimental findings reveal that a bitumen film thins down and ruptures on a glass (hydrophilic) surface in the presence of water. The solid and dashed curves of Fig. 6 correspond to two different pH values of 11 and 3, respectively. The dynamic contact angle of bitumen is seen to change more rapidly at a lower pH value than at higher pH values, e.g., at \( t = 50 \text{ s} \), \( \theta_d = 90^\circ \) for pH 3, whereas, \( \theta_d = 36^\circ \) for pH 11.

4. RESULTS AND DISCUSSION

Qualitative observations on the bitumen film thinning and film rupture are discussed first, followed by a discussion of the quantitative results on the bitumen/water interface displacement rates on a glass plate. Finally, different models of contact line displacement are compared with the present set of experimental data.

4.1. Observations on Film Thin and Film Rupture

A comparison of the extent of bitumen film thinning and film rupture on a glass plate and a PTFE plate is shown in Fig. 5. The glass surface is hydrophilic whereas the PTFE is hydrophobic. Figure 5a shows the result of placing a few drops of water at 50\(^\circ\)C and pH 11 on top of a bitumen film on a glass plate. The bitumen film is seen to thin down entirely on the glass plate. The thinning of the bitumen film on the glass plate is evident by the change in the film’s color from black to light brown. Figure 5b shows the result of a similar
In Fig. 7, a sequence of photographs show the shape and the dynamic contact angle of a bitumen droplet that was exposed to a pH of 3 and 11. Clearly, the receding rate is much higher at a pH of 3, even though the equilibrium contact angle is smaller at this pH.

The variation of the equilibrium contact angle of a bitumen droplet on the glass surface, $\theta_e$, with pH is shown in Fig. 8 for two different temperatures, 40 and 80°C. The equilibrium contact angle of the bitumen drop increases with an increase in pH. Thus at a higher pH value, it would be easier to detach bitumen droplets from the glass surface.

### 4.2.2. Effect of temperature

The effect of temperature on the dynamic contact angle of bitumen for a pH of 11 is shown in Fig. 9. Here too, the dynamic contact angle increases with time toward its new equilibrium value in the presence of aqueous phase. The solid and dashed curves correspond to the two different temperatures, 40 and 80°C, respectively. It can be observed that at the higher temperature the rate of change of the dynamic contact angle of bitumen is much higher than at a lower temperature, e.g., at $t = 50$ s, $\theta_d = 40^\circ$ at 40°C, whereas $\theta_d = 168^\circ$ at 80°C. This is mainly attributed to the decreased bitumen viscosity at the higher temperature.

The variation of equilibrium contact angle, $\theta_e$, with temperature is presented in Fig. 10. It is shown that for a given
pH, the equilibrium contact angle increases slightly with temperature. However for a given temperature, $\theta_e$ is very sensitive to pH changes.

It should be noted that the dynamic contact angle of bitumen depends on the viscosity and the interfacial tension of the bitumen and water through Eq. [14], whereas the equilibrium contact angle depends only on the interfacial tension through the Young–Dupré equation. This is the reason for the great dependence of $\theta_d$ on temperature and, to a large extent, the very low dependence of $\theta_e$ on temperature.

4.2.3. Effect of bitumen volume. In Fig. 11, it is shown that a larger bitumen volume causes a slower movement of the bitumen/water/glass contact line. The decrease in the rate of change in the dynamic contact angle with an increase in the bitumen volume can be explained from Eqs. [12] and [13]. From these two equations, it can be shown through algebraic manipulation that the rate of change in the dynamic contact angle is inversely proportional to $V^{1/3}$. Consequently, a larger bitumen sheet would require a longer time to form a bitumen droplet.

5. MODEL VERIFICATION

5.1. Bitumen Shape

The shape of the bitumen film during the relaxation period is assumed to be a segment of a sphere, i.e., a spherical cap. The validity of this assumption is verified in Fig. 12 by plotting the height of the segment, $h$, from the Eq. [10] against the experimentally measured value of the segment height. The calculated height $h$ in Eq. [10] depends on the measured values of $\theta_d$ (measured with a protractor) and $R$. In Fig. 12, all the data points for different pH, temperature, and bitumen volume coincide with the 45° slope line, justifying the assumption made about the evolving bitumen shape. Further, due to the validity of the “spherical cap”
assumption of the bitumen sheet, the dynamic contact angle was measured conveniently by using Eq. [1].

5.2. Dynamic Contact Angle

5.2.1. Hoffman–Tanner law. Conventionally, the dynamic contact angle, $\theta_d$, is plotted against capillary number, $ca$. Using the form of the Hoffman–Tanner law (Eq. [3]) for a partially wetting system, we plot $\theta^3_3 - \theta^3_d$ against $ca$ for two different temperatures and pH values in Fig. 13. The open and close circular (square) symbols correspond to a pH of 11 (3) for two different temperatures, 80 and 40°C, and they coincide. The equilibrium contact angles at these two temperatures are almost same (Fig. 8). On the other hand the data points corresponding to two different pH values of 11 and 3 at 40°C and also at 80°C do not coincide. In fact, at a pH of 3, the equilibrium contact angle is 106°, which is much smaller than the equilibrium contact angle of 168° at a pH of 11. The intercept of the best-fit lines for two different equilibrium contact angle values gives the value of the constant, $C_T$, in Eq. [3]. The intercept of these two lines is $1.6 \times 10^7$, which is close to the constant, $C_T = 1.56 \times 10^7$, found by Shull et al. (23) based on the experimental data of Hoffman on forced flow in capillaries.

In Fig. 13, a horizontal shift would result in the collapsing of all the data points. A similar horizontal shift of the dynamic contact angle data for different viscosity ratios ($\lambda$) of the inner phase and outer phase for a drop spreading on a solid surface in the presence of a second immiscible liquid is suggested by Foister (24). Many investigators (33, 34) suggested a shift factor in terms of a pseudostatic angle, $\theta^*_p$, which is allowed to depend on speed, i.e., $\theta^*_p = f(\nu)$; since no physical insight is gained by such empirical curve fits we have refrained from attempting similar curve fits.

5.2.2. Cox’s model. In Fig. 14, the dynamic contact angle, $\theta_d$, is plotted against $ca$ for two different pH values of 11 and 3 at 40°C. The different curves pertain to Cox’s model as presented by Eq. [4] for different values of $\epsilon_s$, the length scale ratio. The $\epsilon_s$ is varied in an attempt (not always successful) to match the experimental data with the model prediction. The dynamic contact angle for pH 3 matches reasonably well with Cox’s model for small $ca$ when $\epsilon_s = 10^{-2}$ is used. This value of $\epsilon_s$ corresponds to a microscopic length scale, $s\sim10\mu m$ when the macroscopic length scale, $r_s$, is 1 mm. $s$, the slip length, is a distance from the contact line where slip between liquid and solid occurs. A slip length of 10 $\mu m$ is quite reasonable. For the same case, the match fails when $ca > 0.1$. Further, Cox’s model also fails to match the dynamic contact angles at a pH of 11 with widely different values of $\epsilon_s$. Here, $\epsilon_s$ equal to $10^{-7}$ corresponds to the lower bound of the slip length value of 10 nm. Slip length lower than the order of molecular dimension is not reasonable. Thus a match between the experimental data and Cox’s model appears to be impossible at higher pH values.

Several investigators (39, 40, 41) have observed that in some cases Cox’s formula is inadequate in predicting the dynamic contact angle. A systematic deviation for all the data points from Cox’s prediction occurs at $ca \approx 0.2$, where the calculated $\theta_d$ values increase more rapidly with increasing $ca$ than the measured $\theta_d$ data (11). One may attribute the quantitative discrepancy between the hydrodynamic theory and experiments to the neglect of the higher order correction terms, or even a complete failure of the asymptotic expansions that are formally valid only in the limit $ca \to 1$ (7). In fact, the apparent dynamic contact angles obtained from finite-element solutions of the complete set of Navier–Stokes equations and free-surface boundary conditions indeed agree better with the Hoffman–Tanner law than with the $\theta_d$ values calculated from Cox’s expression [4] (11).

5.2.3. Present model. In Fig. 15, the dynamic contact angle $\theta_d$ of the bitumen/water interface on the glass surface...
is plotted against the capillary number for two different pH values, 3 and 11, at 40 and 80°C, respectively. The two curves (solid and dashed) in Fig. 15 are the predictions from the model (Eq. [14]) for two different pH values. It should be noted that $\theta_0$ is observed to be a strong function of the water pH but it exhibits a weak variation with temperature. Consequently, the change in $\theta_0$ with temperature is neglected and an average $\theta_0$ is used. The value of the parameter $\epsilon_0$ used is 0.03. This $\epsilon_0$ value corresponds to a small-scale cutoff region, $L_0 = 30 \mu m$, whereas the large scale cutoff region is kept equal to 1 mm. This $\epsilon_0$ value was found to predict all the dynamic contact angles for the different temperatures and pH values.

Figure 15 shows that the dynamic contact angle depends on the capillary number through an S-shaped curve. Initially, the contact line velocity increases rapidly and then decreases as the dynamic contact angle approaches towards the equilibrium contact angle value due to the decrease in retracting force. The dependence of the instantaneous radius, $R$, of the bitumen on time would give an idea of the velocity of the bitumen/water contact line. In the present study, $R \approx t^{-0.2}$ when $\theta_0$ is equal to 106° (pH 3), whereas $R \approx t^{-0.8}$ when $\theta_0$ is equal to 168° (pH 11). The negative sign in the exponent of $t$ indicates a dewetting process, i.e., as time progresses the contact radius $R$ decreases. The exponent of $t$ has been found to be 0.1 for silicone drop spreading on glass and silicon wafer surfaces in the presence of air (24, 31, 42). Redon et al. (22) found the value of the exponent to be 0.66 for the dewetting of a microscopic poly(dimethylsiloxane) film (thickness <1 $\mu$m) on silanized silicon wafers.

6. PRACTICAL IMPLICATIONS OF BITUMEN EXTRACTION

In order to liberate bitumen from oil sands, mined oil sands are mixed with hot water under steady shear in a rotating drum. Commercially, one operates a bitumen extraction unit at a pH of 8.2 through the addition of NaOH. In this study we find that the equilibrium contact angle for bitumen on a glass plate in the presence of water is higher at a higher pH value (see Fig. 8). On the other hand, the rate of bitumen displacement is lower at a higher pH value (see Fig. 6). Moreover, the displacement rate is accelerated at a higher temperature. Ideally, one prefers fast bitumen displacement and the formation of a bitumen droplet with a large equilibrium contact angle. A fast bitumen displacement means that the time required to attain complete displacement is small and hence the residence time necessary in an extractor is small. A large equilibrium contact angle allows easy detachment of the bitumen droplets from the sand grains. As the temperature affects the rate of bitumen displacement, a high temperature, 60–80°C, is normally used in a bitumen extraction unit. The use of a high pH to achieve a large bitumen contact angle is essential even though the rate of displacement is lower at the higher pH. The present study suggests that an optimal pH and temperature cycle could be devised to facilitate each step of the bitumen liberation process.

7. CONCLUSIONS

In order to elucidate the mechanism of oil displacement from sand grains, experiments were performed by coating a bitumen film on model surfaces. Bitumen film thinning and film rupture processes were studied on PTFE and glass plates in the presence of water at different pH and temperature. Displacement of the bitumen/water interface on the glass plate was monitored and changes in the dynamic contact angle of bitumen with time were measured. For the same experiment, the equilibrium contact angle of bitumen was also measured.

The displacement of the bitumen/water interface on a glass surface is modeled by a simple force balance model at the three-phase contact line. The driving force (retracting force) for the movement of the three-phase contact line originates due to the inequality in the equilibrium contact angle value after the addition of water to the bitumen. It is assumed that during the bitumen displacement, viscous dissipation takes place in the bitumen close to the glass surface. The viscous force is calculated utilizing lubrication approximation.

The bitumen volume is assumed to be constant during the receding process. This assumption is particularly valid since the formation of daughter droplets is absent and the bitumen is immiscible in water. The viscous loss at the triple-phase contact line is equated to the driving force according to the de Gennes (5) model. The model equation is solved to predict the variation of the dynamic contact angle of bitumen with ca. The experimental results on the dynamic contact angle variation of bitumen are predicted well by the present model. The constant for the Hoffman–Tanner law is estimated to be the same order of magnitude as suggested by Hoffman. Since a single experimental run spans a wide range of ca, Cox’s model (which is valid for small ca) is inadequate in predicting the dynamic contact angle data.

The salient features of all the experimental results and the theoretical model are outlined below.

(i) The bitumen film thins down and then ruptures on the glass surface in the presence of water, whereas on a PTFE surface the bitumen film is stable. A high-pH water value enhances bitumen film thinning and rupture processes.

(ii) The bitumen displacement on the glass surface in the presence of water is faster at a low pH, whereas the equilibrium contact angle of bitumen is larger at a high pH.

(iii) Existing models for the prediction of the dynamic contact angles are tested with the present set of experimental data. The prescribed model based on lubrication approximation predicts the experimental data quite well.

REFERENCES

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