# Dynamic Interfacial Tensions in Acidic Crude Oil/Caustic Systems

## Part I: A Chemical Diffusion-Kinetic Model

A chemical diffusion-kinetic model is developed for the acidic oil/caustic system of alkaline flooding by proposing a set of interfacial reactions leading to *in situ* generation of surfactants. The rate constants of interfacial reactions are independent of aqueous phase compositions. In Part I, the model is applied for determining these rate constants from its correlation with dynamic interfacial tension data obtained using the spinning drop tensiometer. The relative magnitudes of the rate constants characterizing the adsorption/desorption barriers are shown to govern the extent of dynamic interfacial tension minimum.

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## SCOPE

Alkaline flooding is one of the enhanced recovery processes proposed for acidic crude oils. In this process, the neutralization of fatty acids in the crude oil by alkali in the flood water results in *in situ* generation of surfactants which lead to low interfacial tensions. When acidic crude oil is freshly contacted with caustic, the interfacial tension changes continuously with time until equilibrium is attained, often displaying a dramatic dynamic interfacial tension minimum. The question arises as to which interfacial tension is operative in the reservoir during a flood. In Part I we attempt to understand, in terms of the basic mechanisms, the cause of the observed dynamic interfacial tension minima in these systems. This understanding forms the basis of our investigations, reported in Part II, of transient interfacial tensions during alkaline flooding.

Ramakrishnan and Wasan (1983) investigated the equilibrium behavior of the acidic oil/caustic systems, proposed the governing system chemistry and determined the equilibrium constants in the model by correlating the experimental data. By proposing a set of interfacial reactions leading to *in situ* generation of surfactants, we have developed a chemical diffusion-kinetic model that is based on their system chemistry. In Part I, the model is applied to a stagnant (actually, gyrostatic) batch system encountered in the spinning drop tensiometer. The spinning drop tensiometer is the most commonly used apparatus for the measurement of these low dynamic interfacial tensions. The resulting equations are solved with consideration of the changing geometry of the drop accompanying the changes in interfacial tension during an experiment. The rate constants of the interfacial reactions can be determined from a correlation of the model with dynamic interfacial tension data. The rate constants so determined are used in Part II as we attempt to predict the time variation of the interfacial tension between an oil globule and the flood water during a continuous alkaline flood.

Rubin and Radke (1980) developed a physical model to explain the occurrence of dynamic interfacial tension minima in these systems. Theirs being a physical model, the effects of changes in aqueous phase compositions (pH and salinity) were not addressed. Trujillo (1983) developed a pseudochemical model and reported the rate constants as functions of the chemical composition of the aqueous phase. In this paper a truly chemical model is presented. The system chemistry is explicitly incorporated in the model and, thus, the rate

constants are independent of the chemical makeup of the aqueous phase. These kinetic parameters are therefore considered to be the characteristic properties of the surface active acids in the oil phase.

## CONCLUSIONS AND SIGNIFICANCE

A chemical diffusion-kinetic model is developed for the case of the acidic oil/caustic system encountered in alkaline flooding. The model is based on the system chemistry proposed by Ramakrishnan and Wasan (1983). The model is applied to the stagnant batch system of the spinning drop tensiometer.

Parametric study on the model reveals that the observations of dynamic interfacial tension minima in these systems are explicable in terms of the relative magnitudes of the rate constants characterizing the adsorption/desorption barriers. Since the main processes occurring are the interfacial neutralization of the acid from the oil phase by the alkali and the partitioning of the soap formed into the oil phase, the rate constants for the dissociative adsorption of the acid and for the desorption of the soap to the oil represent, respectively, the adsorption and desorption barriers. The higher the desorption barrier is relative to the adsorption barrier, the lower is the minimum interfacial tension.

The procedure for obtaining the extent of these barriers from a correlation of dynamic interfacial tension data is illustrated using data on the acidic Wilmington Field crude oil against caustic solution. This crude exhibits dynamic effects lasting only about 15 min and, furthermore, the dynamic interfacial tension minimum is rather shallow. Being a chemical model, the interfacial reaction rate constants, which represent the adsorption/desorption barriers, are independent of the composition of the aqueous phase. This is a significant improvement over the pseudochemical model of Trujillo (1983). These kinetic parameters are considered to be properties of the surface active acids in the crude oil. The kinetic parameters thus determined for Wilmington Field crude oil are used in Part II to assess the importance of dynamic effects under continuous flow conditions encountered in alkaline floods conducted in laboratory cores as well as in oil fields.

## Introduction

When two immiscible liquid phases, either one containing surfactants, are freshly contacted, the interfacial tension changes continuously with time until it attains the equilibrium value. Unlike gas-liquid systems, in liquid-liquid systems the interfacial tension does not always decrease monotonically to its equilibrium value. If the surfactant is soluble in both phases and initially present in one phase only, a dynamic interfacial tension minimum is often observed within a very short time after the phases are contacted. If it is assumed that the dynamic interfacial tension is always in equilibrium with the surface concentration of the solute, the minimum interfacial tension corresponds to a maximum in surface concentration.

England and Berg (1971) rationalized the occurrence of a maximum in surface concentration of the solute (and concomitant dynamic interfacial tension minimum) in stagnant liquid-liquid systems using a diffusion-kinetic model. A diffusion-kinetic model accounts for diffusional limitations in the stagnant bulk phases as well as activation energy barriers to solute transfer from or to the interface. The activation energy barriers are expressed using kinetics of reversible solute exchanges between the respective sublayers and the interface. Their model explained the occurrence of the dynamic interfacial tension minimum during the physical transfer of surfactant from one phase to another in terms of an activation energy barrier to the transfer of surface active solute from the interface to the receptor phase—the desorption barrier as they called it. In view of the reversible kinetics, there is an adsorption term and a desorption term in every rate process irrespective of whether the net effect is adsorption or desorption. The word "desorption" in the term thus reflects the net effect. These desorption barriers cause the dynamic surface concentration to exceed the equilibrium levels for a short time, giving rise to dynamic interfacial tension minima. Thereafter the surfactant is slowly removed away from the interface into the receptor phase until the surface concentration is reduced to equilibrium levels and the interfacial tension rises to equilibrium levels.

In this series of two papers, we examine the dynamic behavior of a specific liquid-liquid system of practical interest. This is the acidic oil/caustic system encountered in alkaline flooding for enhanced oil recovery. Although several mechanisms have been postulated for oil recovery by alkaline flooding (Johnson, 1976), one of the most important is the reduction in interfacial tension due to the *in situ* generation of surfactant by the reaction of the acid in the crude oil and the alkali in the flood water. Consequently, there have been several studies on both equilibrium and dynamic interfacial tensions of this system under stagnant batch conditions (Jennings, 1975; McCaffery, 1976; Chan, 1978; Rubin and Radke, 1980; Chan and Yen, 1982; Sharma and Yen, 1983; Ramakrishnan and Wasan, 1983; Trujillo, 1983). Also, there have been several observations of a dynamic interfacial tension minimum in these systems (McCaffery, 1976; Chan, 1978; Rubin and Radke, 1980; Trujillo, 1983). However, there is not much known about the importance of these dynamic effects in alkaline flooding; particularly, quantification of the dynamic behavior is lacking. In this paper the dynamic behavior of these systems is investigated under stagnant batch conditions whence the solute transport in the bulk is by molecular diffusion alone. A chemical diffusion-kinetic model is developed to explain the dynamic behavior of these systems, specifically to explain why a minimum in interfacial tension occurs at the beginning of an experiment and what mechanism governs it. The unknown kinetic parameters (rate constants) in the model are obtained by correlation with experimental data. The effects of the chemical makeup of the aqueous phase are explicitly included in the model and, hence, these kinetic constants are characteristic properties of the acidic components in the crude oil. The kinetic parameters so estimated for one such crude oil, Wilmington Field crude oil from California, are used in Part II to assess the importance of dynamic effects under continuous flow conditions encountered in alkaline floods conducted in laboratory cores as well as in oil fields.

The acidic oil/caustic system has many interesting aspects. The interaction of acid in the oil with the alkali in water results in the *in situ* generation of surfactants that are responsible for the lowering of interfacial tension. The surface active species are anions of dissociating electrolytes soluble in either phase (Ramakrishnan and Wasan, 1983). The model developed herein is a chemical model that incorporates the effects of chemical composition of the aqueous phase and also recognizes the existence of an electrical double layer consequent to ionic adsorption. The model is developed for the stagnant (or actually gyrostatic) batch system encountered in the spinning drop interfacial tensiometer. This tensiometer remains the most popular device for measuring the dynamic interfacial tension in these systems where the interfacial tension is usually around one mN/m or lower. The experiments for this work were also carried out using this tensiometer.

In the first part of this paper a phenomenological development of the chemical model based on the diffusion-kinetic approach is presented. A brief parametric study indicates the role of important parameters. Finally, correlation of experimental data to the theoretical model is illustrated.

## The Chemical Diffusion-Kinetic Model

England and Berg (1971) developed the first diffusion-kinetic model for surfactant transport in liquid-liquid systems. They developed a physical model for surfactant transport across the interface between two infinite liquid phases for a linear isotherm with linear kinetics. With their model, they correlated dynamic interfacial tension data on simple surfactant systems obtained using a laminar contacting liquid jet and explained the occurrence of dynamic interfacial tension minima in terms of the desorption barriers. Later, Rubin and Radke (1980) and Brown and Radke (1980) constructed physical models for the case of finite systems by approximating the transport of solute in the bulk using the Nernst film model. Brown and Radke also accounted for the interfacial area changes accompanying the changing interfacial tension in the spinning drop tensiometer. Rubin and Radke were able to assess the effect of phase volume ratio on the dynamic behavior and rationalized the observed minimum in an acidic oil/caustic system, again in terms of desorption barriers. However, being a simple physical model, the effects of the chemical composition of the aqueous phase were not addressed.

Recently, Trujillo (1983) and Sharma et al. (1984) presented dynamic models for the acidic oil/caustic system that took into account these chemical effects. Trujillo superimposed the chemical effects on the physical model of England and Berg, and thus his model may be called as a pseudochemical model. Using this model he examined the effects of pH as well as the presence of divalent ions. The investigation of Sharma et al. appears to be incorrect in that several ionic reactions, which should by nature be instantaneous, are considered as rate processes.

In the next section, a phenomenological development of a truly chemical model of surfactant generation and transport in the acidic oil/caustic system is presented. The underlying approach is the diffusion-kinetic approach detailed elsewhere (Borwankar, 1984). The model is based on the system chemistry proposed by Ramakrishnan and Wasan (1983). They proposed that the adsorbing species in the crude oil/caustic system are anions of long chain fatty acids in the crude. The dynamic model therefore takes into consideration the double layer effects consequent to ionic adsorption. The adsorption isotherm, the equation of state, and the kinetics used are consistent with their equilibrium studies. Finite phase volumes and the area effects associated with the spinning drop tensiometer are considered.

### *Phenomenological development of the chemical model*

Any model of the dynamics of surfactant adsorption should correspond to the equilibrium model as time tends to infinity. Thus, the discussion of the phenomenological chemical model should begin with the equilibrium model. Ramakrishnan and Wasan (1983) presented the equilibrium interfacial activity model for acidic oil/caustic systems and their model forms the basis of the dynamic model developed herein.

*Equilibrium Considerations.* The system chemistry used here is summarized in Figure 1. It is assumed that the mixture of acidic species in the crude leading to the formation of surfactants can be represented as a single component HA with average properties. The acid HA is assumed to distribute itself between the oil and the aqueous phases in a constant distribution ratio under all encountered conditions of the ionic strength. Ideal behavior is assumed in both the phases as well as the interface. The distribution is represented as

$$HA_o \rightleftharpoons HA_w, \quad K_D = \frac{C_{HA_o}}{C_{HA_w}} \tag{1}$$

where the subscripts *w* and *o* stand for aqueous and oil phases, respectively. Obviously, the value of $K_D$ should be high to reflect the fact that the acid is practically unextracted in the case of normal pH water flooding.

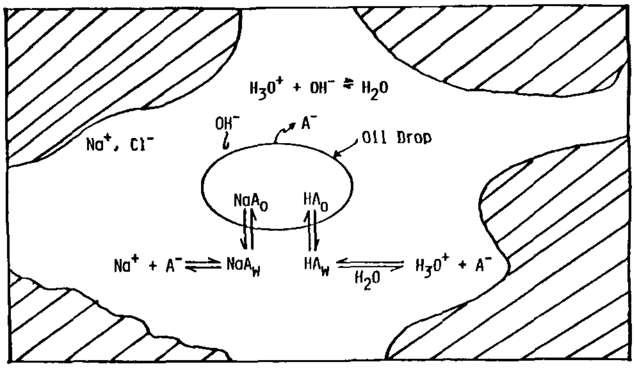

**Figure 1.** ***In situ*** **generation of surfactant in alkaline flooding.**

The acid extracted by the aqueous phase dissociates to form the hydronium ion and the surface active anion $A^-$. This is represented as

$$HA_w + H_2O \rightleftharpoons A^- + H_3O^+, \quad K^D_{HA} = \frac{C_{H_3O^+}C_{A^-}}{C_{HA_w}}. \tag{2}$$

Addition of NaOH reduces the concentration of the hydronium ion and carries forward the dissociation of the acid. This is governed by Eq. 2 and the dissociation constant of water,

$$K_w = C_{H_3O^+}C_{OH^-}. \tag{3}$$

In the presence of a large amount of $Na^+$, undissociated salt NaA is formed. In view of the long hydrocarbon chain (>10 carbon atoms) of A, this salt was presumed to be oil soluble. Moreover, on partitioning to the aqueous phase the salt is assumed to dissociate almost completely to produce the active species $A^-$. Ramakrishnan and Wasan (1983) did not observe any precipitation of this salt in equilibrated samples of Wilmington Field (C-331) crude and caustic even at concentrations of $Na^+$ as high as 400 mol/m³. Thus the formation of NaA and its partitioning is represented by

$$Na^+ + A^- \rightleftharpoons NaA_w, \quad K^D_{NaA} = \frac{C_{Na^+}C_{A^-}}{C_{NaA_w}} \tag{4}$$

and

$$NaA_w \rightleftharpoons NaA_o, \quad K_{s_1} = \frac{C_{NaA_o}}{C_{NaA_w}}, \tag{5}$$

with $K_{s_1} \gg 1$ and

$$K_s = \frac{K^D_{NaA}}{K_{s_1}} = \frac{C_{Na^+}C_{A^-}}{C_{NaA_o}}. \tag{6}$$

This implies that the acid in the crude oil is neutralized by the alkali in water and the salt formed goes back into the crude, and that the acid is practically unextracted into the aqueous phase. Literature data on solubility of sodium palmitate in heptane (Seidell and Linke, 1952) also support the preferential partitioning of the salt into the oil phase. As a consequence of this, the phase volume ratio should have very little effect on the equilibrium interfacial activity except at very low caustic concentrations when the caustic is consumed in the neutralization process. This and more experimental evidence substantiating the preferential partitioning of NaA into the oil phase is presented elsewhere (Borwankar, 1984).

From a correlation of equilibrium data all equilibrium parameters are determined. The dynamic process can now be formulated corresponding to this system chemistry. The following discussion is for the case of stagnant batch systems wherein the bulk transport is by molecular diffusion alone.

*Diffusion-Kinetic Mechanism.* Based on the foregoing discussion of the equilibrium aspects, the diffusion-kinetic mechanism depicted schematically in Figure 2 is proposed. The acid HA in the oil phase diffuses to the oleic sublayer from where it undergoes (reversible) dissociative adsorption. The adsorbed active species $A^-$ can pick up $Na^+$ from the aqueous sublayer and (reversibly) desorb to the oleic sublayer as the soap NaA. Alternatively, the adsorbed $A^-$ can (reversibly) desorb to the aqueous sublayer as any of the two species, $A^-$ itself or undissociated acid HA. Ionic equilibria are assumed to exist in the aqueous phase so that these three species are in local equilibrium. The various species are then transferred away from the respective sublayers by molecular diffusion into the respective bulks.

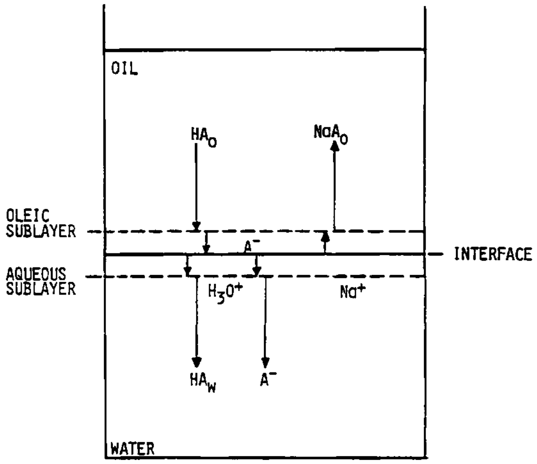

**Figure 2. Diffusion-kinetic transport mechanism.**

The following reversible interfacial reactions can thus be written:

$$HA_0 \rightleftharpoons A_{ads}^- + H_3O^+, \tag{8}$$

$$A_{ads}^- + Na^+ \rightleftharpoons NaA_0, \tag{9}$$

$$A_{ads}^- \rightleftharpoons A_w^-, \tag{10}$$

$$A_{ads}^- + H_3O^+ \rightleftharpoons HA_w, \tag{11}$$

In the aqueous phase $A^-$ and HA are in equilibrium through the ionic equilibria.

It is assumed that the mobilities of $Na^+$, $H^+$, $OH^-$ are very high and that these species essentially have equilibrium composition throughout the aqueous phase. The continuum approach is assumed to be valid. As a result of ionic adsorption the diffuse double layer is set up in the aqueous phase. (The dielectric constant of the oil phase is assumed to be very low.) The diffuse double layer is assumed to be in a quasi-stationary state (Dukhin et al., 1983), i.e., the double layer is assumed to adjust itself instantaneously to the changes in surface charge during the adsorption process. Thus, the potential $\psi_0$ at the aqueous sublayer for a quasi-stationary double layer is given by the Guoy-Chapman theory as (Adamson, 1982)

$$\frac{F\psi_0}{RT} = 2\sinh^{-1}\left(\frac{-F\Gamma}{2\sqrt{2\epsilon_0\epsilon_r RTC}}\right), \tag{12}$$

where $\Gamma$ is the instantaneous surface concentration and $C$ is the total electrolyte concentration in the aqueous phase. (The surface concentration of ionic surface active species is equal to its surface excess concentration less the contribution from the diffuse double layer [Borwankar, 1984]. Since these ions are expelled from the double layer, the double layer's contribution to the surface excess is negative and the surface concentration of an ionic surfactant is greater than its surface excess concentration.) The electrostatic double layer is assumed to have a very small thickness, thus the double layer effects appear only as the boundary conditions and bulk transport equations are unaffected by the existence of the double layer (Newman, 1969). All the ionic concentrations calculated from the bulk transport equations with disregard to the double layer need to be corrected with Boltzmann factors in the double layer.

From phenomenological extension of the equilibrium model, the rate of the interfacial reaction represented by Eq. 10 can easily be written by considering that for every ion of $A^-$ adsorbed, a water molecule is removed from the interface (Borwankar, 1984). Then, the rate of the reaction representing the adsorption of $A^-$ from the aqueous sublayer (Eq. 10), for ideal behavior existing in the bulk as well as the interface, can be equated to the flux of $A^-$ to the aqueous sublayer to yield (Borwankar, 1984)

$$-D_{A^-}\frac{\partial C_{A^-}}{\partial n}\bigg|_s = k_A\left[C^s_{A^-}\exp\left(\frac{F\psi_0}{RT}\right)(\Gamma_\infty - \Gamma) - \frac{\Gamma}{K_A}\right], \quad (13)$$

where $C^s_{A^-}$ is the concentration of $A^-$ at the sublayer obtained with disregard to the double layer, $k_A$ is the rate constant, $K_A$ is the equilibrium constant and $\Gamma_\infty$ is the saturation adsorption.

The rate expressions for the other interfacial reactions can now be written easily. Since $Na^+$, $H^+$, and $OH^-$ are assumed to exist at equilibrium compositions throughout the aqueous phase, their concentrations are uniform in the aqueous phase except for the Boltzmann correction in the electrostatic double layer. Then equating the diffusive fluxes to the rates of respective interfacial reaction yields

$$-D_{HA_o}\frac{\partial C_{HA_o}}{\partial n}\bigg|_s = k_{HA}\left[C^s_{HA_o}(\Gamma_\infty - \Gamma) - \frac{\Gamma}{K_{HA}}C_{H^+}\exp\left(-\frac{F\psi_0}{RT}\right)\right], \quad (14)$$

$$-D_{NaA_o}\frac{\partial C_{NaA_o}}{\partial n}\bigg|_s = k_{NaA}\left[C^s_{NaA_o}(\Gamma_\infty - \Gamma) - \frac{\Gamma}{K_{NaA}}C_{Na^+}\exp\left(-\frac{F\psi_0}{RT}\right)\right], \quad (15)$$

$$-D_{HA_w}\frac{\partial C_{HA_w}}{\partial n}\bigg|_s = k_{HA_w}\left[C^s_{HA_w}(\Gamma_\infty - \Gamma) - \frac{\Gamma}{K_{HA_w}}C_{H^+}\exp\left(-\frac{F\psi_0}{RT}\right)\right]. \quad (16)$$

Here $k_{HA}$, $k_{NaA}$, and $k_{HA_w}$ are the kinetic rate constants and $K_{HA}$, $K_{NaA}$, and $K_{HA_w}$ are the equilibrium constants for the reactions represented by Eqs. 8, 9, and 11, respectively. The subscript *o* is dropped from $k_{HA}$, $k_{NaA}$, $K_{HA}$, and $K_{HA}$ in the oil phase for the sake of simplicity. Also, for consistency, all the rate constants refer to the adsorption terms in the reversible kinetic processes. The desorption rate constants in Eqs. 13–16 are simply adsorption rate constants divided by the corresponding equilibrium constants.

In view of the ionic equilibria existing in the aqueous phase, the species $A^-$ and HA are in equilibrium in this phase. Thus, Eqs. 13 and 16 are not independent. The overall rate of exchange between the interface and the aqueous phase is then obtained by adding the individual rates of exchange for these two species. Using Eq. 2, Eqs. 13 and 16 can be combined to yield

$$-D_w\left[\exp\left(-\frac{F\psi_0}{RT}\right) + \frac{C_{H^+}}{K^D_{HA}}\right]\frac{\partial C_{A^-}}{\partial n}\bigg|_s = k_A\alpha\left[C_{A^-}(\Gamma_\infty - \Gamma) - \frac{\Gamma}{K_A}\exp\left(-\frac{F\psi_0}{RT}\right)\right], \quad (17)$$

where

$$\alpha = 1 + \frac{C_{H^+}}{K^D_{HA}}, \quad (18)$$

$$D_w = D_{A^-} = D_{HA_w}, \quad (19)$$

$$k_A = k_{HA_w} \quad (20)$$

and

$$K_A = \frac{K_{HA_w}}{K^D_{HA}}. \quad (21)$$

Here, Eqs. 19–21 are assumed to be true for simplicity. Therefore, there is a single rate constant $k_A$ and a single equilibrium constant $K_A$ governing the transfer to the aqueous phase.

For the sake of simplicity the terms adsorption barriers and desorption barriers will be used in this work with the understanding that they refer to the net effect produced by the reversible kinetic steps. Then, for this system, $k_{HA}$ characterizes the adsorption barrier and $k_{NaA}$ and $k_A$ are measures of the desorption barriers.

With the diffusion-kinetic transport mechanism proposed and the kinetics of the various steps established, the discussion now proceeds to the geometry encountered in the spinning drop tensiometer wherein the bulk diffusion equations are to be solved.

*Spinning Drop Geometry.* Measurement of interfacial tension by the spinning drop technique was first proposed by Vonnegut (1942). The technique essentially consists of rotating a cylindrical glass tube—containing a droplet of the lighter (oil) phase in the continuous, transparent, denser (aqueous) phase—about its horizontal axis. If the rotational speeds are high enough (>5000 rpm), gravitational effects can be neglected (Manning and Scriven, 1977). The oil drop is then under the gyrostatic equilibrium wherein the shape of the drop is such that the rotational forces are counterbalanced by the interfacial forces. If the length of the drop is more than four times its diameter, the drop may be assumed to be a cylinder with hemispherical ends. Then the interfacial tension $\sigma$ is related to the drop radius $R_d$, the rotational speed $\Omega$, and the density difference between the two phases $\Delta\rho$ according to the equation

$$\sigma = \frac{R_d^3\Omega^2\Delta\rho}{4}. \quad (22)$$

When this criterion is not satisfied the drop has an ellipsoidal shape. Several authors (Princen et al., 1967; Cayias et al., 1975;

Slattery and Chen, 1978) have treated the drop shapes and indicated the means of obtaining the interfacial tension for ellipsoidal drops.

McCaffery (1976) and Chan (1978) have shown that the spinning drop technique is suitable for measurement of the dynamic interfacial tension. In a dynamic experiment, when the two phases are freshly contacted in the tensiometer, the interfacial tension has a very high initial value and the drop is ellipsoidal in shape. The interfacial tension then falls rapidly from this high value and, when the interfacial tension is low enough that the length of the drop is more than four times its diameter, the drop can be assumed to be a cylinder with hemispherical ends. As the interfacial tension continues to fall, the radius of the drop changes continuously with time, obeying Eq. 22. If there exists a dynamic interfacial tension minimum, the interfacial tension increases with time after the minimum and the drop begins to shorten in length until the final state of equilibrium is attained. By proper choices of drop volume and rotation speed it can be ensured that at equilibrium the drop is a cylinder with hemispherical ends. Thus, once the above criterion is satisfied and the drop is assumed to be a cylinder, this criterion is not violated in that experiment at a later time.

### *Formulation of the problem*

At initial times when the drop shape is ellipsoidal and changing, the penetration theory approximation is used to account for the diffusion in the bulk phases. For surfactant transport in stagnant, batch systems involving gas-liquid surface, Borwankar and Wasan (1983) have shown that this approximation is fairly good for the diffusion-kinetic case. It is assumed to be true here for the liquid-liquid case, especially if it is ensured that the volume of the drop introduced in the spinning drop tube is such that the cylindrical shape is attained fairly quickly in an experiment. In such a case, the error, introduced by the use of this simplified approach for short initial times, is not expected to affect the results substantially at larger times. It should also be noted that in the short time when the penetration theory approximation is used, the penetration length for diffusion is much smaller than the dimensions of the system so that the finiteness of the system does not pose any problem in this regard.

Brown and Radke had used the exact drop shapes as given by Princen et al. in terms of elliptic integrals to account for area variations. However, their model was for a simple physical transport process and involved the use of the Nernst film model to approximate the bulk transport. Treatment of ellipsoidal shapes in the case of this chemical model without making use of the Nernst film model is a formidable problem. In view of the fact that the penetration theory approximation needs to be used for short times only—often so short that the experimental data are not available for these times—a rigorous treatment of changing drop shapes with accompanying complexities may be unnecessary.

The diffusion-penetration theory approximates the outward flux of any species as

$$-D\frac{\partial C}{\partial n}\bigg|_s = \sqrt{\frac{D}{\pi t}}\,(C^b - C^s), \tag{23}$$

where $C^b$ and $C^s$ are concentrations of that species in the bulk and at the sublayer, respectively. Using this approximate expression for the fluxes of HA and NaA in the oil phase and for combined transport of $A^-$ and HA in the aqueous phase, and equating these fluxes to the rates of the respective interfacial reactions yields

$$\sqrt{\frac{D_{HA_o}}{\pi t}}\,(C^b_{HA_o} - C^s_{HA_o}) = k_{HA}\left[C^s_{HA_o}(\Gamma_\infty - \Gamma) - \frac{\Gamma}{K_{HA}}C_{H^+}\exp\left(-\frac{F\psi_0}{RT}\right)\right], \tag{24}$$

$$\sqrt{\frac{D_{NaA_o}}{\pi t}}\,(C^b_{NaA_o} - C^s_{NaA_o}) = k_{NaA}\left[C^s_{NaA_o}(\Gamma_\infty - \Gamma) - \frac{\Gamma}{K_{NaA}}C_{Na^+}\exp\left(-\frac{F\psi_0}{RT}\right)\right], \tag{25}$$

$$\sqrt{\frac{D_w}{\pi t}}\left[\exp\left(-\frac{F\psi_0}{RT}\right) + \frac{C_{H^+}}{K^D_{HA}}\right](C^b_{A^-} - C^s_{A^-}) = k_A\alpha\left[C_{A^-}(\Gamma_\infty - \Gamma) - \frac{\Gamma}{K_A}\exp\left(-\frac{F\psi_0}{RT}\right)\right]. \tag{26}$$

Furthermore, the total rate of outflux from either phases to the interface equals the rate of adsorption of $A^-$, thus

$$\frac{d\Gamma}{dt} = \sqrt{\frac{D_{HA_o}}{\pi t}}\,(C^b_{HA_o} - C^s_{HA_o}) + \sqrt{\frac{D_{NaA_o}}{\pi t}}\,(C^b_{NaA_o} - C^s_{NaA_o}) + \sqrt{\frac{D_w}{\pi t}}\left[\exp\left(-\frac{F\psi_0}{RT}\right) + \frac{C_{H^+}}{K^D_{HA}}\right](C^b_{A^-} - C^s_{A^-}). \tag{27}$$

Initially, the acid HA is uniformly distributed throughout the oil phase at its original acid number, while NaA in the oil phase and $A^-$ and HA in the aqueous phase are absent. Also, the surface concentration is zero. Thus,

$$C^b_{HA_o} = C^0_{HA_o}, \tag{28}$$

$$C^b_{NaA_o} = 0, \tag{29}$$

$$C^b_{A^-} = 0, \tag{30}$$

$$\Gamma = 0. \tag{31}$$

Equation 27 is an ordinary differential equation coupled to the algebraic Eqs. 24–26 and is easily integrated with explicit schemes like the Runge-Kutta methods for the initial conditions represented by Eqs. 28–31.

Once the drop assumes a cylindrical shape, the exact diffusion equations are solved in both the bulk phases in the cylindrical geometry. Figure 3 shows a schematic diagram of the cylindrical oil drop in gyrostatic equilibrium with the continuous aqueous phase in a cylindrical spinning capillary tube of radius $R_T$. The axial variation of concentration is neglected as well as the transfer to and across the interface at the hemispherical ends of the drop. Essentially, the transfer to the region outside the one bounded by the planes *AA*' and *BB*' in either phase is neglected. This is not a serious limitation since very little surfactant is extracted into the aqueous phase and the phase volume change

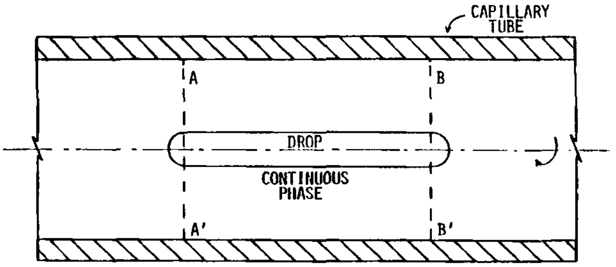

**Figure 3. Spinning drop geometry.**

accompanying this approximation thus has negligible effect on the solution. The elongation and contraction of this cylindrical drop is taken into account at the time of numerical solution, as are the area effects.

In the oil phase, the two independent diffusion equations for the acid HA and the soap NaA are written as

$$\frac{\partial C_{HA_o}}{\partial t} = D_{HA_o}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_{HA_o}}{\partial r}\right) \qquad (32)$$

and

$$\frac{\partial C_{NaA_o}}{\partial t} = D_{NaA_o}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_{NaA_o}}{\partial r}\right). \qquad (33)$$

In the aqueous phase, for the case of uniform concentrations of $H^+$ and $Na^+$, the combined equations for diffusion of $A^-$ and HA, which are in equilibrium, take the following form (note that the double layer effects do not appear in the bulk transport equation):

$$\frac{\partial C_{A^-}}{\partial t} + \frac{\partial C_{HA_w}}{\partial t} = \frac{D_{A^-}}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_{A^-}}{\partial r}\right) + \frac{D_{HA_w}}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_{HA_w}}{\partial r}\right) \qquad (34)$$

or

$$\alpha\frac{\partial C_{A^-}}{\partial t} = D_w^*\frac{\partial}{\partial r}\left(r\frac{\partial C_{A^-}}{\partial r}\right), \qquad (35)$$

where

$$D_w^* = D_w\left(1 + \frac{C_{H^+}}{K_{HA}^D}\right) \qquad (36)$$

and $\alpha$ is defined in Eq. 18.

The boundary conditions for Eqs. 32, 33, and 35 at the interface are given by Eqs. 14, 15, and 17, respectively, together with the species balance at the interface. From species conservation at the interface, the total rate of outflux equals the rate at which $A^-$ is adsorbed at the interface and, in view of the changing interfacial area,

$$\frac{1}{S}\frac{d[S\Gamma]}{dt} = -D_{HA_o}\left.\frac{\partial C_{HA_o}}{\partial r}\right|_s - D_{NaA_o}\left.\frac{\partial C_{NaA_o}}{\partial r}\right|_s + D_w^*\left.\frac{\partial C_{A^-}}{\partial r}\right|_s, \qquad (37)$$

$S$ being the interfacial area. The boundary conditions at the center of the drop (for the oil phase) and at the tube wall (for the aqueous phase) are no-flux conditions. The initial conditions for these equations are given by the solution of the approximate penetration theory equations at the time the drop assumes the cylindrical shape and the solution of these exact equations is begun.

### *Method of solution*

As indicated previously, for initial times when the penetration theory approximation is used, the Runge-Kutta fourth-order method was used to integrate the equation.

When the interfacial tension becomes low enough and the drop assumes cylindrical shape (the satisfaction of this criterion of length to diameter ratio exceeding four was checked for within the program), Eqs. 32, 33, and 35, are solved with the corresponding boundary conditions using a finite difference scheme. The initial conditions for this case are the profiles in the bulk and the interfacial concentration obtained from the penetration theory solution at the previous time. These equations are written in a finite-difference form of the Crank-Nicholson scheme. It can be seen that the interfacial boundary conditions represented by Eqs. 14, 15, and 17, make the system nonlinear. The problem is further complicated by the fact that the radius of the drop changes with time as the interfacial tension changes. In the technique adopted here, the secant method is used to iterate on the interfacial concentration Γ. When Γ is assumed as a guess, these equations become linear. Again, guessing Γ allows calculation of the new interfacial tension through the equation of state. The new radius of the drop at time $t + \Delta t$ is then calculated using the Vonnegut equation (Eq. 22) and the mean value of the radius for the interval $t$ to $t + \Delta t$ is used for computations. With change in drop radius the length of the drop also changes and particularly the continuous phase volume of interest (that bounded between planes *AA'* and *BB'* in Figure 3) increases with a decrease in the drop radius. At each time interval, the finite-difference grid is adjusted to simulate the effect of the changing drop dimensions and the aqueous phase concentrations are corrected to satisfy the overall conservation of species. This is an approximate method but it is used here in preference to the more complicated two-dimensional approach. This method is not expected to give significant errors in view of the fact that the concentrations in the aqueous phase are small. Thus, once the entire system is linearized, the finite-difference equations can be solved by matrix inversion using the Thomas algorithm (Finlayson, 1980), and the guessed Γ is checked against the integrated form of Eq. 38. The integration is achieved using the trapezoidal rule. The details of this procedure are given elsewhere (Borwankar, 1984).

## Results and Discussion

The chemical diffusion-kinetic model predicts the surface concentration if the various parameters are known. It is necessary to relate the surface concentration to the interfacial tension. We assume that the dynamic interfacial tension is in equilibrium with the instantaneous surface concentration irrespective of the sublayer concentrations. Then, the dynamic interfacial tension $\sigma$ is related to the instantaneous surface concentration Γ of the solute by the surface equation of state (ob-

**Table 1. Constants Used in Parametric Study**

| Parameter | Symbol | Value |
|---|---|---|
| Distribution constant of HA | $K_D$ | $4.1 \times 10^4$ |
| Equilibrium constant of NaA | $K_s$ | 0.1 mol/m$^3$ |
| Dissociation constant of HA | $K_{HA}^D$ | $3.1 \times 10^{-7}$ mol/m$^3$ |
| Equilibrium constant for A$^-$ adsorption | $K_A$ | $1.976 \times 10^4$ m$^3$/mol |
| Saturation adsorption | $\Gamma_\infty$ | $4.0 \times 10^{-6}$ mol/m$^2$ |
| Temperature | $T$ | 298 K |
| Initial concentration of HA in oil phase | $C^0_{HA_o}$ | 14.3 mol/m$^3$ |
| Caustic concentration in aqueous phase | $C_{OH^-}$ | 250 mol/m$^3$ |
| Salt concentration in aqueous phase | | 170 mol/m$^3$ |

**Table 2. Constants Used in Study of Effect of Rate Constants**

| Parameter | Symbol | Value |
|---|---|---|
| Diffusivity of HA in oil | $D_{HA_o}$ | $5.0 \times 10^{-12}$ m$^2$/s |
| Diffusivity of NaA in oil | $D_{NaA_o}$ | $5.0 \times 10^{-12}$ m$^2$/s |
| Diffusivity in water | $D_w$ | $1.0 \times 10^{-9}$ m$^2$/s |
| Volume of oil drop | | $2.0 \times 10^{-9}$ m$^3$ |
| Speed of rotation | $\Omega$ | 800 s$^{-1}$ |
| Density difference | $\Delta_\rho$ | 84 kg/m$^3$ |

tained from equilibrium considerations) (Borwankar, 1984) as

$$\sigma_0 - \sigma = -RT\Gamma_\infty \ln\left(1 - \frac{\Gamma}{\Gamma_\infty}\right) + \frac{4RT\sqrt{2\epsilon_0\epsilon_r RTC}}{F}\left[\cosh\left(\frac{F\psi_0}{2RT}\right) - 1\right], \quad (38)$$

where $\sigma_0$ is the interfacial tension in the absence of surface active solute at the interface. It is easily seen that in a dynamic experiment at a given ionic strength, the dynamic interfacial tension minimum corresponds to a maximum in the surface concentration.

### *Parametric study*

Computer calculations were performed using the chemical diffusion-kinetic model to study the effect of the various parameters involved. There are six transport parameters in this model: the rate constants $k_{HA}$, $k_{NaA}$, and $k_A$, and the diffusion coefficients $D_{HA_o}$, $D_{NaA_o}$, and $D_w$. The various equilibrium constants are held fixed at the values given in Table 1. The equilibrium constants used herein correspond to those reported by Ramakrishnan and Wasan (1983) for the Wilmington Field (C–331) crude oil. The initial acid concentration of 14.3 mol/m$^3$ corresponds to the acid number 0.86 for this crude.

The results of the study conducted to examine the effects of the three rate constants are presented first. For this study the diffusivities and other variables in the model are held fixed at the values reported in Table 2. It should be mentioned that the diffusivities in the oil phase are assumed to be so small primarily because the oil is highly viscous (100–110 mPa · s at room temperature).

Figure 4 shows the effect of varying the rate constant $k_{NaA}$ representing desorption into the oil phase on interfacial tension. Decreasing the value of $k_{NaA}$ implies increasing the desorption barrier. It is seen that with increase in desorption barrier the dynamic interfacial tension minimum is lowered. This can be explained as follows: When the desorption barrier is increased, the rate of supply of the solute to the interface becomes greater than its rate of desorption from the interface. Thus, the surface concentration $\Gamma$ rises beyond the equilibrium value until the driving force for desorption increases to the extent that the desorption rate becomes greater than the adsorption rate. Then the surface concentration begins to fall as the solute desorbs, and eventually approaches the equilibrium value. The maximum surface concentration attained is higher when the desorption barrier is higher or the desorption rate constant is lower.

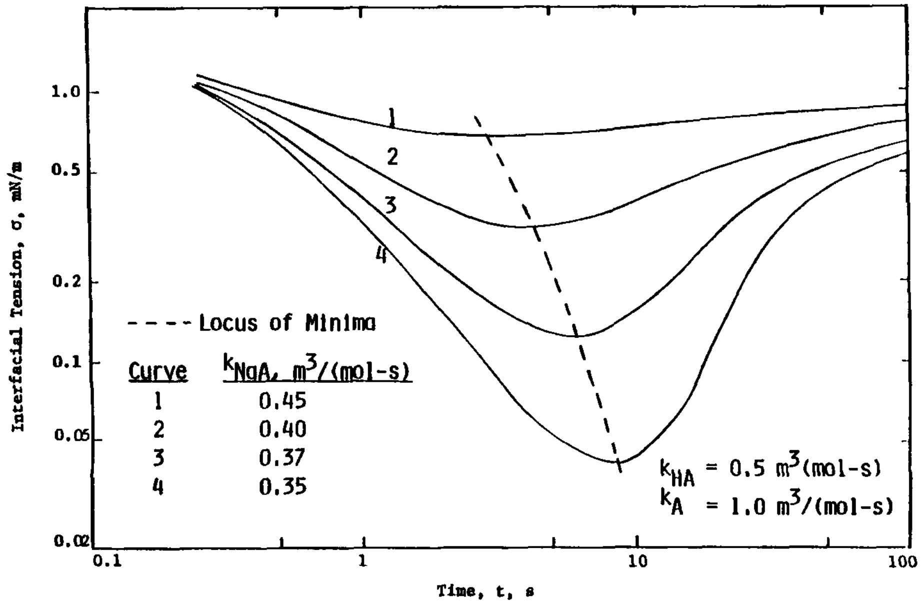

**Figure 4. Effect of desorption rate constant $k_{NaA}$ on dynamic interfacial tension.**

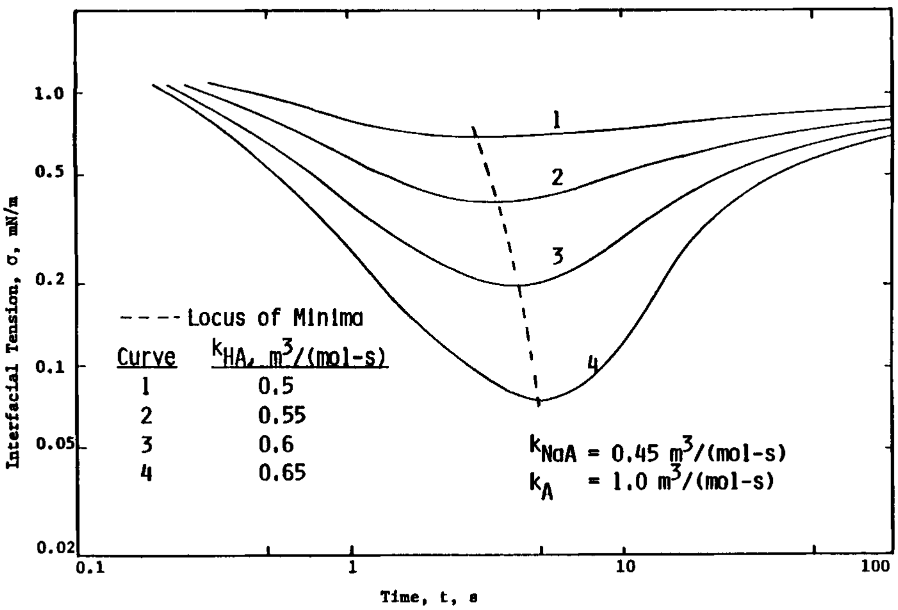

**Figure 5. Effect of adsorption rate constant $k_{HA}$ on dynamic interfacial tension.**

In the case of infinite desorption barriers, or zero desorption rate constants, the surface concentration corresponding to the one in equilibrium with the original acid number would be attained. The maximum in surface concentration corresponds to the observed minimum in interfacial tension.

Furthermore, decrease in $k_{NaA}$ or increase in the desorption barrier leads to a slight increase in the time at which the minimum interfacial tension is attained. This is shown by the dashed line *MM'* in Figure 4, which is the locus of the minimum interfacial tension.

The same effect of increasing the desorption barrier can be obtained by decreasing the adsorption barrier since it is their magnitude relative to each other that causes the dynamic interfacial tension minimum. This is shown in Figure 5. When adsorption barrier is decreased, or the adsorption rate constant $k_{HA}$ is increased, the dynamic interfacial tension minimum is lowered. Again, decreasing the adsorption barrier causes the time at which the minimum interfacial tension is attained to increase.

It was mentioned earlier that the soap NaA partitions preferentially into the oil phase. The concentrations of HA, NaA, and $A^-$ are, therefore, very low in the aqueous phase, which implies that very little transfer occurs from the interface to the aqueous phase. As such, the rate constant $k_A$ governing this transfer is not expected to affect the interfacial tension considerably. In fact, changing the value of $k_A$ by one order of magnitude at fixed values of $k_{HA}$ and $k_{NaA}$ caused the interfacial tension to change less than 2%.

A parametric study of diffusion coefficients revealed that the interfacial tension is less sensitive to them than it is to the corresponding rate constants. The model was also found to be fairly sensitive to the drop volume and the speed of rotation; hence, these should be measured as accurately as possible (Borwankar, 1984).

### *Correlation of experimental data with the model*

The chemical diffusion-kinetic model developed earlier can be used to correlate the dynamic interfacial tension data obtained using the spinning drop tensiometer. Data were taken for several concentrations of caustic and salt in the aqueous phase against Wilmington Field (C–331) crude (Borwankar, 1984). It is seen that the interfacial tensions of this crude against caustic solutions are lower than that of the crudes examined by Trujillo (1983). The various equilibrium constants for this system have been reported earlier in Table 1. It is assumed that the various diffusivities are independent of compositions in the phases. Since the effects of the aqueous phase composition have been explicitly incorporated in the model through the system chemistry, the various rate constants in the model are also independent of the aqueous phase composition. Thus, the correlation of the model to experimental data lies in determining the values of the various transport parameters that best fit the data over all aqueous phase compositions studied. This is a significant advantage of this model over the pseudochemical model of Trujillo wherein the desorption rate constant and the distribution coefficient were computed as functions of the aqueous phase composition. The kinetic parameters can therefore be considered to be characteristic properties of the surface active acids in the crude oil.

The parametric study had shown that the diffusivities have less effect on interfacial tension than the rate constants. Thus, the diffusivities are assumed to be equal to those reported by Trujillo, which are the same as those given in Table 2. The desorption rate constant $k_A$ for transfer to the aqueous phase also does not affect dynamic interfacial tension significantly. This rate constant was therefore assumed to be 1 $m^3/mol \cdot s$. The correlation with experimental data thus lies in finding the values of the adsorption rate constant $k_{HA}$ and the desorption rate constant $k_{NaA}$ that best fit the experimental data over several concentrations of caustic and salt.

It should be noted that the equilibrium model of Ramakrishnan and Wasan agrees with equilibrium interfacial tension data with a fairly large relative error. This problem plagues all models when applied to low interfacial tension systems. This is because the model predicts surface pressure while the spinning drop tensiometer measures interfacial tension. Thus, for com-

Table 3. Experimental Conditions for Dynamic Interfacial Tension Measurements

| Aqueous Phase Composition NaOH mol/m$^3$ | Aqueous Phase Composition NaCl mol/m$^3$ | Rotation Speed s$^{-1}$ | Drop Volume $10^{-9}$ m$^3$ |
|---|---|---|---|
| 25.0 | 170.0 | 604 | 1.9 |
| 62.5 | 170.0 | 653 | 2.1 |
| 125.0 | 170.0 | 684 | 2.0 |
| 250.0 | 85.0 | 646 | 2.0 |
| 250.0 | 42.5 | 672 | 1.8 |

parison between the two, predicted interfacial tension is obtained from the predicted surface pressure by subtraction from $\sigma_0$, which is the interfacial tension when no surfactant is present at the interface. An interfacial activity model for as complicated a system as the crude oil with a spectrum of surface active acids is not expected to be accurate. Furthermore, the assumption of ideal behavior existing in the bulk aqueous phase is suspect at the high ionic strengths encountered. (No significant improvement resulted, however, when we included the mean ionic activity coefficients as predicted by the modified Debye-Hückel theory [Adamson, 1979].) Thus, there is some error in the predicted surface pressures. Also, the values of $\sigma_0$ are functions of the aqueous phase composition. For example, Haydon and Taylor (1960) have reported a small increase in interfacial tension of petroleum ether against water with increasing concentration of sodium chloride. Since it is impossible to measure the actual values of $\sigma_0$ for the system under consideration in view of the *in situ* surfactant generation, Ramakrishnan and Wasan took the interfacial tension of crude oil against distilled and deionized water to correspond to the $\sigma_0$ value. Thus, there is a small error in the $\sigma_0$ values used. Then, when the predicted surface pressures are subtracted from $\sigma_0$ to obtain the predicted interfacial tensions, a large discrepancy is imminent.

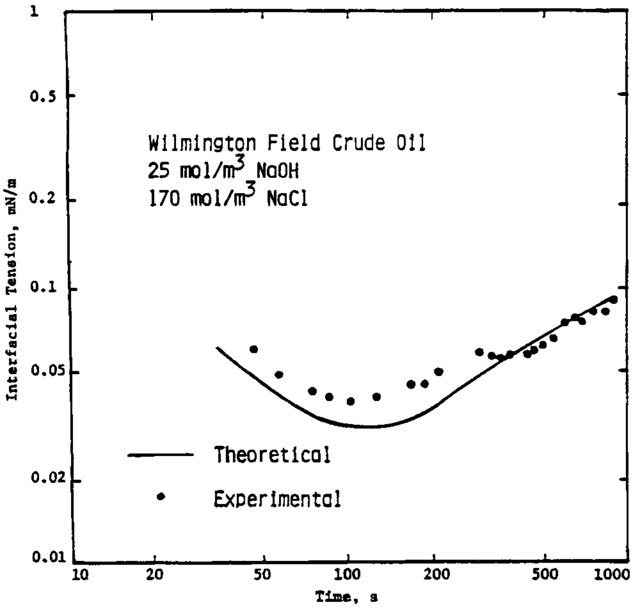

Figure 6. Comparison of model with dynamic interfacial tension data for Wilmington Field crude oil against specified caustic solution.

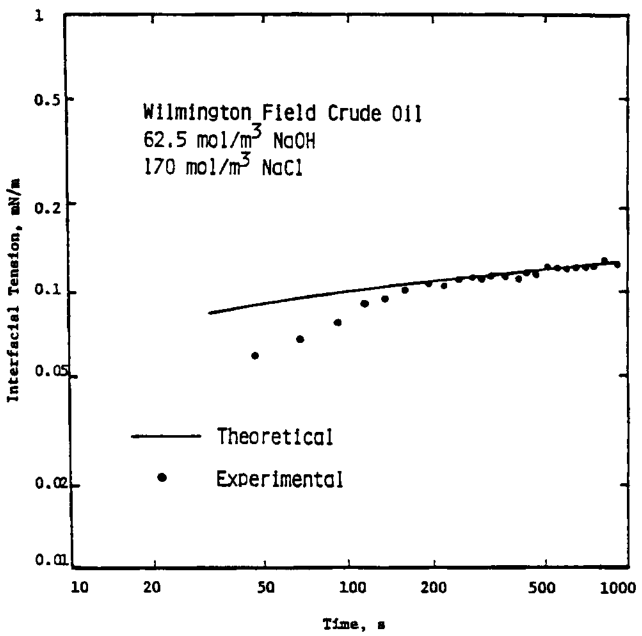

Figure 7. Comparison of model with dynamic interfacial tension data for Wilmington Field crude oil against specified caustic solution.

While the procedure described above for comparing the present model with dynamic interfacial tension data is a general one, a direct use of it is precluded in view of the discrepancy between the equilibrium interfacial activity model and the equilibrium tensions. The comparison of the present model with the experimental data will be meaningless if the model predictions and the experimental dynamic interfacial tensions approach different values at long times. Therefore, a variation of this procedure is used. It is proposed that the model predictions be multiplied by a factor that corrects for this discrepancy in the equilibrium data.

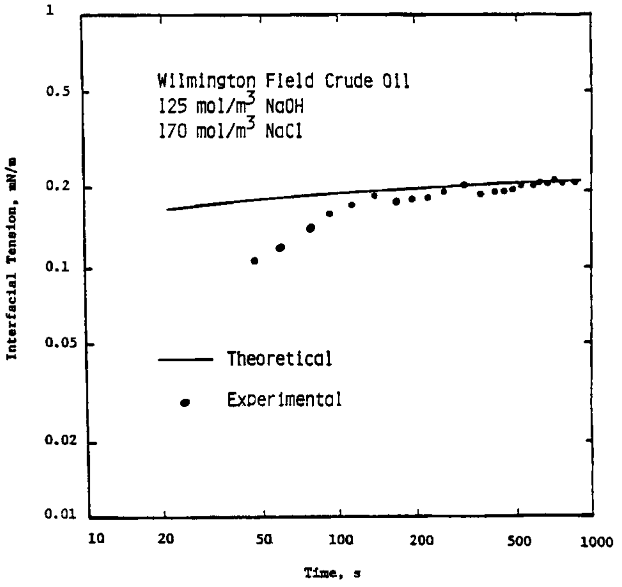

Figure 8. Comparison of model with dynamic interfacial tension data for Wilmington Field crude oil against specified caustic solution.

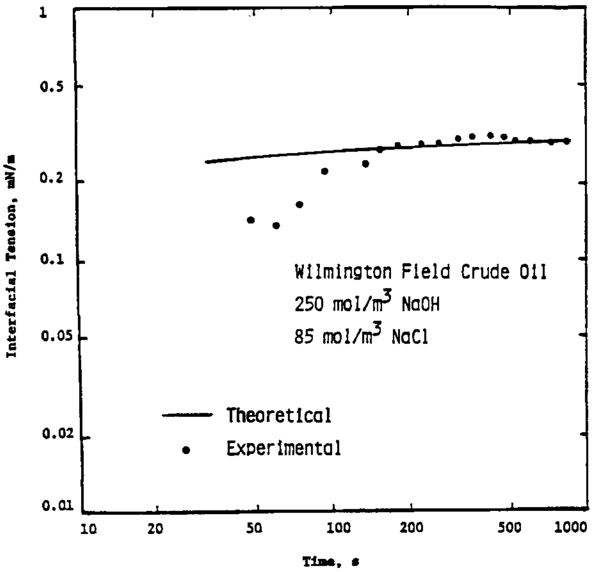

**Figure 9. Comparison of model with dynamic interfacial tension data for Wilmington Field crude oil against specified caustic solution.**

Since in most cases equilibrium is attained in about 15 min, the interfacial tension values at this time were used to compute the correction factor.

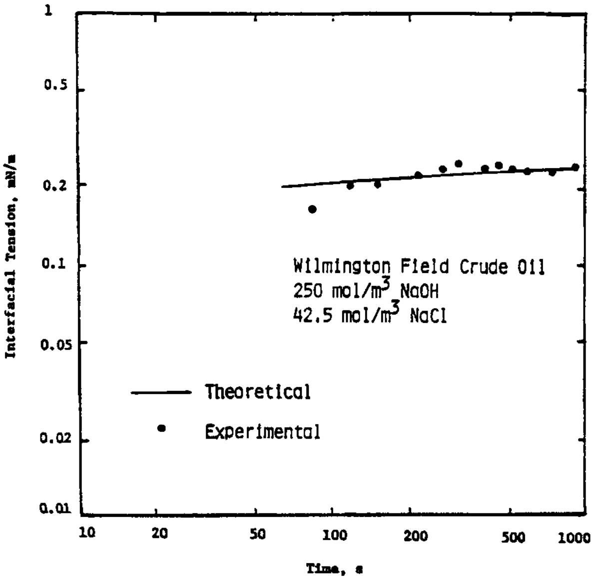

**Figure 10. Comparison of model with dynamic interfacial tension data for Wilmington Field crude oil against specified caustic solution.**

**Table 4. Transport Parameters for Wilmington Field Crude Oil**

| Parameter | Symbol | Value |
|---|---|---|
| Diffusivity of HA in oil | $D_{HA_o}$ | $5.0 \times 10^{-12}$ m²/s |
| Diffusivity of NaA in oil | $D_{NaA_o}$ | $5.0 \times 10^{-12}$ m²/s |
| Diffusivity in water | $D_w$ | $1.0 \times 10^{-9}$ m²/s |
| Adsorption rate constant | $k_{HA}$ | 0.46 m³/mol · s |
| Desorption rate constant | $k_{NaA}$ | 0.433 m³/mol · s |
| Desorption rate constant | $k_A$ | 1.0 m³/mol · s |

Table 3 shows the experimental conditions for the runs used in this correlation. The best correlation of the experimental data under these conditions was obtained with $k_{HA} = 0.46$ m³/mol · s and $k_{NaA} = 0.433$ m³/mol · s. The comparison between the model predictions using these values to the experimental data is shown in Figures 6–10. It is seen that only the experimental data for 25 mol/m³ (0.1 wt.%) NaOH and 170 mol/m³ (1 wt.%) NaCl actually showed a dynamic interfacial tension minimum. All other data showed only the rising trend. It can be seen that the transport parameters summarized in Table 4 correlate the experimental data fairly well. Since this model yields, from a comparison with the experimental data, the rate constants which do not vary with the aqueous phase composition, they can be regarded as characterizing the fatty acids in the crude oil at the temperature used in the study. It should be noted that the dynamic effects in the case of Wilmington Field (C–331) crude last only about 15 min in most cases investigated. This behavior is quite different from that observed by Trujillo for some other crudes wherein the dynamic effects lasted for up to 24 h. Although his dynamic effects lasted over longer times than in our case, on closer examination it can be seen that the value of the desorption rate constant $k_{NaA}$ is in the same range as his pseudoconstant at high pH. (It is at high pH that the pseudoconstant of Trujillo approaches its true, physically meaningful value.) Also, the values of the rate constants are indicative of a rather shallow dynamic interfacial tension minimum for this system.

## Acknowledgment

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## Notation

$C$ = total electrolyte concentration, mol/m³
$C_i$ = concentration of $i$, mol/m³
$D_i$ = diffusivity of $i$, m²/s
$D_w$ = diffusivity in the aqueous phase, m²/s
$F$ = Faraday constant, C/mol
$k_A$ = rate constant for adsorption of $A^-$, m³/mol · s
$k_{HA}$ = rate constant for adsorption of HA from oleic sublayer, m³/mol · s
$k_{HA_w}$ = rate constant for HA adsorption from the aqueous sublayer, m³/mol · s
$k_{NaA}$ = rate constant for adsorption of NaA from oleic sublayer, m³/mol · s
$K_A$ = equilibrium constant for $A^-$ adsorption, m³/mol
$K_D$ = distribution coefficient of HA
$K_{HA}$ = equilibrium constant for HA adsorption from oleic sublayer
$K_{HA_w}$ = equilibrium constant for HA adsorption from the aqueous sublayer
$K_{HA}^D$ = dissociation constant of HA, mol/m³
$K_{NaA}$ = equilibrium for NaA adsorption from oleic sublayer
$K_{NaA}^D$ = dissociation constant of NaA, mol/m³
$K_s$ = equilibrium constant, Eq. 6, mol/m³
$K_{s_1}$ = distribution coefficient of NaA
$K_w$ = dissociation constant of water, mol²/m⁶
$n$ = direction normal to the interface, m
$r$ = radial coordinate, m
$R$ = gas constant, J/mol · K
$R_d$ = radius of drop, m
$S$ = interfacial area, m²
$t$ = time, s
$T$ = temperature, K

### *Greek letters*

$\alpha$ = constant, Eq. 18
$\Gamma$ = surface concentration, mol/m$^2$
$\Gamma_\infty$ = saturation adsorption, mol/m$^2$
$\Delta\rho$ = density difference, kg/m$^3$
$\epsilon_r$ = relative permittivity
$\epsilon_0$ = permittivity of vacuum, C$^2$/N · m$^2$
$\sigma$ = interfacial tension, N/m
$\sigma_0$ = interfacial tension when no surfactant is present, N/m
$\psi_0$ = interfacial potential, V
$\Omega$ = speed of rotation, s$^{-1}$

### *Subscripts/superscripts*

$b$ = bulk
$o$ = oil
$s$ = sublayer
$w$ = water

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