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Surfactant-Enhanced Alkaline Flooding for Light Oil Recovery

**Annual Report
1992-1993**

**by
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MASTER

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EXECUTIVE SUMMARY

In this report, we present the results of our experimental and theoretical studies in surfactant-enhanced alkaline flooding for light oil recovery. The overall objective of this work is to develop a very cost-effective method for formulating a successful surfactant-enhanced alkaline flood by appropriately choosing mixed alkalis which form inexpensive buffers to obtain the desired pH (between 8.5 and 12.0) for ultimate spontaneous emulsification and ultralow interfacial tension. In addition, we have (1) developed a theoretical interfacial activity model for determining equilibrium interfacial tension, (2) investigated the mechanisms for spontaneous emulsification, (3) developed a technique to monitor low water content in oil, and (4) developed a technique to study water-in-oil emulsion film properties. The results of the studies conducted during the course of this project are summarized below.

Interfacial Activity Model

A new interfacial activity model which predicts equilibrium interfacial tension both qualitatively and quantitatively has been developed. The ultralow value of interfacial tension is shown to result from the simultaneous adsorption of ionized and unionized acid on the interface, and the lowering results from the formation of mixed micelles of ionized and unionized acid. This theoretical model can also be used to determine micellization parameters.

Interfacial Turbulence and Spontaneous Emulsification

Observation of roll cells indicates that the mechanism for spontaneous emulsification is interfacial turbulence. The effect of pH on roll cell formation is explained in terms of the concentration gradient of unionized acid in the oil phase, the sensitivity of interfacial tension to preformed surfactant concentration, and the rate of acid ionization. The added preformed surfactant creates an interfacial resistance to mass transfer, and it also makes the interface more rigid. It also makes the interfacial tension more sensitive to the ionized and unionized acid. It is shown that interfacial turbulence is a necessary but not sufficient condition for spontaneous emulsification. Low interfacial tension is also a necessary condition for spontaneous emulsification, if the rotational velocity of the cell is too slow for emulsion snap-off. Therefore,

there is a trade-off between interfacial tension and rotational velocity. This study shows that reacting alkali/acidic oil systems are ideal for investigating interfacial turbulence and to test theories, because roll cell size, rate of amplification, rate of reaction, etc. can be controlled by controlling the pH, unionized acid concentration, ionic strength, added preformed surfactant concentration and type, etc. In addition, interfacial turbulence appears to improve penetration of an aqueous solution between an oil and solid surface leading to oil removal from the solid surface.

Low Water Content determination

Simple exact solutions to the microwave interferometric transmission equations have been derived, thus allowing determination of complex dielectric constant without time consuming iterative procedures. Moisture levels are shown to be detectable with an accuracy of about 0.5 volume percent water content using microwave interferometric dielectrometry. The ease of obtaining the data, the noninvasivity of the measurement technique, and the rapidity with which results are obtainable makes low water content determination using dielectrometry highly desirable in comparison to a wet technique such as Karl Fisher titration.

Demulsification of Water-In-Crude Oil Emulsions

A new technique has been developed for the study of the film properties governing the water-in-crude oil emulsion film stability. With the technique, the film properties in the presence of demulsifiers were measured and the factors governing the rate of film thinning and its stability of the water-in-crude oil emulsion film have been discussed. The performance of three differently blended oil soluble demulsifiers on the water separation from the emulsions and the emulsion film rheology have been studied. It has been found that there is a direct correlation between the demulsifier performance and the rheology of water/crude oil/water emulsion film in the presence of the demulsifier. Also, to improve the demulsifier efficiency, the demulsifier components need to create a low emulsion film elasticity (dilatational film modulus), higher film diffusivity and low film tension.

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PRACTICAL APPLICATIONS

1. A new theoretical model for prediction of interfacial tension has been developed, which can be incorporated into a chemical flood predictor model for prediction of flood performance.
2. Understanding that spontaneous emulsification is caused by the interfacial turbulence mechanism will allow better control over the emulsification process and better control over the duration of ultralow interfacial tension during a surfactant-enhanced alkaline flood by better controlling acid extraction rate through pH and roll cell formation characteristics.
3. Post flood evaluation of the dryness of crude oil can be achieved by use of our newly developed interferometric dielectrometer for low water content determination.
4. A new instrument has been developed for measuring thin liquid film rheological properties, which have direct one-to-one correlation with emulsion stability in water-in-crude oil emulsions.

CHAPTER 1
INTERFACIAL ACTIVITY MODEL

INTRODUCTION

Rudin and Wasan¹ conducted experimental studies in order to determine the physicochemical mechanisms responsible for lowering of interfacial tension in alkali/acidic oil systems. Ionic strength, pH, alkalinity, acid concentration and type were investigated for their effect on interfacial and surface tension. It was shown that interfacial tension goes through an ultralow minimum with NaOH (initial pH) at constant ionic strength. Unionized acid was shown to be present in the system at these NaOH concentrations. The overwhelming evidence suggested that the unionized acid adsorbs onto the interface together with the ionized acid, resulting in ultralow transient and equilibrium interfacial tension.

Current theories do not consider simultaneous adsorption of unionized acid on the interface, dimerization of acid in the oil, and micelle formation, and as a result, they do not adequately describe the effect of pH on equilibrium interfacial tension. Chan and Yen² considered adsorption of only ionized acid on the interface, and the minimum in interfacial tension results from precipitation of the ionized acid. The modeling of Ramakrishnan and Wasan³ is basically the same as Chan and Yen² except instead of precipitation of the ionized acid, it is believed to partition into the oil. Qutubuddin et al.,⁴ have developed a simplified model to describe the effect of pH and salinity on interfacial tension behavior. The pH is believed to effect interfacial tension behavior by allowing more acid to be ionized, making the system more hydrophilic.

It is known that a mixture of ionic and nonionic surfactants such as sodium dodecyl sulfate and an alcohol form a mixed interfacial layer, and this mixed layer reduces interfacial tension below that for either surfactant alone. The presence of a nonionic will also reduce the critical micelle concentration of the ionic surfactant, which will also effect interfacial tension. These physicochemical phenomena are what Hua and Rosen⁵ refer to as a synergism in binary surfactant mixtures.

SYSTEM CHEMISTRY

Figure 1-1 shows the proposed system chemistry for the contacting of an acidic oil with an alkaline solution. The unionized acid species (or just acid) is represented as HA . It is well known that nonionics, such as alcohols and acids dimerize in oil⁶. This dimerization is represented as

and

$$K_d = \frac{C_{(HA_o)_2}}{C_{HA_o}^2} , \quad (1-1)$$

where for convenience HA_o is used to represent the unionized acid in the oleic phase, and C_i is the concentration of species i at equilibrium. The acid is assumed to distribute between the aqueous and the oleic phase according to the relation

and

$$K_D = \frac{C_{HA_o}}{C_{HA_w}} , \quad (1-2)$$

where HA_w is used to represent the unionized acid in the aqueous phase.

The acid which is extracted into the aqueous phase, dissociates to form hydronium ions, H^+ and the ionized acid, A^- . This is represented as

and

Figure 1-1. Alkali/Acidic Oil Interactions.

$$K_A = \frac{C_H \cdot C_{A^-}}{C_{HA_w}} , \quad (1-3)$$

The addition of an alkali, such as NaOH, leads to the reduction of H^+ and carries forward the dissociation of HA .

The dissociation constant for water is K_w , which is given by

$$K_w = C_H \cdot C_{OH^-} . \quad (1-4)$$

The ionized acid may form an undissociated salt which partitions into the oil phase. This partitioning may take place when the acid species is very high molecular weight, alkylated, or has groups on the hydrogen tail, such that the head group can be pulled into the oil phase. When this occurs, the partitioning of the ionized acid depends upon the sodium ion (i.e., ionic strength), Na^+ and the dependency is given by

and

$$K_s = \frac{C_{NaA_o}}{C_{Na^+} \cdot C_{A^-}} , \quad (1-5)$$

where NaA_o is the sodium salt of the acid in the oil phase.

When the alkali and added salt are NaOH and NaCl, their dissociation is assumed to be complete. In that case, no equilibria are necessary. By using concentrations, we have assumed that the activity coefficients are unity. If the ionic strength is maintained constant and high, the activity coefficients of the various species should not change over the pH range of the experiments⁶⁻⁸.

As acid is extracted into the aqueous phase, it becomes ionized. As the pH of the

aqueous phase increases, the ionized acid will reach a critical concentration to form micelles. In the conservation and charge balance equations that follow, explicit representation for micellization need not be accounted for in the equations themselves. A separate well-known semi-empirical equation for micellization is presented to complete the required set of equations to solve for the unknowns.

Conservation of Species A

If V_w and V_o are the volumes of the aqueous and oleic phases, respectively, a molar balance for A^- leads to

$$V_w C_{HA_w} + V_o C_{HA_o} + 2V_o C_{(HA_o)_2} + V_o C_{NaA_o} + V_w C_{A^-} + M_A = V_o C_{(HA_o)_0} \quad (1-6)$$

where M_A is the moles of A in the micellar phase and $C_{(HA_o)_0}$ is the initial concentration of acid in the oil. Rearrangement of Equation (1-6) with use of the equilibrium relationships yields

$$M_A = V_o C_{(HA_o)_0} - 2V_o K_d \left[\frac{K_w K_D}{K_A} \right]^2 \frac{C_{A^-}^2}{C_{OH^-}^2} - \left[V_w + \frac{K_w (V_w + V_o K_D)}{K_A C_{OH^-}} + V_o K_s C_{Na^+} \right] C_{A^-} \quad (7)$$

Conservation of Species Na

If C_1 and C_2 are the initial concentrations of NaOH and NaCl in the aqueous phase, then a molar balance for sodium leads to

$$V_o C_{NaA_o} + V_w C_{Na^+} + M_{Na} = V_w (C_1 + C_2) \quad (1-8)$$

and

$$M_{Na} = (1 - \alpha) M_A \quad (1-9)$$

where M_{Na} is the moles of Na bound in the micellar phase, and α is the fraction of unbound

sites on the micelles. Rearranging Equation (1-8) with the use of Equation (1-7) and the equilibrium relationships yields

$$C_{Na^+} = \frac{C_1 + C_2 - (1-\alpha)pl}{1 + \alpha V_R K_s C_{A^-}}, \quad (1-10)$$

where

$$pl = V_R C_{(HIA)_0} - 2V_R K_d \left[\frac{K_w K_D}{K_A} \right]^2 \frac{C_{A^-}^2}{C_{OH^-}^2} - \left[1 + \frac{K_w (1 + V_R K_D)}{K_A C_{OH^-}} \right] C_{A^-},$$

and $V_R = V_o/V_w$.

Charge Balance

A charge balance in the aqueous phase yields

$$V_w C_{Na^+} + V_w C_{H^+} = V_w C_{OH^-} + V_w C_{A^-} + V_w C_2 + M_C, \quad (1-11)$$

and

$$M_C = \alpha M_A, \quad (1-12)$$

where M_C is the moles of charges in the micellar phase. Upon rearrangement with the use of Equation (1-7) and the equilibrium relationships

$$C_{Na^+} = \frac{C_{OH^-} + C_{A^-} + C_2 + \alpha(pl)}{1 + \alpha V_R K_s C_{A^-}}. \quad (1-13)$$

The OH Balance

On combining Equations (1-10) and (1-13), we get

$$C_{OH^-} = C_1 - V_R C_{(HA)_0} + (1 + V_R K_D) \frac{K_w}{K_A} \frac{C_{A^-}}{C_{OH^-}} + 2V_R K_d \left[\frac{K_w K_D}{K_A} \right]^2 \frac{C_{A^-}^2}{C_{OH^-}^2} \quad (1-14)$$

Here we see that the effect of the partitioning of the acid-salt out of the aqueous phase (i.e., K_s) does not influence the relationship between C_{A^-} and C_{OH^-} . In fact, Equation (1-14) holds in either the presence or absence of micelles. Equation (1-14) is just

$$C_{OH^-} = (\text{total hydroxide added}) - (\text{total acid ionized}) \quad (1-15)$$

Equation (1-14) is a quadratic in C_{A^-} which is solved to get

$$C_{A^-} = \frac{C_{OH^-} \left[-\frac{K_w(1+V_R K_D)}{K_A} + (p2)^{1/2} \right]}{4V_R K_d \left[\frac{K_w K_D}{K_A} \right]^2} \quad (1-16)$$

where

$$p2 = \left[\frac{K_w(1+V_R K_D)}{K_A} \right]^2 - 8V_R K_d \left[\frac{K_w K_D}{K_A} \right]^2 (C_1 - V_R C_{(HA)_0} - C_{OH^-})$$

Equation (1-16) has imaginary roots when (since $K_D \gg 1$)

$$C_{OH^-} < C_1 - \frac{V_R}{8K_d} - V_R C_{(HA)_0} \quad (1-17)$$

This arises because the last two terms in Equation (1-14) vanish (i.e., no acid remains in the oil), and the solution (i.e., Equation (1-16)) comes from these terms. Under conditions where Equation (1-17) applies, Equation (1-14) becomes

$$C_{OH^-} = C_1 - V_R C_{(HA)_0} \quad (1-18)$$

Equation (1-14) along with either Equation (1-10) or (1-13) provide two equations and three unknowns. To solve for the unknowns and completely describe the system chemistry, another equation needs to be specified. The proposed relationship between these unknowns comes from the formation of micelles.

Micellar Relationships

Assuming that the ionized acid and the unionized acid dissolve each other in a state of regular solution, we obtain

$$\frac{C_{A^-}}{C'_{A^-}} = (1-x) , \quad x \ll 1, \quad (1-19)$$

where C'_{A^-} is the concentration of ionized acid in solution equilibrium with the ionized acid micelle, C_{A^-} is the concentration of ionized acid in solution equilibrium with the mixed micelle, and x is the mole fraction of acid in the mixed micelle. A mixed micelle contains ionized and unionized acid molecules.

The acid is considered to undergo partitioning between the micellar and bulk phase. The partitioning follows

$$\frac{C_{HA_w}}{x} = K'_0 \exp\left[-\frac{m'\omega}{kT}\right] , \quad (1-20)$$

where K'_0 is a constant, m' is the number of carbon atoms in the acid, ω is the free energy change per methylene group transferred from the water into the micelle, k is the Boltzmann constant, and T is the temperature. Here, C_{HA_w} is the unionized acid in the mixed solution, which is assumed to equal that in the absence of micelles. If the concentration of ionized acid monomer is constant after the CMC, the phase separation model for micellization can be applied. It was shown by Rudin and Wasan¹ with an interfacial tension isotherm for

sodium oleate that the ionized acid monomer is indeed constant above CMC. Since the phase separation model for micellization is applied, Equations (1-19) and (1-20) hold at CMC and are assumed to hold above CMC. This is true provided that the unionized acid concentration in the micelle does not become too great so that the micelle can no longer be treated as a separate phase.

On combining Equations (1-19) and (1-20), we get

$$C_{A^-} = -K_0 C'_{A^-} C_{HA_w} + C'_{A^-} \quad (1-21)$$

where

$$K_0 = \frac{1}{K'_0} \exp\left(\frac{m'\omega}{kT}\right) .$$

Due to the phase separation theory, C_{A^-} is equal to the CMC, and Equation (1-21) is then recognized as the semi-empirical relationship developed by Shinoda^{9,10} for an alcohol in a micellar solution of anionic surfactant. Here, the unionized acid in the water is analogous to an alcohol.

System chemistry shows that when micelles form, C_{Na^+} will decrease because of counterion binding. The value of C'_{A^-} will alter, and the extent can be related to C_{Na^+} by considering the following equilibria,

and

$$K_1 = \frac{C'_m}{(C'_{A^-})^n (C'_{Na^+})^{n(1-\alpha)}} , \quad (1-22)$$

where n is the aggregation number for the ionized acid, and C'_m is the concentration of micelles. Taking the logarithm of Equation (1-22) yields

$$\log(C'_{A^-}) = K_2 - (1-\alpha)\log(C'_{Na^+}) , \quad (1-23)$$

where

$$K_2 = \frac{1}{n} \log\left(\frac{C'_m}{K_1}\right) .$$

Considering again the phase separation theory, C_{A^-} is equal to the CMC at and above the CMC. This equation is then recognized as the well-known relationship between CMC and ionic strength¹⁰. It has also been shown experimentally that K_2 is a constant¹¹. Rearrangement of Equation (1-23) yields

$$C'_{A^-} = K_3 \left[\frac{1}{C'_{Na^+}} \right]^{(1-\alpha)} , \quad (24)$$

where $K_2 = \log(K_3)$. On combining Equations (1-21) and (1-24), we get

$$\frac{C_{A^-}}{K_3 \left[\frac{1}{C'_{Na^+}} \right]^{(1-\alpha)}} = -K_0 C_{HA_w} + 1 . \quad (1-25)$$

Making appropriate substitutions into Equation (1-25) results in

$$C_{A^-} = \frac{K_3}{C_{Na^+}^{(1-\alpha)} + \left[\frac{K_3 K_0 K_w}{K_A} \right] \left[\frac{1}{C_{OH^-}} \right]} \quad (1-26)$$

Equations (1-14) and (1-26) are solved together with either Equation (1-10) or (1-13) to obtain C_{A^-} , C_{OH^-} , and C_{Na^+} .

At low concentrations of alkali or low initial acid concentrations, it may be possible that the total concentration of ionized acid is below its critical micelle concentration (CMC). In that case, the conservation equations, which are presented in the previous section, are solved, excluding the presence of a micellar phase. The conservation of species A, the conservation of species Na, and the charge balance comprise a set of nonlinear algebraic equations in three unknowns, C_{A^-} , C_{OH^-} , and C_{Na^+} which can be solved with a Newton-Raphson numerical scheme.

At this point, all important species are known for the bulk chemistry. The surface concentrations are next related to the interfacial tension through the adsorption isotherms.

ADSORPTION EQUATIONS

The bulk concentrations of surface active species can be related to the surface concentrations by an adsorption isotherm. The surface active species are considered to be A^- and HA . Davies¹² has derived the following adsorption isotherm to relate C_{A^-} to the surface concentration as

$$C_{A^-} = \frac{k_{12}}{k_{11}} \frac{n_{A^-}}{(1-f)} \exp \left[-\frac{[W_1 + N\epsilon\psi(0)]}{RT} \right], \quad (1-27)$$

where k_{11} is the adsorption rate constant, k_{12} is the desorption rate constant, W_1 is the energy barrier for desorption of A^- per mole, ϵ is the electronic charge, N is Avogadro's

number, R is the gas constant, and f is the fractional surface covered by adsorption and is related to the surface species by

$$f = \frac{n_{A^-}}{n_{A_{\max}}} + \frac{n_{HA}}{n_{HA_{\max}}} \quad (1-28)$$

where n_{A^-} and n_{HA} are the number of moles of A^- and HA per unit area at the surface, respectively. Also, $n_{A_{\max}}$ and $n_{HA_{\max}}$ are the maximum number of moles that can be adsorbed per unit area for A^- and HA , respectively. In Equation (1-28), it is assumed that the interface behaves ideally. This assumption is reasonable based on the results of Lucassen-Rynders¹³ for a single ionic surfactant. However, a mixed interfacial layer of ionized and unionized acid may not behave ideally⁵.

The key to understanding the behavior of interfacial tension is the realization that the unionized acid species adsorbs onto the interface mainly from the oil-side of the interface. Adsorption from the water-side will be negligible compared to the oil-side adsorption, because C_{HA_w} is too low to influence interfacial tension. The adsorption isotherm for HA is

$$C_{HA_o} = \frac{k_{22}}{k_{21}} \frac{n_{HA}}{(1-f)} \exp\left[-\frac{W_2}{RT}\right], \quad (1-29)$$

where W_2 is the energy barrier for head-group desorption of HA per mole. According to Davies and Rideal¹⁴, the hydrodynamics of the adsorption process will alter k_{21} and k_{22} separately, but their ratio will remain constant. This implies that $k_{21}/k_{22} = k_{11}/k_{12}$.

The double layer is described by the Gouy-Chapman theory, where the Gouy potential at a distance zero from the interface, $\psi(0)$ is given by

$$\psi(0) = -\frac{2kT}{\epsilon} \sinh^{-1} \left[\frac{(n_{A^-}) \epsilon N^{1/2}}{2^{3/2} (\epsilon_r \epsilon_0)^{1/2} (kT)^{1/2} C_{Na^+}^{1/2}} \right], \quad (1-30)$$

where ϵ_r is the relative permittivity of the medium and ϵ_0 is the permittivity of vacuum.

Equations (1-27) through (1-30) are solved to calculate the values of n_{A^-} and n_{HA} .

These surface concentrations are next related to the surface pressure.

SURFACE PRESSURE RELATIONSHIP

By considering the equation of state approach, the concentrations of adsorbed species can be related to the surface pressure, which is in turn related to interfacial tension. Davies and Rideal¹⁴ for an oil/water interface consider the surface pressure as

$$\pi = \pi_K + \pi_E, \quad (1-31)$$

where π_K is the kinetic contribution to surface pressure, obtained by considering a hypothetical uncharged film, and π_E is the contribution to surface pressure from the electrical double layer.

For immobile films, the kinetic contribution is given by the Frumppkin isotherm (Frumppkin¹⁵; Volmer¹⁶) as

$$\pi_K = RT n_{\max} \ln \left(\frac{1}{1-f} \right), \quad (1-32)$$

where

$$n_{\max} = \frac{n_{A^-} + n_{HA}}{f}, \quad (1-33)$$

The electrical contribution is expressed with the relationship given by Davies¹⁷ as

$$\pi_E = \frac{4\sqrt{2}}{\epsilon} (kT)^{3/2} (N\epsilon_r \epsilon_o C_{Na^+})^{1/2} [\cosh(\frac{\epsilon\psi(0)}{2kT}) - 1] . \quad (1-34)$$

Finally the interfacial tension is given by

$$\gamma = \gamma_0 - \pi , \quad (1-35)$$

where γ_0 is the interfacial tension in the absence of both A^- and HA .

MATERIALS AND METHODS

The sodium hydroxide and sodium chloride were obtained from Fisher Scientific Company with ACS purity. The decane (99+% pure) and the oleic acid (99% pure) were obtained from Sigma Chemical Company.

Pre-equilibrated samples were made by periodically shaking equal volumes of aqueous and oil phases for 1 month with the temperature maintained at 25 °C. The interfacial tensions were measured for these equilibrated samples using the Wilhelmy plate and the spinning drop technique. Readings were made when the interfacial tension had reached a steady value. The pH was measured using an Orion microprocessor ionalyzer/901 with a Ross combination electrode designed for low sodium error. Ionized acid concentrations in the water were determined using the dichlorofluorescein titration technique, and the unionized acid concentrations in the oil were determined using ASTM procedure D-664. All solutions were made on a w/v basis with respect to the initial phase, and the initial ionic strength was kept constant by adjustment with sodium chloride. All experiments were performed at 25 °C.

Throughout this chapter, oleic acid refers to unionized acid and soap refers to the ionized form of the acid.

RESULTS AND DISCUSSION

In the Absence of Alkali

One way to independently determine and check the known parameters is to consider the system in the absence of any added alkali. Under these conditions, the concentration of ionized acid will be negligible and no micelles will be formed. As a result, A^- will not influence interfacial tension, and can be neglected. This assumption is rechecked in the next section where alkali is present, and it is confirmed to hold true. Under these conditions, Equation (1-6) is a quadratic, which is solved to obtain C_{IIA_o} . Next, Equation (1-29) is solved for n_{HA} . Then from Equations (1-31) with $\pi_E=0$, (1-32) and (1-35), the interfacial tension is obtained.

By considering the interfacial tension in the absence of added alkali, we are able to independently check the literature values for K_D , K_d , W_2 , and $n_{IIA_{max}}$. These values are listed in Table 1-1. It should be mentioned that the value for $n_{IIA_{max}}$ given by Ananthapadmanabhan¹⁸ is for an air/water surface, which is approximately the diameter of the molecule. It should be within 20% of the value for the water/oil interface. Beunen and White⁸ have used a value of $21.3 \text{ \AA}^2$ for an unionized acid molecule at the oil/water interface.

The interfacial tension of decane against a 171 mol/m^3 solution of NaCl in the absence of acid was measured to be 43.1 mN/m . This is slightly lower than the literature value of 50 mN/m for the interfacial tension against distilled water¹⁴, and indicates the presence of impurities. The value of 43.1 mN/m is used for γ_0 , which is the interfacial tension in the absence of A^- and HA . For k_{11}/k_{12} , the value was taken from Davies and Rideal¹⁴ to be $2 \times 10^{-9} \text{ m}$.

Shown in Figure 1-2 is the comparison of the theory with the experiments for the interfacial tension as a function of initial acid concentration at constant ionic strength and no added alkali. Here, the initial acid concentration can be considered as that at equilibrium. As the concentration of acid increases, interfacial tension decreases, due to the

Table 1-1. Constants in the Absence of Alkali

Constants	This Investigation	Literature	
K_D	4.5×10^5	2.28×10^5	[5]
K_d	20.0 (m ³ /mol)	20.0 (m ³ /mol)	[5]
W_2	22700 (J/mol)	20900 – 23000 (J/mol)	[13]
$n_{HA_{max}}$	8.3×10^{-6} (mol/m ²)	8.3×10^{-6} (mol/m ²)	[17]
		7.8×10^{-6} (mol/m ²)	[7]

Figure 1-2. Effect of Acid on Interfacial Tension Against 171 mol/m³ NaCl.

surface activity of the unionized acid. In this range of acid concentrations investigated, no CMC is observed. Comparison between theory and experiment appears to be very good in the limit of no added alkali.

In the Presence of Alkali

When the concentration of alkali is increased, the initial pH of the aqueous solution will correspondingly increase. As the hydroxide ion is consumed by the acid ionization, the initial pH will decrease to some equilibrium value, corresponding to the amount of acid which has been ionized. The mathematical description for the system chemistry, adsorption isotherms, and surface pressure can be tested by a simple procedure. First, the experimentally determined equilibrium pH provides values for C_{OH^-} , which, when used in Equation (1-14), yield values for C_{A^-} . Once C_{A^-} is obtained, the use of either Equation (1-10) or (1-13) along with the equilibria provide a complete description of all bulk species. Next, C_{A^-} and C_{HA_0} together with the adsorption equations and the equation of state determine the value of interfacial tension. This procedure tests the model without directly considering the micellar phase. Although the micellar phase enters into the system chemistry through the species balances, one needs to know only the fraction of unbound sites on the micelles. Once the chemical species concentrations are known, the micellar relationships can be tested to establish their validity.

The parameters used in this investigation, in addition to those in Table 1-1, are shown in Table 1-2. All values are the same or differ only slightly from the literature values. The value for α was estimated from Vold and Vold¹¹, and the value is typically around 0.2, but depends on the surfactant chain length, the ionic strength, the surfactant head-group, etc.

Figure 1-3 shows a comparison between the theoretically used hydroxide ion values and the experimentally measured values, represented as the equilibrium pH. The values for 13.0 mol/m^3 initial acid were used to obtain exactly the experimentally measured interfacial

Table 1-2. Constants in the Presence of Alkali

Constants	This Investigation	Literature	
K_A	$1.1 \times 10^{-2} \text{ (mol/m}^3\text{)}$	$1.1 \times 10^{-2} \text{ (mol/m}^3\text{)}$	[5,17]
		$1.7 \times 10^{-2} \text{ (mol/m}^3\text{)}$	[20]
K_s	$0.0 \text{ (m}^3\text{/mol)}$	$0.0 \text{ (m}^3\text{/mol)}$	[21]
K_w	$1.02 \times 10^{-7} \text{ (mol}^2\text{/m}^6\text{)}$	$1.02 \times 10^{-7} \text{ (mol}^2\text{/m}^6\text{)}$	[22]
W_1	48000 (J/mol)	48900 (J/mol)	[23]
$n_{A_{\max}}$	$4.0 \times 10^{-6} \text{ (mol/m}^2\text{)}$	$4.0 \times 10^{-6} \text{ (mol/m}^2\text{)}$	[24]
α	0.1	0.1	[10]

Figure 1-3. Comparison of Theory with Experiments for the Effect of Alkali on the Equilibrium pH at Different Initial Acid Concentrations.

tension values shown in Figure 1-4. It is here that the constants shown in Table 1-2 were obtained. Then, the initial acid concentration in the oil was changed to 5.0 and 40.0 mol/m³, and the model yielded the results shown without any modification to the constants. It can be seen from Figures 1-3 and 1-4 that the theoretical model accurately predicts that the effective pK_A of the system occurs slightly after the minimum in interfacial tension, there exists a linear relationship between the equilibrium pH, initial pH and the logarithm of the initial acid concentration at the minimum in interfacial tension, and the width of the minimum corresponds to the slope of the pH verses NaOH curve at the minimum. One may think that the acid should be mostly converted at very low pH (i.e., pH of 5), so why does the apparent pK_A of the system appear at a pH of about 10.5 (see Figure 1-3)? It is because of the last two terms in Equation (1-14) (i.e., the partitioning of the unionized acid into the oil and the dimerization in the oil) that the pK_A of the system occurs at a higher equilibrium pH than in the absence of the excess oil phase. It can be seen that more hydroxide is needed to reach the minimum in interfacial tension (i.e., optimum ionization ratio) when the initial acid concentration is increased.

Figure 1-5 shows the comparison between the theory and experiments for the concentration of unionized acid in the oil and ionized acid in the aqueous phase as a function of NaOH for 13.0 mol/m³ initial acid. The theory compares with the experiments very well. Figure 1-6 shows the normalized concentrations for the three levels of initial acid. In every case, the theory predicts that the minimum in interfacial tension occurs at half-ionization of the acid, occurring when the NaOH concentration is half of the initial acid concentration. The theory also shows that, when the NaOH is equal to the initial concentration of acid, the acid is at the point of complete ionization, and interfacial tension is constant from this point onward with increasing NaOH.

The occurrence of the minimum in interfacial tension at half-ionization of the acid may be just a coincidence. Figure 1-7 shows the total surface pressure with the kinetic and electrostatic contributions to it. Interfacial tension is minimized when π is maximized. However, the maximization of π results from a trade-off between π_K and π_E . The

Figure 1-4. Effect of Alkali on Interfacial Tension for Different Initial Acid Concentrations.

Figure 1-5. Comparison of Theory with Experiments for the Ionization Curves of 13.0 mol/m^3 initial acid.

Figure 1-6. Theoretical Predictions of the Ionization Curves for Different Initial Acid Concentrations.

Figure 1-7. Theoretical Predictions of the Surface Pressure for 13.0 mol/m^3 Initial Acid.

maximum in π_K occurs at about 2.5 mol/m^3 NaOH, but π_E continuously increases. As a result, π reaches a maximum at about 6.25 mol/m^3 NaOH. We see that it is not just the presence of the molecules at the interface that solely determines the position or the depth of the minimum. The electrical charge at the interface plays a vital role as well. As further seen in Figure 1-8, the interfacial tension is not minimum when the fractional surface coverage is maximum, because the fractional surface coverage is maximized at about 8.0 mol/m^3 NaOH, indicating again that the presence of the surface molecules does not solely govern the interfacial tension minimum.

Micellization Analysis

At this point, all of the bulk species are known. So, let us rearrange them in such a way as to investigate the micellization phenomena. In doing so, we can establish a means for estimation of micellization parameters.

Although the initial ionic strength was kept constant, the counter ion binding on the micelles will lower the ionic strength proportionally to the micellar concentration. By using different initial acid concentrations with a solution at high pH, the micellar concentration, and therefore ionic strength, can be varied in a meaningful way. At a high pH of 125 mol/m^3 NaOH, all of the acid is ionized, and Equation (1-23) applies. To establish the validity of this relationship, the logarithm of C_{A^-} verses the logarithm of C_{Na^+} . (i.e., model predictions) is shown in Figure 1-9. Figure 1-9 shows that the relationship is indeed linear with a slope of -0.905 and an intercept of 0.346 . This slope results in a value of α of 0.095 , which is surprisingly, the value of α (i.e., $\alpha=0.1$) input to the model. It should be mentioned that varying the input value has little or no effect on the output value after interfacial tension readjustment. This correlation can be tested by considering the CMC of sodium oleate. For sodium oleate, C_{A^-} equals C_{Na^+} at the CMC, and Equation (1-23) yields 1.52 mol/m^3 for the CMC of sodium oleate. Flockhart and Graham¹⁹ experimentally determined the CMC of sodium oleate to be 1.5 mol/m^3 by conductivity measurements.

Figure 1-8. Theoretical Predictions of the Interfacial Concentrations and Fractional Interfacial Coverage for 13.0 mol/m³ Initial Acid.

Figure 1-9. Effect of Ionic Strength on Ionized Acid Monomer Concentration at High pH.

Also, if we assume phase separation, then the CMC of sodium oleate for an initial acid concentration of 13.0 mol/m^3 oleic acid and 171 mol/m^3 initial sodium is 0.0225. It was shown experimentally by Rudin and Wasan¹ for these same conditions that the CMC is about 0.023 mol/m^3 .

When the concentration of alkali is such that unionized acid is present in the system, then Equation (1-25) is applicable. A plot of the left-hand-side versus C_{HA_w} should yield a straight line with intercept of unity. Figure 1-10 shows this plot of the theoretically predicted values. The relationship is indeed a straight line with a slope of $2.88 \times 10^5 \text{ m}^3/\text{mol}$ and an intercept of 1.1. This correlation is good for NaOH concentrations at and after the point where the minimum in interfacial tension just starts. These points are 6.6×10^{-7} , 1.1×10^{-6} , and $2.1 \times 10^{-6} \text{ mol/m}^3$ C_{HA_w} for 5.0, 13.0 and 40.0 mol/m^3 initial acid concentration, respectively. The minimum in interfacial tension occurs at 5.3×10^{-7} , 2.2×10^{-7} , and $1.5 \times 10^{-6} \text{ mol/m}^3$ C_{HA_w} for 5.0, 13.0 and 40.0 mol/m^3 initial acid concentration, respectively. For NaOH concentrations (or initial pH) at and before the start of the minimum in interfacial tension, these points do not follow the micellar relationship. It should be mentioned that the model predicts ionized acid concentrations high enough for micelle formation, even at low alkali concentrations.

The model does not predict higher concentrations of HA_w than shown by experiment. Lucassen²⁰ has shown that the solubility of oleic acid (i.e., C_{18} minus one carbon for the double bond) in water is $5.9 \times 10^{-6} \text{ mol/m}^3$. The highest concentration of HA_w at 40.0 mol/m^3 initial acid is $2.2 \times 10^{-6} \text{ mol/m}^3$, occurring at 0.25 mol/m^3 NaOH.

Figure 1-11 shows that when the ratio of the unionized to the total ionized acid in the aqueous phase is greater than about 9.5×10^{-6} , the micellar relationship does not hold. This nonconformity may result because either the phase separation assumption is invalid (negating Equation (1-19)) in this region and/or the distribution of HA between solution and micelle is no longer linear (negating Equation (1-20)). The discrepancy between theory and experiments may also have resulted from assuming an ideal interface⁵. The β parameter

Figure 1-10. Normalized Ionized acid Monomer Concentration as a Function of Unionized Acid Concentration in the Alkaline Solution.

Figure 1-11. Theoretical Predictions of the Ratio of Unionized Acid in the Water to the Total Ionized Acid as a Function of Alkali Concentration.

used in regular solution theory was not adequate in correcting this discrepancy, however.

Summary

Even at low alkali concentrations, enough acid is extracted for the ionized acid to be above its CMC. Then, why does interfacial tension go through a minimum? The interfacial tension goes through a minimum with pH (see Figure 1-12) because, at low pH, the high concentration of unionized acid reduces the CMC of the ionized acid, resulting in lower interfacial coverage and higher interfacial tension. As pH increases, the unionized acid concentration decreases, and the CMC of the ionized acid increases, resulting in increased interfacial coverage and a reduction in interfacial tension. With further increase in pH, the acid is completely ionized, and interfacial tension rises because of its loss to contributing to interfacial tension. Thereafter, interfacial tension is constant, and results from only adsorption of ionized acid.

SIGNIFICANT FINDINGS

1. The effective pK_A of the system occurs slightly after the minimum in interfacial tension.
2. The width of the interfacial tension minimum corresponds to the slope of the pH versus NaOH curve at the minimum.
3. The concentration of unionized acid in the aqueous phase is high enough to cause a reduction in the critical micelle concentration of the ionized acid.
4. The concentration of unionized acid on the interface is high enough to result in interfacial tension lower than the effective tension due to ionized acid alone.

CONCLUSIONS

1. The new interfacial activity model predicts equilibrium interfacial tension both qualitatively and quantitatively well.
2. The ultralow value of interfacial tension results from the simultaneous adsorption

Figure 1-12. Illustration of the Synergistic Effect.

of ionized and unionized acid on the interface, and the lowering results from the formation of mixed micelles of ionized and unionized acid.

3. This theoretical model can be used to determine micellization parameters.

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CHAPTER 2
INTERFACIAL TURBULENCE AND SPONTANEOUS EMULSIFICATION

INTRODUCTION

Sherwood and Wei¹ determined overall mass transfer coefficients for extraction of n-butyric acid from benzene and acetic acid from isobutyl alcohol by water. They found that the addition of sodium hydroxide to the water resulted in mass transfer rates four to five times those given by either film or penetration theory. Other researchers (Olander and Reddy²; Bakker *et al.*³; Bakker *et al.*⁴) have reported similar findings for other liquid-liquid systems where the measured overall mass transfer coefficient was found to increase by as much as a factor of four with an increase in the concentration driving force. These unusually high mass transfer rates are caused by a phenomena known as interfacial turbulence resulting from the Marangoni effect.

Orell and Westwater⁵, using a Schlieren technique, studied spontaneous interfacial cellular convection accompanying mass transfer in an ethylene glycol-acetic acid-ethyl acetate system. Schlieren photography revealed the finer structure of the interfacial convection, in which the interfacial patterns were found to be made up of polygonal cells, stripes and ripples.

Sternling and Scriven⁶, in their classical paper, developed a simplified mathematical model and established criteria upon which to predict the occurrence of interfacial turbulence, which originates from the Marangoni effect. They found that interfacial turbulence is usually promoted by 1) solute transfer out of the phase of higher viscosity, 2) solute transfer out of the phase in which its diffusivity is lower, 3) large differences in kinematic viscosity and solute diffusivity between the two phases, 4) steep concentration gradients near the interface, 5) interfacial tension highly sensitive to solute concentration, 6) low viscosities in both phases, 7) absence of surface active agents. Sternling and Scriven⁶ as well as most other researchers consider thermal or concentration gradients in the bulk phases as destabilizing factors for interfacial turbulence in theories of the Marangoni effect, ignoring interfacial reaction also as a destabilizing factor.

Vedove and Sanfeld⁷ found that the perturbations leading to fully developed flow can be initiated by a coupling between the convective and surface reaction kinetic processes, in which a feedback loop is induced by the convective contribution in the surface mass balance equations. Here, concentration gradients in the bulk phases are not the destabilizing factors, and linear surface kinetic schemes can never induce aperiodic Marangoni instabilities (Vedove *et al.*⁸). Ruckenstein and Berbente⁹ developed theory for interfacial turbulence where diffusion is

accompanied by chemical reaction. They found that even small values of the reaction rate constant change the conditions in which instability occurs.

Davies and Rideal¹⁰ state three mechanisms responsible for spontaneous emulsification. They are: 1) interfacial turbulence, 2) diffusion and stranding, and 3) negative interfacial tension. Ruschak and Miller¹¹ demonstrate that spontaneous emulsification can occur when diffusion produces a region of local supersaturation near the interface. Rubin and Radke¹², among others (Sharma *et al.*¹³; Cambridge *et al.*¹⁴), have measured transient interfacial tensions of an acidic oil against an alkaline solution and found low but positive interfacial tensions. They hypothesized that interfacial turbulence was a possible mechanism for spontaneous emulsification and developed a simplified model to predict transient interfacial tension.

In this chapter, we investigate interfacial instability occurring between an oil containing an organic acid and an alkaline aqueous solution. Two model oils (i.e., one with low viscosity and the other at high viscosity), and a crude oil have been used. This study provides additional parameters by which to characterize the interfacial turbulence phenomena and to provide reasons for spontaneous emulsification.

MATERIALS AND METHODS

In this study, two model oils and a crude oil containing an organic acid were contacted with an alkaline pH aqueous solution. The model oils used in this study were n-decane (99+% pure) obtained from Sigma Chemical Company and heavy mineral oil obtained from Fisher Scientific Company. The crude oil used in this investigation was a Long Beach crude oil obtained from THUMS Long Beach Company, having an acid number of 1.0 determined from ASTM procedure D-664 and an API gravity of 24.9. It was centrifuged at 40,000 G's for 30 minutes to remove water and clays. The viscosity of the crude oil after centrifuging was 52 cp at 25 °C, and the interfacial tension against deionized water was 24.5 mN/m.

The alkaline solutions were a mixture of sodium hydroxide, sodium chloride, and Trona, which is an industrial grade chemical being 94% sodium bicarbonate. All alkalis were obtained from Fisher Scientific Company, except Trona, which was obtained from Kerr-McGee Chemical Company.

Two surface active compounds, an organic acid and a preformed surfactant were used.

The organic acid was oleic acid (99% pure), which was obtained from Sigma Chemical Company. The preformed surfactant, a petroleum sulfonate, Petrostep B-105 (55.0% active) was obtained from Stepan Chemical Company. The preformed surfactant solutions were made on a 100% active basis.

The spinning drop technique was used to measure transient (non-equilibrated) interfacial tension. The volumetric ratio of water to oil in the spinning drop tensiometer is about 140. If all the acid that is in the oil drop went into the water phase during transient interfacial tension measurements, the concentration of ionized acid would be 0.12 mol/m^3 . Percent transmittance was measured using a Beckman spectrophotometer set at 600 nm with deionized water as the reference. The pH was measured using an Orion microprocessor analyzer/901 with a Ross combination electrode designed for low sodium error. All experiments were performed at 25 °C.

During this investigation two experimental techniques were used to study interfacial turbulence. The first technique uses reflected light and is shown in Figure 2-1. The glass container was placed on the stage of a metallographic microscope (model N11, Unitron Scientific Co.), which is mounted on a vibration-free table. Here, light is projected from the objective, and the illuminated image is reflected back from the interface to the objective. This technique is useful when the lighter phase (i.e., oil phase) is too dark to transmit light. In the case where the lighter phase is transparent, it is possible to use transmitted light. The experimental set-up used to study interfacial instability in transmitted light is shown in Figure 2-2. Here, a microscope slide containing a hemispherical groove is used for free movement of the interface. The objective is focused through a coverslip and onto the oil/alkali interface.

RESULTS AND DISCUSSION

Observations on Cellular Convection

When the acidic crude oil and alkali come into contact, the interface instantaneously begins to twitch. A few cases studied did not exhibit twitching, and these were either at very low pH or very high pH and high ionic strength (i.e., much under optimum pH or over optimum pH). The rod-like twitches homogeneously covered the interface, and the length of a twitch was about 5 μm .

Seconds after the interface is formed and the twitches begin, small black aggregates of

Figure 2-1. Experimental Technique Used to Study Interfacial Instability in Reflected Light

Figure 2-2. Experimental Technique Used to Study Interfacial Instability in Transmitted Light

either trapped asphaltene particles or flocculated emulsions are distributed across the interface as sketched in Figure 2-3a. After a lag-period which parallels the time for roll cell formation, vacancies are born at various locations on the interface, usually randomly spaced. These vacant areas grow or expand radially, pushing the black aggregates away from the center as shown in Figure 2-3b. Each vacant area grows until it is restricted from expanding further by another neighboring vacancy. The resulting configuration is one which resembles that shown in Figure 2-3c, where the borders are made-up of the constricted aggregates, and the cell areas are clear, except for the twitching.

Alkali at a pH of 11.57 was contacted with the acidic crude oil. A photograph of a resulting roll cell (approximately 500 μm) is shown in Figure 2-4. The high level of pentagonal order observed here likely results from an orderly spacing and uniform growth rate of the vacancies. Figure 2-5 shows a photograph of the same system. These cells are obviously less ordered, resulting from vacancies being unevenly spaced and/or their growth rate being not the same for each. The growth rate may be different for different cells because of the inhomogeneities in the alkali/crude oil interface. The sharp contrast of the hexagonal border (i.e., field diaphragm), indicates that the focus is precisely on the interface. One can see from the cells in the bottom half of the photograph that the center of the cell is recessed and the edges are protruding, except where the aggregates have collected recessing occurs.

After the cells are formed, they usually propagate, and this rate depends upon the particular system under investigation. The cells drift to the edge of the glass container, where they vanish. Macroscopic observations of the mixing cylinders (See Figure 2-6), which have not been shaken, reveal that the aqueous phase is spreading up the glass wall of the container between the crude oil and the solid surface. The crude oil is observed to move away from the cylinder wall and to allow the spontaneously formed oil-in-water emulsion to be drawn up into this gap at various time intervals. Over a period of hours, the oil-in-water emulsion is observed to "dance" between the crude oil and glass wall. When the gravitational forces overcome the forces holding the aqueous phase in this gap, the crude oil is observed to move away from the glass, but this time, instead of drawing the aqueous phase up into the gap, the aqueous phase is expelled out of the gap. This draining continues for the remainder of the spontaneous emulsification process, indicating that interfacial turbulence may be a mechanism for enhancing

Figure 2-3. Sketch of the Stages in the Process of Roll Cell Formation

Figure 2-4. Pentagonal Roll Cell at the Alkali/Acidic Crude Oil Interface

Figure 2-5. Interfacial Turbulence Patterns at the Alkali/Acidic Crude Oil Interface

Figure 2-6. Effect of Interfacial Turbulence on the Removal of Oil From a Solid Surface

oil removal from a solid surface, similar to the findings of Carles and Cazabat¹⁵.

Explanation of Observations

It has been known since the time of Benard¹⁶ that the internal structure of the patterns on the interface consist of circulation cells. When viewed perpendicular to the interface, these polygonal cells have borders that are higher than the mean level of the interface, indicating high interfacial tension, and the center of the cell is recessed, indicating low interfacial tension. When viewed parallel to the interface, the fluid is found to roll in a circular motion on both sides of the interface.

Sternling and Scriven⁶ consider interfacial turbulence to result from hydrodynamic instability of the bulk phases, in which small, ever present random fluctuations about the interface may be amplified into fully developed flows by the Marangoni effect. They have shown that the stability of the disturbed system depends on the viscosity ratio, the diffusivity ratio, the direction of solute transfer, and the sign and rate of change of interfacial tension with concentration. Once a disturbance causes the local interfacial concentration of preformed surfactant to be high relative to surrounding interfacial areas, the interface will expand (due to the high surface pressure in this region), if interfacial tension decreases with increasing preformed surfactant concentration, and it will contract, if interfacial tension increases with increasing preformed surfactant concentration. If the interface contracts, the disturbance is dampened, and if it expands, the disturbance will be amplified. It is the amplification of the disturbance that eventually leads the fully developed flows in the vicinity of the interface shown in Figure 2-7.

Shown in Figure 2-7 are the hydrodynamic flow patterns and the resulting interfacial configuration envisioned by Velarde and Normand¹⁷ that develop from interfacial tension gradients during the heat transfer process. In our investigation, mass transfer is taking place, and although the source of the disturbance (i.e., mass verses heat transfer) is not the same, the resulting convective cells are the same because they both result from the Marangoni effect. As fluid rich in preformed surfactant travels towards the interface and the preformed surfactant is adsorbed there, the interface will expand away from the center of high preformed surfactant concentration and low interfacial tension along a path of decreasing preformed surfactant concentration and increasing interfacial tension to a distance which defines the width of roll cell.

Figure 2-7. Hydrodynamic Flow Patterns Resulting From Interfacial Turbulence

At the edge of the cell, where interfacial tension is the greatest and preformed surfactant concentration is the least, the fluid descends back into the bulk of the liquid to repeat the cycle. The movement of the interface transfers momentum to adjacent bulk fluid elements, thus setting them into motion and creating the roll cells which occur on both sides of the interface.

Figures 2-4 and 2-5 show that indeed these interfacial pattern configurations are present, indicating that cellular convection is occurring in the bulk phase. Of the seven criteria of Sternling and Scriven⁶ described in the introduction section, one through five apply in this system. The interfacial patterns are curved towards the oil side of the interface, where mass transfer of unionized acid is originating. However, the unionized acid must become at least partially ionized to create a high enough surface pressure to bring about interfacial expansion. This requires a sufficient supply of hydroxide ions from the aqueous phase to maintain this rapid interfacial movement. Thus, it can be reasoned that bulk convective flow must exist in the aqueous phase as well.

Figure 2-8 shows the alkali/acidic oil interface for an aqueous phase containing 20 mol/m³ NaOH (171 mol/m³ Na⁺) contacting an oil phase containing 40 mol/m³ oleic acid in decane. Of the seven criteria of Sternling and Scriven⁶ described in the introduction section, four, five and six apply in this system. Oil-in-water emulsions, acting as natural tracers, clearly show cellular convection on the aqueous side of the interface (i.e., left half of the photograph). Water-in-oil emulsions on the oil side of the interface show bulk fluid movement also, when viewed during a VHS movie of the captured images. Figure 2-9 shows that when the roll cell size is greater than the distance separating the emulsion droplets, the roll cells will deform and remain outside of the gap. It was observed experimentally that the oil-in-water emulsions are more stable in the initial stages of the phase contacting. It was also observed in the VHS movie that the rotational velocity of the roll cells increases with increase in pH.

The cellular patterns resulting from bulk cellular convection are viewed normal to the interface, and these are shown in Figure 2-10. Here, the oil phase has a higher viscosity (heavy mineral oil). With this mineral oil system, the roll cells are rectangular, and the spontaneously produced emulsions are larger. Also, amazingly beautiful 'explosions' of oil-in-water emulsions at the interface are commonly observed in the initial stage of contacting, similar to those reported by Benton *et al.*¹⁸. Except for the explosions, the heavy mineral oil system behaves very similar

Figure 2-8. Roll Cells with $0.02 \text{ mol/m}^3 \text{ NaOH}$ ($\text{Na}^+ = 171 \text{ mol/m}^3$) Against 0.04 mol/m^3 Oleic Acid in Decane

Figure 2-9. Effect of Roll Cells Between Two Emulsion Droplets

Figure 2-10. Roll Cell Patterns with $0.02 \text{ mol/m}^3 \text{ NaOH}$ ($\text{Na}^+ = 171 \text{ mol/m}^3$) Against 0.04 mol/m^3 Oleic Acid in Heavy Mineral Oil

to the crude oil system.

Effect of pH and Ionic Strength

Figures 2-11a and 2-11b show the effect of pH on transient interfacial tension for 171 mol/m³ total sodium. Interfacial tension goes through a minimum with both pH and time. Several researchers (Rubin and Radke¹²; Sharma *et al.*¹³; Cambridge *et al.*¹⁴; Rudin¹⁹, 1991) have reported similar interfacial tension minima and have developed simplified models based on the occurrence of interfacial turbulence to explain transient interfacial behavior by treating the organic acid transfer as a convective-diffusive process. Rubin and Radke¹² concluded that transient interfacial tension minima with respect to time arise whenever the solute mass transfer resistance is higher and/or a large desorption barrier exists in the phase towards which transfer is occurring. Since interfacial turbulence is present and arises from interfacial tension gradients on the interface, what really is the value of the transient interfacial tension being measured? The values are likely averages over the droplet surface.

Rudin and Wasan²⁰ have recently developed a theoretical model for equilibrium interfacial tension between an oil containing an organic acid and an alkaline solution. They show that the interfacial tension goes through an ultralow minimum with the pH of the aqueous phase. The ultralow interfacial tension results from the simultaneous adsorption of ionized and unionized acid on the interface, and the lowering results from the formation of mixed micelles of ionized and unionized acid, which is depicted in Figure 2-12. By changing the pH, the ratio of unionized to ionized acid is altered, and an optimum pH exists for which interfacial tension is minimized. Rudin²⁰ has shown that, the pK_A of the alkali/crude oil system is at an equilibrium pH of about 10.6. This is the lowest equilibrium pH where the acid is mostly ionized.

Figure 2-13 shows the roll cell size as a function of the initial pH and total sodium concentration. The roll cell size, which is the initial size, decreases as the pH increases until the pH of about 10.7. After this value, roll cell size is constant and independent of sodium ions. Roll cell size decreases because an increase in pH, which causes an increase in the rate of reaction (i.e., rate of ionization) at the interface, resulting in a higher concentration gradient of unionized acid in the oil phase. Sternling and Scriven⁶ found that steeper preformed surfactant concentration gradients promote smaller cells and more rapid amplification. It should be

Figure 2-11a. Effect of pH on Transient Interfacial Tension for 171 mol/m³ Total Sodium

Figure 2-11b. Effect of pH on Transient Interfacial Tension for 171 mol/m³ Total Sodium

Figure 2-12. Illustration of the Synergistic Effect Between Ionized and Unionized Acid

Figure 2-13. Effect of pH on Roll Cell Size.

mentioned that interfacial turbulence is not present in the absence of added alkali, and the interface is calm and devoid of twitches.

The roll cell formation time or amplification time is defined as the time it takes for the roll cells to become fully developed after contacting of the two phases. Shown in Figure 2-14 is the roll cell formation time as a function of the pH and total sodium concentration. As roll cell size decreases, the time for formation also decreases with increase in pH. This trend comes about because of the shorter distance over which the fluid travels.

Another finding of Sternling and Scriven⁶ is that stronger variation of interfacial tension with preformed surfactant concentration (i.e., smaller area per molecule of surfactant) promotes smaller roll cells. This becomes evident if we plot the interfacial tension at the time of roll cell formation. By using the data from Figures 2-11a and 2-11b along with similar data for different ionic strengths, this interfacial tension is depicted in Figure 2-15. The interfacial tension is decreasing or leveling off before a pH of 10.7. This is because both ionized and unionized acid are simultaneously adsorbing onto the interface, making interfacial tension more sensitive to variations in the total concentration of preformed surfactant species (i.e., smaller area per molecule) as pH is increased. This is evident from such low interfacial tensions. After a pH of about 10.7, the unionized acid at the interface is vanishingly small or nonexistent. This means that the interfacial tension after the pH of about 10.7 depends mainly on the ionized acid (remember that these are transient not equilibrium interfacial tensions), making the unionized acid bulk concentration gradient constant. This explains why the roll cell size shown in Figure 2-13 remains constant after a pH of about 10.7.

Effect of Added Preformed surfactant

Figures 2-16a and 2-16b show the effect of pH on transient interfacial tension for 343 mol/m³ total sodium concentration with 0.1% added preformed surfactant (petroleum sulfonate). Interfacial tension goes through a minimum with pH and with time, just like that without added preformed surfactant. Interfacial tensions are, in general, lower than those without added preformed surfactant, and these ultralow tensions generally occur for longer times. At these longer times when the interfacial tension is below about 10⁻³ mN/m, the elongated droplet in the tube of the spinning drop tensiometer broke-up. Before breaking-up, the droplet developed a

Figure 2-14. Effect of pH on Roll Cell Formation Time

Figure 2-15. Effect of pH on Interfacial Tension at the Time for Roll Cell Formation

Figure 2-16a. Effect of pH on Transient Interfacial Tension for 343 mol/m^3 Total Sodium with Petrostep B-105

Figure 2-16b. Effect of pH on Transient Interfacial Tension for 343 mol/m^3 Total Sodium with Petrostep B-105

sinusoidal shaped interface. The interfacial tension for 343 mol/m^3 total sodium at high pH begins to decrease substantially after a long period of time. This behavior was nonexistent in the absence of added preformed surfactant, suggesting that the added preformed surfactant creates an interfacial resistance to acid transfer, thus reducing the rate of transfer.

The roll cell size as a function of the pH is shown in Figure 2-17. The roll cell size, which is the initial size, is a function of both pH and ionic strength. It decreases with an increase in pH up to a certain pH which will be explained later. After this certain pH, no apparent roll cells were present, however the interface had very deep creases going from one container edge to the other. These creases suggest that the roll cells may be larger than the configuration of the glass container. Future experiments are planned to test this possibility.

Figure 2-18 shows the roll cell formation time as a function of the pH. As before without added preformed surfactant, the roll cell formation time decreases with decreasing roll cell size, however with added preformed surfactant the correlation is much more striking.

In Figure 2-19, interfacial tension at the time of roll cell formation is shown as a function of the pH. Both roll cell size and time for formation correlate nicely with the sensitivity of interfacial tension to the preformed surfactant concentration and with the absolute value of interfacial tension. The certain pH mentioned earlier is the pH where slope of interfacial tension changes sign. These correlations are not related to the pK_A ($pH=10.6$) of the system. However, when acid is ionized, the ionized acid will form mixed micelles with the added preformed surfactant, which will alter the ratio of monomeric interfacially active species in the bulk and on the interface. This changes the average area/molecule on the interface and therefore the sensitivity of the interfacial tension to preformed surfactant concentration. It may be that increasing the ionized acid past a certain ratio causes the added preformed surfactant monomer concentration to decrease. The ratio being different for different ionic strengths. This may, in turn, cause interfacial tension to increase with increasing ionized acid concentration (i.e., pH). In that case, a disturbance will be dampened instead of amplified, resulting in no interfacial turbulence.

Figure 2-20 shows the roll cell formation time as a function of the roll cell size. The line drawn through the data is a least square fit, and the correlation coefficients are 0.84 and 0.67 with and without added preformed surfactant, respectively. For a given cell size, the addition

Figure 2-17. Effect of pH on Roll Cell Size with Petrostep B-105

Figure 2-18. Effect of pH on Roll Cell Formation Time with Petrostep B-105

Figure 2-19. Effect of pH on Interfacial Tension at the Time for Roll Cell Formation with Petrostep B-105

Figure 2-20. Roll Cell Formation Time as a Function of Roll cell Size with and without Added Surfactant

of preformed surfactant increases the time it takes for the cell to form. The preformed surfactant increases the interfacial resistance to mass transfer, and it possibly increases interfacial viscosity. Thomas and Wasan²¹ have shown that the addition of preformed surfactant completely eliminated interfacial turbulence. They measured interfacial shear viscosity with and without added preformed surfactant and concluded that the dampening effect is related to increased interfacial viscosity. Sternling and Scriven⁶ state that surface active agents tend to reduce the violence of the upsets, sometimes suppressing them completely. In the present system, the addition of 0.1% preformed surfactant did not eliminate interfacial turbulence completely, however it did slow down the development of it. Higher concentrations may eliminate interfacial turbulence completely.

If the cellular growth rate is plotted as a function of the cell size, we see an interesting trend, which is shown in Figure 2-21. The line drawn is a least squares fit of the data. The cellular growth rate or amplification rate is nearly constant with cellular size, however, there is a slight dependance on cellular size. Smaller cells have a slightly slower amplification rate. This is inconsistent with Sternling and Scriven's⁶ conclusions that smaller cells have more rapid amplification, which comes from the inertia of the smaller volume of fluid per cell. The faster reaction rate at the interface for smaller cells may be a reason for the observed trend here. Also, the interfacial shear viscosity may be higher at higher pH.

The Resulting Phase Behavior

In the initial stages of contacting of the two phases, primary and secondary emulsions are produced. The secondary emulsions result from the energy supplied by interfacial turbulence, and they are smaller than 1 μm in diameter. Secondary emulsions are usually very stable. Primary emulsions, on the other hand, result from the energy supplied by physical mixing of the system, and they are larger than 1 μm in diameter. The primary emulsions are not stable, so the systems separates into two phases. The lower phase is aqueous and contains secondary oil-in-water emulsions if spontaneous emulsification occurs, if not, then it is clear. The upper phase is oil and contains secondary water-in-oil emulsions if spontaneous emulsification occurs, and it may contain primary water-in-oil emulsions, which settle slowly because of the high oil viscosity.

Figure 2-21. Roll Cell Growth Rate as a Function of Roll cell Size with and without Added Surfactant

During interfacial turbulence, spontaneous emulsification may or may not take place. The extent of emulsification depends upon the magnitude of the interfacial tension, and the rate of reaction, which governs the rotational velocity of the cells. Figure 2-22 shows the extent of secondary oil-in-water emulsification measured as the percent transmittance of the aqueous phase. Interfacial turbulence was observed over the whole range of pH shown here, however, spontaneous emulsification did not occur over the whole range of pH. The percent transmittance remains relatively constant after the pK_A of the system. After the pH of 10.6, both 86 mol/m³ sodium and 1000 mol/m³ sodium had the same roll cell size, but the former spontaneously produced emulsions whereas the latter did not. This behavior results from the 86 mol/m³ sodium having a lower transient interfacial tension and a higher cellular rotational velocity than the 1000 mol/m³ sodium system. With a lower interfacial tension, the mechanical energy supplied by the bulk cellular movement is enough to cause snap-off of emulsions from the interface.

Figure 2-23 shows the percent transmittance as a function of pH with 0.1% added preformed surfactant. The percent transmittance follows the same general trends as that without added preformed surfactant. In general, lower interfacial tension means more oil-in-water emulsion production with smaller and faster forming roll cells. In going from under-optimal pH to optimal pH (highest emulsion production), the size of the emulsions appear to increase, and at optimal pH, the size of the emulsions are on the average about 0.5 μm . By increasing the total sodium concentration, the region for spontaneous emulsification shifts to lower pH.

Figures 2-22 and 2-23 also show the effect of adding preformed surfactant to the 1000 mol/m³ sodium system. Although interfacial turbulence occurs in both cases, the spontaneous production of colloidal sized emulsions occurs only with added preformed surfactant, and only at the appropriate pH. The rate of reaction and cellular rotational velocity should be about the same in both cases at this pH, so it will not be a reason for the observed behavior. At this pH however, interfacial tension is lower. **This then indicates that interfacial turbulence is a necessary but not sufficient condition for spontaneous emulsification.** Low, but not necessarily negative, interfacial tension is also a necessary condition for spontaneous emulsification.

Bakker *et al.*⁴ measured the concentration change of acetic acid in isobutylalcohol when contacted with aqueous sodium hydroxide. They report that the ratio of the measured

Figure 2-22. Effect of pH on the Extent of Emulsification

Figure 2-23. Effect of pH on the Extent of Emulsification with Petrostep B-105

concentration change of acetic acid with chemical reaction and the calculated concentration change without chemical reaction (defined as G) has a maximum when plotted against the hydroxide concentration divided by the acetic acid concentration (See Figure 2-24). The increase is explained as due to interfacial turbulence, and the decrease results from excess of reactant causing the interfacial concentration of the acetic acid to be zero, so that no interfacial tension differences occur, thus no interfacial turbulence. Sherwood and Wei¹ investigated the same system and found that G increases and levels off at a high value. Although our system and the system used by these researchers is not the same, the transfer of an acid by chemical reaction is the same, therefore the trends should be the same. Figure 2-13 shows that the roll cell size decreases and levels off when pH is increased, indicating that interfacial turbulence does indeed occur at high pH. If roll cell size characterizes the rate of acid transfer, assuming constant interfacial area, then the results of Sherwood and Wei¹ can be interpreted in terms of roll cell size.

Figure 2-25 shows the alkali/acidic oil interface for 125 mol/m³ NaOH (171 mol/m³ Na⁺) aqueous phase contacting 40 mol/m³ oleic acid in decane. When the two phases are contacted, interesting emulsion types are formed. Seen in the photograph are multiple emulsions of oil droplets surrounded by a water film in oil (O/W/O emulsion). When the oil/water interface tugs on the emulsion in Figure 2-25a, the water film surrounding the oil drop breaks in Figure 2-25b, leaving behind in the oil some aqueous phase in Figure 2-25c. Notice that the large emulsion on the left has smaller O/W/O emulsions in it, verifying that these are indeed O/W/O emulsions. Notice also in Figure 2-25c how flexible is the water film. Not only is the water film very stable, but so is the oil film separating the emulsion droplets in Figure 2-25a.

SIGNIFICANT FINDINGS

When an oil containing an organic acid is contacted with an alkaline aqueous solution, spontaneous emulsification may take place. Interfacial turbulence has been observed in these reacting systems and some findings associated with it follow.

1. Roll cell size depends strongly on the pH of the aqueous solution. Without added preformed surfactant, the size decreases with an increase in pH until the pK_A of the system, where it remains constant with further increase in pH. When preformed

Figure 2-24. Measure of the Mass Transfer Rate as a Function of Normalized Alkali Concentration

Figure 2-25. Stages in the Breaking of an O/W/O emulsion

surfactant is added, the size decrease follows interfacial tension decrease until the minimum in interfacial tension is reached, and with further increase in pH, where the cells are either nonexistent or are larger than the experimental set-up.

2. As roll cell size decreases, the time it takes for roll cells to form also decreases.
3. For a given cell size, the addition of preformed surfactant increases the time it takes for the cell to form.
4. Cellular rotational velocity increases with increase in pH.
5. The spontaneously produced emulsions are very stable at equilibrium.

CONCLUSIONS

1. The observation of roll cells indicates that the mechanism for spontaneous emulsification is interfacial turbulence.
2. The effect of pH can be explained in terms of the concentration gradient of unionized acid in the oil phase, the sensitivity of interfacial tension to preformed surfactant concentration, and the rate of acid ionization.
3. The added preformed surfactant creates an interfacial resistance to mass transfer, and it also makes the interface more rigid. It also makes the interfacial tension more sensitive to the ionized and unionized acid.
4. Interfacial turbulence is a necessary but not sufficient condition for spontaneous emulsification. Low interfacial tension is also a necessary condition for spontaneous emulsification, if the rotational velocity of the cell is too slow for emulsion snap-off. In other words, there is a trade-off between interfacial tension and rotational velocity.
5. Reacting alkali/acidic oil systems are ideal for investigating interfacial turbulence and to test theories, because roll cell size, rate of amplification, rate of reaction, etc. can be controlled by controlling the pH, unionized acid concentration, ionic strength, added preformed surfactant concentration and type, etc.
6. Interfacial turbulence appears to improve penetration of an aqueous solution between an oil and solid surface leading to oil removal from the solid surface.

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CHAPTER 3
LOW WATER CONTENT DETERMINATION

INTRODUCTION

The ability to determine on-line moisture content and structure of dispersed systems is important in a number of areas, such as, cost-effective drying in process industries, bound moisture determination for safety of food and drugs, dryness of crude oil, emulsion type and composition determination, such as in the treatment of oily sludge or in-line process control.

The dielectric constant of a sample containing water can be determined accurately down to about 10% water content, using microwave interferometry¹. This arises because the attenuation of the sample is low when the moisture level is low. The detection limit of the instrument is reached when attenuation of the sample equals the instrument noise. The noise can arise from several sources. The principle contribution to noise arises from multiple reflections from the sample surfaces. The purpose of this chapter is to develop a technique for determining the low water content (0 to 10 vol%) of a water-in-oil emulsion using microwave interference dielectrometry.

METHOD

The oil phase consisted of a blend of 19.2% carbon tetrachloride in 80.8% light mineral oil of which was made a 2% solution of Span 80. The water-in-oil emulsion was made with deionized water and ranged from 0 to 10%. The emulsion was prepared by drop-wise addition of water into the stirring oil phase. All solutions were made on a volume (v/v) percent basis.

The microwave interference dielectrometer constructed and described by Perl et. al¹ was used in this study. Operation was at a frequency of 23.48 GHz. The teflon cell used to contain the sample was modified for temperature control. Experiments were carried-out at 30 °C.

The microwave transmission equations¹ are given for the real part of the complex dielectric constant as

$$\epsilon' = \left(\frac{1}{A} + \frac{2\beta_g \left(\frac{\Delta L}{\Delta t} \right)}{\beta_g A} \right)^2 \quad [1]$$

Where, $\Delta L/\Delta t$ is the slope of the phase shift versus path length. Also, $\beta_g = 2\pi/\lambda_g$ and $\lambda_g = 1.597$ cm as determined by slotted line measurements of the distance between successive

minima. Here, $\beta_0 = 2\pi/\lambda_0$, where $\lambda_0 = C/F$ and C is the speed of light and F is the frequency. Therefore, $\lambda_0 = 1.278$ for $F = 23.48$ GHz. Also,

$$A = \left[\frac{1 + (1 + (\epsilon''/\epsilon')^2)^{\frac{1}{2}}}{2} \right]^{\frac{1}{2}} \quad [2]$$

Equation (3-1) then becomes

$$\epsilon' = \left[\frac{1}{A} + \frac{(1.601)(\frac{\Delta L}{\Delta f})}{A} \right]^2 \quad [3]$$

and the imaginary part is given by

$$\epsilon'' = \alpha_s \sqrt{\epsilon'} A (0.0469) \quad [4]$$

where, α_s is the slope of the attenuation versus path length.

As reported by Perl et. al.¹, the determination of the complex dielectric constant requires an iterative solution to solve Equations (3-3) and (3-4), which convert the experimentally measured attenuation and phase shift into real and imaginary parts of the complex dielectric constant. Equations (3-3) and (3-4), however, can be combined to obtain an exact solution given by

$$\epsilon' = [1 + 1.601(\frac{\Delta L}{\Delta f})]^2 - [0.0234\alpha_s]^2 \quad (5)$$

and

$$\epsilon'' = 0.0469\alpha_s [1 + 1.601(\frac{\Delta L}{\Delta f})] \quad (6)$$

Where, ϵ' and ϵ'' are the real and imaginary parts of the dielectric constant.

RESULTS AND DISCUSSION

Microwave transmission dielectric interferometry as a tool to measure water content operates on the basis of a large difference in the dielectric constants between the dispersed (i.e.,

water) phase and the continuous (i.e., oil) phase. At 23.45 GHz, the real part of the dielectric constant for water is 33.28¹ and that for oil is 2.

In the determination of the real and imaginary parts of the complex dielectric constant, the slotted line for signal phase shift and precision attenuator for signal amplitude is balanced after insertion of the sample into the dielectrometer. The slope of the attenuation versus path length (see Fig. 3-1) and the slope of the phase shift versus path length (see Fig. 3-2) can be used to calculate the complex dielectric constant. However, resonance effects become very pronounced at low water content. Resonance takes place mainly between the sample surfaces, which causes an oscillation of the attenuation as path length is varied as shown in Figure 3-1 for a 3% water-in-oil emulsion. As a result, the complex dielectric constant cannot be determined.

Figure 3-2 shows that the phase shift varies linearly with the path length at low water content. If this slope is plotted versus water content, the results can be seen in Figure 3-3. Figure 3-3 shows that phase shift measurements alone are accurate enough to determine water content to within 0.5%.

SUMMARY

Simple exact solutions to the transmission equations have been derived, thus allowing determination of complex dielectric constant without time consuming iterative procedures. Moisture levels are shown to be detectable with an accuracy of about 0.5 volume percent water content using microwave interferometric dielectrometry. The ease of obtaining the data, the noninvasivity of the measurement technique, and the rapidity with which results are obtainable makes low water content determination using dielectrometry highly desirable in comparison to a wet technique such as Karl Fisher titration.

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Figure 3-1. Attenuation Versus Path Length at 23.48 GHz and 30 °C.

Figure 3-2. Phase Shift Versus Path Length at 23.48 GHz and 30 °C.

Figure 3-3. Slope of Phase Shift Versus Path Length as a function of water content at 23.48 GHz and 30 °C.

CHAPTER 4
DEMULSIFICATION OF WATER/CRUDE OIL EMULSIONS

INTRODUCTION

The importance of understanding the mechanisms governing water-in-crude oil emulsion stability/instability has been of scientific interest for a long time and has precipitated a wealth of published literature on the subject. Water droplet/droplet flocculation (the formation of a crude oil lamella between the water droplets) takes place because, under gravity settling, the water droplets approach and the capillary force deforms their surfaces, the surfaces hydrodynamically interact and the oil lamellae of the "biliquid foam" form (See Figure 4-1). The dispersed water phase is trapped in polyhedron shaped, crude oil lamellae cells. Under the gravity and capillary forces, the crude oil lamellae begins to break, the water polyhedron droplets coalesce and the "biliquid foam" lamellae polydispersity increases. Then, when the crude oil lamellae separating the water bulk phase from the water polyhedron drops break, the real separation process occurs.

The process of chemical demulsification of a water-in-crude oil emulsion leads to the acceleration of flocculation and the rate of "biliquid foam" lamellae rupture. The hydrodynamic interaction between the droplets depends on: capillary pressure (drop size, dynamic interfacial tension, drop polydispersity), asphaltenes-resins particle suspension rheology, and interfacial rheology (interfacial viscosity and interfacial tension gradient, this last one is known as Marangoni-Gibbs effect). An analysis of the factors governing the hydrodynamic film stability and rheology is presented in the book recently published by Edwards, Brenner, and Wasan, Interfacial Transport Processes and Rheology ¹.

In the presence of an efficient oil soluble demulsifier, the interfacial tension gradient, and the interfacial viscosity are usually decreased^{2,3}. In other words, in the presence of an efficient oil soluble demulsifier, the rate of film thinning increases and the time it takes the film to reach a certain thickness decreases^{4,5}.

In the hydrodynamic droplet/droplet interactions, high film thickness (about 1 μ m)

Figure 4-1. **Formation of the "biliquid foam" during the gravitational water separation from the water-in-crude oil emulsions.**

causes the approaching droplet interfaces to more or less behave as a deformable single interface, and a dimple is formed. When the thinning film ruptures at high film thickness, correlation with the rheology of the single interface may be observed and indeed, in some cases, such a correlation has been found⁶. This may not be, however, the only governing mechanism when the asphaltenes and resins (submicron particle/particle) have a high effective volume (deviation from the ideal positive second virial coefficient).

The experimental observations show that the stability of water-in- crude oil emulsion depends on the effective volume concentration of asphaltenes and resin and on their polydispersity⁷. In some cases, the asphaltenes and resins (submicron particles) first form a layered type structure inside the thinning oil emulsion film and, after a certain effective volume concentration, the layering structure inside the film becomes colloid crystal-like. The particle layering inside the film creates in the normal direction to the film surfaces an additional disjoining pressure which stabilizes the film and stops the film thinning, thus causing the formation of a very stable film with a thickness of $> 0.1\mu\text{m}$. Such film thins in a stepwise manner.

To reduce the film stability (thickness), one needs to improve the attractive particle/particle interactions by adding efficient oil soluble flocculent or by reducing the " Θ -temperature" point (particle/solvent interactions) and particle effective volume⁸. By improving the attractive particle/particle interactions, the particle film stabilizing effect diminishes and the stability of such films will then depend on the interactions between the adsorbed layers (formed at the water/oil interfaces).

These interactions in oil film are basically stearic types and, until now, the understanding of water-in-crude oil emulsion has been based on stearic stabilization governed by the adsorbed asphaltene-resins at the water/oil interfaces. Depending on the crude oil aliphatic/aromatic ratio (which governs the solubility of asphaltenes-resins and their interfacial activity), one can expect two major crude oil film stabilizing mechanisms: 1) stearic stabilization by the adsorbed asphaltenes-resins at the water/oil interface; and

2) long-range particle structure formation inside the film (see Figure 4-2). By using the curved crude oil emulsion film (which models the emulsion polydispersity), the role of each component of the demulsifier and the blend demulsifier can be analyzed by studying the dynamics of the film tension and surfactant diffusivity at the emulsion film surfaces. The results of the dynamic film properties, dynamic film tension measurements for the various demulsifier packages and demulsifier components are compared with their performance in the field. The dynamic film tension data provide a good guideline for optimizing demulsifier composition.

EXPERIMENTAL

Field Information

The crude oil is produced by gas lift. The crude oils have an average API gravity of 28. The w/o emulsion contains close to 54 V% water and requires around 25 - 45 ppm of emulsion breaker to drop water and dehydrate the crude oil. The dehydration requirement for the refinery is normally about 99%. The typical particle size distribution of the water in this crude oil observed by microscopic imager is shown in Figure 4-3. The crude oil and water analysis (by IATRO Scan Analysis) is listed in Tables 4-I and 4-II. Crude oil contained 20.4 wt% hydrocarbon, 44.8 wt% aromatics, 34.1 wt% heterocyclics, 0.37 wt% asphaltenes, 0.04 wt% resins and 22.66 wt% water. The water phase contained 66,000 ppm sodium chloride, 3,100 ppm calcium chloride. Hence the partitioning of the demulsifier in the water phase can be ignored. The production system consists of an L.P. bulk separator and a surge tank. The pressure of the production system varies from 68 - 76 pounds and the temperature is between 27 - 35 °C. The residence time of the crude oil in the separator varies between 6 - 9 minutes.

Performance of Emulsion Breakers by Bottle Tests

Bottle tests were performed at the Chevron Bay Marchand field platforms

Figure 4-2. Schematic diagram of stabilized water/crude oil emulsion film by 1) steric stabilization by the adsorbed asphaltene-resin particles and 2) long-range particle formation inside the film.

Figure 4-3. Drop Size Distribution of the Water-in-Crude Emulsions.

Table 4-1. Composition of Gulf Coast Louisiana Crude Oil.

TLC/FID Analysis "latroscan"

Hydrocarbon	Aromatics	Heterocyclics
wt%	wt%	wt%
20.4	44.8	34.1

Colloidal Analysis

Dispersion Media	Resins	Asphaltenes
wt%	wt%	wt%
76.93	0.04	0.37

Table 4-2. Composition of the Water Phase of the Crude Oil Emulsions at 25 °C.

Metals	ppm
Iron(Fe)	17.0
Copper(Cu)	0.08
Chromium(Cr)	.02
Barium(Ba)	39.0
Aluminum(Al)	0.1
Potassium(K)	410
Calcium(Ca)	3,100
Magnesium(Mg)	980
Manganese(Mn)	1.0
Silica(Si)	9.2
Strontium(Sr)	47.0
Antimony(Sb)	0.3
Lead(Pb)	0.2
Tin(Sn)	0.2
Sodium(Na)	66,000
Sulfur(S)	4.5
Phosphorous(P)	4.3
Chloride(Cl)	111,000

Tango/HH/Victory (Gulf Coast Louisiana). Details of the bottle tests can be found elsewhere⁹. The 25 demulsifier packages that could destabilize the Chevron Bay Marchand emulsion were tested. The tests were performed at least 20 times on each demulsifier package. The demulsifier concentration in the test was 30 ppm. The demulsifier performance was defined as following 'response' value in terms of the rate of water separation in 3 hours at different temperatures: at 40 °C (hot coalescence) and 25 °C (cold coalescence) and the final dryness of oil, which is defined as final remained water volume % in oil phase at 25 °C. The values of the response of the coalescence rate and the dryness have been calculated based on the equation (4-1).

$$response^* = \frac{(\bar{u}_{specific} - \bar{u}_{all})}{S_{all}} \quad (4-1)$$

(*: (+) for the water separation rate and (-) for the dryness)

where, $\bar{u}_{specific}$: average value of rate of water separation or dryness for a specific demulsifier

$\bar{u}_{all}$: average value of rate of water separation or dryness for all demulsifiers (25 packages)

S : standard deviation of the data of water separation rate or dryness for all demulsifiers.

Three Nalco blended demulsifiers - blend-2, blend-15, and blend-19 were chosen to correlate the demulsifier performance and the demulsifier properties (on the effect of rheological properties of W/O emulsion film) because they represent emulsion breaker packages covering the entire spectrum of efficiency. The selected three demulsifiers are listed with their individual components in Table 4-III. All the chemicals used are oxyalkylated derivatives of phenol/formaldehyde resins with branch structure, except for N-499 and N-428 are EPON cross link derivatives. The demulsifier performances for the

Table 4-3. Blend Demulsifiers and Individual Components.

demulsifier components	blend-2	blend-15	blend-19
N-100	7	5	5
N-253	-	-	3
N-428	-	1	0.5
N-499	3	2	-

*** numeric number represents volumetric blending ratio of the components**

three blend demulsifiers are shown in Figure 4-4.

Before using the crude oil for experiments conducted in the laboratory, solid particles in the crude oil were removed by centrifugation.

Apparatus for Film Property Measurement

An interfacial/film tension tensiometer developed at Illinois Institute of Technology (See Figure 4-5) was used to measure the water-in-crude oil emulsion film rheology. The device consists of a glass capillary, a sensitive pressure transducer, and an assembled linear actuator which drives the plunger of a gas-tight micro syringe to control the formed oil film shape at the tip of the capillary. All manipulations of the instrument and gathering of the experimental data were performed by a fully automatic computerized system.

The glass capillary has an internal diameter of $6.4 \times 10^{-2} \pm 1\%$ cm and a wall thickness of 0.5×10^{-2} cm. A horizontal microscope with magnification X 60 (Cole Parmer Model 3890) is attached to the instrument, and it enables the measurement of the size of the film and the film curvature during the measurement. To observe the oil film on the tip of the capillary, the tip is fixed in the optical part of the instrument.

Before the experiment, the capillary assembly (a part of the instrument) was first cleaned with xylene and then with heptane and with fresh water to remove any traces of organic material. The presence of impurities has been tested by measuring the interfacial tension of pure water (purified by Milipore Water Purify System Serial-01245) and dodecane (Aldrich 99+% dodecane) which was purified in laboratory with active charcoal. After the capillary was cleaned, the capillary was connected to the pressure transducer and the capillary was then filled with water phase pre-equilibrated with the oil phase. After thermal equilibrium is reached (± 0.2 °C), the oil film at the capillary tip in the water phase was formed for the film rheological experiment.

The oil film formation procedure at the capillary tip is depicted in Figure 4-6.

Figure 4-4. Performances of Blend Demulsifiers for Water Separation Efficiency from The Water-in-Crude Emulsions.

Figure 4-5. Schematic diagram of the film experimental apparatus.

Figure 4-6. **Procedure of oil film formation on the capillary tip.**

First, the capillary tip was immersed into a cuvette containing an oil layer (about 1 mm) at the top level (Figure 4-6(a)). Then, to form an oil layer on the tip of capillary, the capillary was immersed into the water phase at the lower part of the cuvette, this capillary tip immersion was performed by adding water phase from out of a cuvette using a syringe. At this moment, an oil layer initially forms at the tip of capillary (Figure 4-6(b)). After several minutes, thin oil film was obtained which is formed (Figure 4-6(c)) from the relatively thick oil layer by releasing remnant oil induced by the buoyancy force effect at the capillary tip. Attention is paid to the oil film meniscus so as to wet only the capillary tip and to avoid wetting the capillary walls. The film meniscus is necessary to maintain a regular three-phase contact line at the rim of the capillary tip. The oil film formed at the tip of the capillary was expanded, very slowly, up to a certain curvature, usually before the hemisphere position. This expansion of the curved film was performed by pressing the plunger of the micro-syringe actuated under the control of a computerized system. After a sufficient amount of time, of the order of less than an hour, the capillary pressure of the curved oil film reached a constant value indicating that film/interfacial tension equilibrium has been reached. After equilibrium was reached, two types of experiments were performed to model the phenomenon governing the process of water separation under gravity settling (Figure 4-7):

- 1) dynamic film tension experiment at a constant rate of expansion, which models the thinning film phenomenon during the "oil lamellae" drainage, where the area of crude oil lamellae slowly increases as time progresses, and a oil lamellae with rhomboidal dodecanhedron unit cell is formed.
- 2) stress relaxation experiment to model the phenomenon of the new lamella formation. During the oil lamellae drainage, the gravity and capillary stresses break some of the oil lamellae to balance the inter-lamellae tension and a new

Figure 4-7. Schematic Diagram of Foam Lamella Rupture Process

lamella is formed.

RESULTS AND DISCUSSION

Emulsifier Performance and the Role of Film Dilatational Modulus and Demulsifier Diffusivity

In this study, attention is paid to the role of oil soluble demulsifier components and blends on the asphaltenes/resins film adsorbed layers destabilization and particularly, their effect on film dilatational modulus and diffusivity for improving the destabilization of water-in-oil emulsion. During gravity settling, a "biliquid lamellae" type water-in-crude oil emulsion is formed¹⁰, and over time, the area of crude oil lamellae, under gravitational and capillary force stresses, is slowly expanded. The oil emulsion curved film is used to represent the emulsion polydispersity. Expansion and film stress-relaxation experiments are conducted to model the phenomena such as expansion and breaking of the crude oil lamellae which occur in biliquid lamellae under the gravity and capillary forces. For the three blended demulsifiers, the dynamic film tension of oil emulsion film vs. the normalized rate of film area expansion ($\ln(A/A_0)$) is shown in Figure 4-8. The slope of the film tension- $\ln(A/A_0)$ curve provides information on the film dilatational modulus. When blend-19 demulsifier is present in the crude oil, the dilatational modulus is about 7.9 mN/m and is smaller than the other two blends. One can expect that oil film with a low dilatational modulus will have a low film stability and thus gives better demulsification performance. Indeed, there exists a correlation between the film dilatational modulus and the demulsifier performance for water separation (See and compare Figures 4-4 and 4-8 for curves representing blend-19). With low film elasticity (calculated from dynamic film tension experiments at constant film expansion rate), one can correlate film tension gradient (Marangoni effect). To reduce the film tension gradient and to improve the rate of film thinning, demulsifier components need to have higher film

Figure 4-8. **Dynamic film tension as a function of film area expanded in the presence of blended demulsifiers.**
 (Rate of film expansion is $2.7 \times 10^{-4} \text{ cm}^2/\text{sec}$)

surface diffusivity and interfacial activity and the experimental results for the film stress-relaxation experiment shown in Figure 4-9 for blended demulsifiers show that this is, indeed, the case for the adsorbed layer stabilizing mechanism. In Figure 4-9, the best demulsifier (blend-19) has the curve with the steepest initial slope. It is important to note that, for a particular crude oil; film emulsion stability, the diffusivity of the demulsifier at the film interfaces plays a critical role in the demulsifier efficiency. For example, if the diffusivity is too low at the higher rate of film expansion, the demulsifier component will not be adsorbed at the film interfaces and one can expect a higher film dilatational modulus and, thus, higher film stability. By presenting the curves shown in Figure 4-10, the apparent diffusivity of the demulsifier can be calculated from the slope of $1/\Delta\gamma$ versus $t^{-1/2}$. By fitting the film stress relaxation data to a kinetic adsorption model¹¹, the demulsifier diffusivity was calculated, and the data are presented in Table 4-IV. The calculated value of the diffusivity of the three demulsifiers studied follows the sequence: blend-19>blend-15>blend-2. The data presented in Figure 4-10 showing linear behavior with $t^{-1/2}$ suggests that the adsorption kinetics is controlled by the diffusion in the controlling mechanism.

Individual Component Film Dilatational Modulus and Diffusivity

As we mentioned before, the blended demulsifier contained several components and it is important to determine which of these components has higher diffusivity of the film surface and thus, it reduces the film elasticity. To reveal that, dynamic film tension and film relaxation experiments with the demulsifier components were conducted using the component concentration in the blend demulsifiers (See Tables 4-III and 4-IV). The dynamic film tension vs. film area expanded and the fitting of the stress relaxation data to the diffusion control model is presented in Figure 4-11.

The results of the dynamic film properties, calculated apparent diffusivities and film dilatational modula for all the blended demulsifiers and the components are summarized

Figure 4-9. **Stress relaxation curves in the presence of blended demulsifiers.**

Figure 4-10. Fitting of stress relaxation data to the adsorption model to calculate the diffusivity of demulsifier.

Table 4-4. Summary of dynamic film properties for the component and blended demulsifiers

COMPONENT		BLEND-19					BLEND-15					BLEND-2				
type	M.W	vol. ratio	ppm	E	D x 10 ⁴	vol. ratio	ppm	E	D x 10 ⁴	vol. ratio	ppm	E	D x 10 ⁴			
N-100 branched	8,400	5.0	17.7	10.4	1.1	5.0	18.75	10.1	1.4	7.0	21	9.58	1.4			
			30	10.1	1.5		30	10.1	1.5		30	10.1	1.5			
N-253 cross-linked	135,000	3.0	10.6	9.0	42.0											
				9.8	40.0											
N-428 cross-linked	15,400	0.5	1.7	7.0	4.2	1.0	3.75	6.7	5.0							
			30	10.9	8.0		30	10.9	8.0							
N-499	400,000					2.0	7.5	10.0	1.0	3.0	9	9.09	1.2			
							30	10.7	1.1		30	10.7	1.1			
properties of blend-->				7.9	20.0			9.9	6.8			10.5	3.6			

where, D: diffusivity (cm /sec), E: film modulus (mN/m), and M.W.:molecular weight.

Figure 4-11. Dynamic film tension vs. film area expanded and fitting of the stress relaxation data for the components of blend-2, blend-15, and blend-19.

in Table 4-IV.

By comparing the film dilatational modulus of the components with the properties of the blended demulsifiers, one finds that the dynamic film elasticities of the components are of approximately the same magnitude (9 to 10 mN/m). Note that the elasticity of the most efficient demulsifier, Blend-19, is 7.9 mN/m and is less than the film dilatational modulus of the single component. Also note that the film dilatational modulus in the studied concentration region does not depend on the concentration. This shows that when the single components are mixed, a synergistic effect on the film rheology properties is observed, and for optimal efficiency, the film dynamic elasticity needs to be studied vs. component volume ratios. In fact, the most efficient demulsifier, Blend-19, contains, relatively, the highest amount of component N-253 (See Table 4-III or Table 4-IV) and the calculations show that this component has the highest apparent diffusivity, $42 \times 10^{-4} \text{ cm}^2/\text{sec}$. For higher demulsifier efficiency, film surface diffusivity is an important parameter (See the above discussion). The apparent diffusivities of all the components, which were calculated from the stress-relaxation curves as shown in Figure 4-11, are presented in Table 4-IV. The highest diffusivity, $42 \times 10^{-4} \text{ cm}^2/\text{sec}$ at 10.6 ppm, was calculated for component N-253. The diffusivities of the other components are less than one order of magnitude of that of N-253. It should be pointed out that the calculated apparent diffusivity does not depend on the concentration (See Table 4-IV).

Effect of Interfacial Tension on Demulsifier Efficiency

Finally, it is also important to discuss the effect of interfacial tension value on the demulsifier efficiency. It is important to note that, in some cases, a correlation between the rate of interfacial tension lowering and the demulsification efficiency of demulsifier has been found^{6,12}. The effect of the blended demulsifiers and their components on the film tension relaxation experiment shown in Figures 4-9 and 4-12 provide information about the demulsifier interfacial activity. In the case of the stearically stabilized oil film,

Figure 4-12. **Film relaxation for the blend-19 demulsifier and individual components at 30 ppm.**

the measured film tension is equal to two times the interfacial tension and thus, the data presented in Figures 4-9 and 4-12 provide information about oil/water interfacial tension. The data for blend-19 which is a mixture of N-100, N-253, and N-428 (See Table 4-III) at the ratio of 5:3:0.5 confirms the existence of interfacial tension synergism (See Figure 4-12). For example, at the same concentration of 30 ppm, the interfacial tension of each single component of blend-19 is higher than that of the mixture, blend-19. Note that, in Figure 4-12, the initial slope of the film tension curve in the presence of blend-19 is steeper than that of any other single component and, in Table 4-IV, the film dilational modulus of blend-19 is even lower than that of any other components blend-19 at 30 ppm. The interfacial tension synergism is governed by the adsorbed intermolecular interactions and depends on the composition ratio of the adsorbed layer. From this point of view, the observed correlation between the lowering the interfacial tension and the efficiency of blend-19 can also be optimized.

CONCLUSIONS

1. By measuring the dynamic properties of crude oil emulsion film (Gulf Coast Louisiana crude oil), the stearic stabilization role of the adsorbed asphaltenes-resin at water/crude oil interface has been studied.
2. In order to optimize the demulsifier efficiency, the rate of water gravity separation of the water-in-crude oil emulsion and the curved oil film dynamic properties such as diffusivity of demulsifier and film modulus have been studied.
3. To improve the demulsifier efficiency, the demulsifier components need to create a lower emulsion film elasticity (dilational film modulus), higher film diffusivity and lower film tension.

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