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**BASIC STUDIES IN THE DISPLACEMENT OF
RESIDUAL OIL BY CHEMICAL FLOODING**

Annual Report, February 1, 1978—January 31, 1979

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University of Houston
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U. S. DEPARTMENT OF ENERGY

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**BASIC STUDIES IN THE DISPLACEMENT OF
RESIDUAL OIL BY CHEMICAL FLOODING**

**Annual Report
for the Period
February 1, 1978—January 31, 1979**

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Under Contract EY-76-S-05-5075**

U.S. DEPARTMENT OF ENERGY

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ABSTRACT

Research studies at the University of Houston are concerned with (1) the role of dynamic interfacial properties on the displacement and reconnection processes occurring in surfactant flooding processes and (2) the analytical description of multiphase displacement dynamics using ganglia population balance models and simulation algorithms. During the past year, progress has been made in:

1) Measurement of interfacial viscosities.

Tests on oil-water-surfactant systems using both a drop deformation and orientation method and the viscous traction method indicate the largest interfacial viscosities at salt concentrations in the neighborhood of the optimal salinity. Values of interfacial viscosities for crude oil systems were considerably larger than those associated with iso-octane systems.

2) Coalescence studies of oil-water-surfactant systems.

A new technique involving the use of a spinning drop apparatus has been developed for controlled coalescence tests. Tests to date on several iso-octane-brine-surfactant systems and one crude oil-brine-surfactant system indicate that the fastest coalescence occurs at salt concentrations near the point of optimal salinity. Also, the crude oil systems coalesce at significantly slower rates than the iso-octane systems.

3) Displacement tests

Capillary displacement tests involving iso-octane drops being displaced by water have been attempted in both constant pressure drop and constant displacement rate systems. The results to date have been quite varied and have not been reproducible, even though extensive measures have been taken to eliminate contaminant surface active agents.

4) Studies of oil ganglia population dynamics during immiscible displacement

Work has continued in the development of a theoretical description of the dynamics of mobilized oil ganglia, their breakup, coalescence, and entrapment. Improvements in the mobilization criteria have been effected, and hundreds of computer-aided stochastic realiza-

tions have been performed for solitary ganglia of all sizes of interest moving in a 100 x 200 sandpack. These realizations show clearly that a solitary ganglion gets slenderized as it moves, and that either it gets restranded whole after a few rheons, or that it first breaks into two daughter ganglia, which eventually get stranded.

INTRODUCTION

The efficient recovery of residual oil by low tension processes generally requires four key steps: (1) The mobilization of the residual oil by reductions of the oil/water interfacial tension, (2) the reconnection of the mobilized oil through coalescence, (3) the formation and maintenance of a stable oil bank, and (4) the uniform sweep of the oil bank through the reservoir zone. Although the mobilization step is essential to the displacement process, the achievement of this condition, in itself, does not insure the realization of an efficient recovery. Model studies of ganglia dynamics and breakup by investigators in this laboratory [1-5] have clearly demonstrated that without coalescence, the probability of breakdown and re-entrapment of isolated ganglia in a random porous structure is essentially unity. Obviously, any factors which affect the reconnection processes or alter the kinetics of oil bank formation can have significant consequences on the ultimate success of a given process.

In any given application, there are a number of factors which can seriously affect the dynamic stages of the displacement process, including surfactant adsorption on the rock, thermodynamic phase behavior, bulk phase viscous effects, dynamic wetting effects, dynamic oil-water interfacial properties, interfacial adsorption and bulk phase mass transfer, as well as in situ hydrodynamic phenomena (dispersion, coalescence, etc.). At the University of Houston, we have focused on two major objectives relating to the dynamic behavior of residual oil during chemical flooding. Objective A is concerned with the particular role of dynamic interfacial effects such as interfacial viscous effects, interfacial elasticity, and dynamic interfacial tension as well as interfacial tension gradient effects. When sufficiently large, such effects can seriously alter the effective interfacial tension of an advancing interface through converging-diverging channels [6], as well as alter the trapping and displacement mechanisms [7], plus, play significant roles in the in situ hydrodynamic phenomena of ganglia breakdown and coalescence [8]. The work here is centered on clarifying these roles through (1) the development and utilization of methods for the measurement of interfacial viscous and elastic properties, as well as dynamic interfacial tension effects, and (2) the determination of the nature and magnitude of such effects on the coalescence, breakup, and capillary displacement processes. Such studies should contribute to our basic understanding of the dynamic stages of displacement, and

particularly to the reconnection and breakup processes associated with oil bank formation and stability. Reliable utilization and design of low tension flooding processes require careful consideration of such factors, their nature, and their variance with surfactant system and displacement conditions.

Under Objective B we are concerned with (1) the development of theoretical models and simulation algorithms for the motion, stranding, breakup and coalescence of oil ganglia in porous media, and (2) identification of displacement mechanics and oil ganglia population dynamics from experimental observations in porous networks. Clearly, the fate of a mobilized oil ganglion and, much more importantly, the collective fate of a population of oil ganglia engulfed by a chemical flood are problems of fundamental significance in understanding the formation of an oil bank and elucidating the mechanisms through which significant amounts of oil remain entrapped. Successful oil bank formation depends on the outcome of the competition between the process of oil ganglia deterioration through breakup and stranding on one hand, and the process of oil ganglia collision and coalescence on the other [4]. The studies here attempt to provide a framework for the analysis and description of such oil ganglia population processes.

In the sections which follow, we summarize the progress during the past year on Objectives A and B and indicate directions for future work.

INTERFACIAL VISCOSITY MEASUREMENTS

Although there appears to be considerable incentive for the determination of the magnitude of interfacial viscous effects in low tension surfactant systems, the current status of experimental interfacial viscometry does not, as yet, allow for reliable and reproducible measurements of interfacial shear and dilational viscosities of such systems. The viscous traction method of Mannheimer & Burton [9] and Mannheimer & Schechter [10], as applied to liquid-liquid systems [11,12], appears to give reliable results for interfacial shear viscosity measurements, although inter-laboratory verification for a specific oil-water-surfactant system has not yet been obtained. Measurements of this type are being conducted at Northwestern University, Illinois Institute of Technology (IIT), and in this laboratory.

In the case of interfacial dilational viscosity, measurements have been limited largely to the drop deformation and orientation methods employed in this laboratory [12-17], and the capillary wave methods of Wasan and co-workers at IIT [18, 19]. Both methods have been developed under DOE sponsorship and are aimed specifically for application to oil-water-surfactant systems.

The drop deformation and circulation method stemmed from a suggestion by Wei et al. [20] that a combination of interfacial viscosities $3\kappa + 2\varepsilon$ could be obtained from circulation measurements at the surface of drops suspended in simple shear fields. Although previous investigators [21], including some in this laboratory [22], had observed significantly retarded circulation in drops in shear fields, Wei et al. were the first to theoretically relate such effects to interfacial viscous effects.

Following the work of Wei et al., several developments followed in this laboratory. First, preliminary studies clearly indicated that circulation experiments, particularly at the drop surface, were not attractive because of experimental difficulties and because of the strong dependence of circulation time on the tracer position near the interface. We then proceeded to extend the theoretical work of Wei et al. and obtained, in addition to internal and external circulation behavior, the drop deformation in terms of the applied shear rate G , the original drop radius a , the bulk phase viscosities μ and $\hat{\mu}$, the interfacial tension σ , and the interfacial viscosities κ and ε [13]. This was a small capillary number theory ($N_{ca} \equiv \frac{\mu Ga}{\sigma} \sim 0(0.1)$). A series of tests then followed by Phillips [14] to verify these relations and to establish the

test methods. These studies defined the experimental constraints and demonstrated the accuracy of the method when applied to viscous "pure" systems.

More recently, the theory was extended even further, and a higher order solution was obtained for the deformation and orientation [16]. This required a more rigorous analysis of the coupled mass and momentum transfer problem, and solutions were obtained for diffusion controlled and adsorption controlled regimes, as well as conditions of small surfactant concentration variations on the interface. The approach was based upon a perturbation solution in terms of deformation, instead of the capillary number as before [13]. Since small deformations could be realized over a full range of capillary numbers depending on the magnitudes of the viscosity ratio ($N_\mu = \frac{\hat{\mu}}{\mu}$), the dimensionless interfacial shear viscosity ($N_\varepsilon \equiv \varepsilon/\mu a$), and the dimensionless apparent interfacial dilational viscosity ($N'_K \equiv \kappa'/\mu a$), the theory had a wide range of validity. In particular, the previous small capillary number theory represents a special case in this more general theory. The deformation and orientation results obtained from this extended theory are given by (refer to Figure 1):

$$D = \frac{5N_{ca} (24N'_K + 8N_\varepsilon + 19N_\mu + 16)}{16(6N'_K + 4N_\varepsilon + 5N_\mu + 5)} \left\{ \frac{1}{[1+(19\lambda RN_{ca}/20)^2]^{1/2}} \right\} \quad (1)$$

$$\alpha = \frac{\pi}{4} + \frac{1}{2} \tan^{-1} \left(\frac{19\lambda RN_{ca}}{20} \right) \quad (2)$$

where $\lambda \equiv N_\mu + \frac{2}{5} (3N'_K + 2N_\varepsilon)$ (3)

$$R \equiv \frac{1}{19\lambda^2} (19N_\mu^2 + 23N_\mu N'_K + 26N_\mu N_\varepsilon + 16N'_K N_\varepsilon) \quad (4)$$

Here N'_K , the dimensionless interfacial dilational viscosity, represents both intrinsic and apparent dilational effects. In terms of these contributions, this group can be written

$$N'_K = N_K + \frac{N_M E_c}{N_{ca} \sigma_o} \quad (5)$$

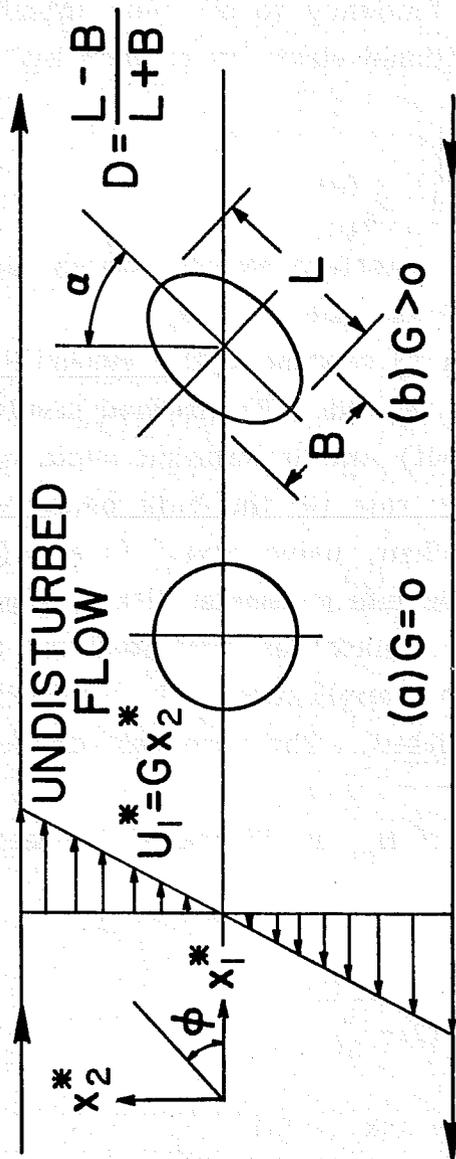


Figure 1. Illustration of drop deformation and orientation in shear field.

The first term on the right is the intrinsic interfacial dilational viscosity group ($N_{\kappa} \equiv \kappa/\mu a$). The second term represents the contributions stemming from variations of σ on the drop interface. The term N_M in Eq.(5) is associated with the rates of bulk phase/interface surfactant transfer (see [16] for specific form and discussion); the faster these processes, the lower the value of N_M , and the more the tendency to eliminate interfacial tension gradients. The term E_c is the compositional elasticity defined by

$$E_c \equiv - \left[\frac{\partial \sigma}{\partial \ln \rho_A}(\sigma) \right] \bigg|_{\rho_{A_0}}(\sigma) \quad (6)$$

where $\rho_A(\sigma)$ represents the interface excess concentration of surfactant; $\rho_{A_0}(\sigma)$ being a reference concentration where $\sigma = \sigma_0$.

Eqs. (1) and (2) above represent the essential relations for the drop deformation and orientation method. The method involves measurements of the deformation $D = (L-B)/(L+B)$ and orientation angle α along with initial drop radius a , the applied shear rate G , the bulk phase viscosities μ and $\hat{\mu}$, and the interfacial tension σ . Then, using Eqs. (1) and (2), the values of ε and κ can be obtained by appropriate parameter fitting algorithms [17].

During the past year, work has continued on the development of this method both in theory and application. In addition, testing of oil-water-surfactant systems was initiated. The progress can be summarized as follows:

1) Extensions of Method

It was observed that if N_{ca} is eliminated between Eqs. (1) and (2), we obtain

$$F = \frac{19D}{20} \left[1 + \frac{1}{\tan^2 (2\alpha - \frac{\pi}{2})} \right]^{1/2} \quad (7)$$

$$\text{and} \quad F = \frac{5(24N'_{\kappa} + 8N_{\varepsilon} + 19N_{\mu} + 16)}{16(6N'_{\kappa} + 4N_{\varepsilon} + 5N_{\mu} + 5)} \frac{1}{\lambda R} \quad (8)$$

The last equation represents F in terms of κ' , ε , μ , $\hat{\mu}$, and a . Hence, from measurements of D and α , one can calculate F from Eq. (7) and then use it in Eq. (8) to obtain a relation between κ' and ε ; the important point being that σ and G data are not required in this determination. Also, the quantity F is

a sensitive function of the dynamic interfacial properties and the initial drop radius a [15]; hence, accurate determinations of κ' and ε should be possible from deformation and orientation tests on different size drops. The data of Phillips and Graves, as well as more recent data, have been analyzed using Eqs. (7) and (8) to accurately identify the existence of dynamic interfacial effects [15].

Another modification of the method has been recognized recently for cases involving very small drops. In particular, as a is decreased, the groups N'_K and N'_ε increase with the following limits being realized if a is sufficiently small [16]:

$$D = \frac{5}{8} \left(\frac{3N'_K + N'_\varepsilon}{N'_\varepsilon N'_K} \right) \quad (9)$$

$$\alpha = \frac{\pi}{2} - \frac{1}{4} \left(\frac{3N'_K + 2N'_\varepsilon}{N'_K N'_\varepsilon ca} \right) \quad (10)$$

Also, for small values of a , the surfactant bulk phase-interface diffusion processes become quite fast, with the result that interfacial tension gradients are diminished and $N'_K \rightarrow N_K$. Hence, if deformation and orientation experiments are possible for sufficiently small drops, Eqs. (9) and (10) can be used to determine the intrinsic interfacial viscosities ε and κ .

2) Experimental observations. Tests on an oil (iso-octane + CCl_4)/brine/surfactant (Exxon C12 orthoxylene sulfonate)/tertiary butyl alcohol system showed very low interfacial viscosities (κ' , $\varepsilon < 10^{-3}$ s.p.) outside the region of optimal salinity. In the region of optimal salinity, higher values were noted ($\kappa' = 0.007$ s.p. and $\varepsilon = 0.004$ s.p.). Similar results (ε only) were found for tests on the viscous traction instrument with an oil (iso-octane)/brine/surfactant (Witco TRS 10-80)/tertiary butyl alcohol system. In this case, the value of ε outside the region of optimal salinity was $< 10^{-4}$ s.p., and ε was measured as high as 0.04 s.p. in the optimal salinity region. Also, indirect determinations of $(\kappa' + \varepsilon)$ from coalescence experiments (discussed below) showed similar behavior. Evidently, for these iso-octane systems, the interfacial viscosities assume their largest values when the interfacial tension is lowest.

Extensive testing of oil/water/surfactant systems was prevented because of difficulties in carrying out deformation experiments in the Couette apparatus. The relatively large density differences and the low continuous phase viscosities produced drop rise velocities which made continuous focusing of the microscope and camera almost impossible. Various techniques were tried to alleviate these difficulties, but none were very satisfactory. Further, the large volume of fluids required for this system made mixing and pre-equilibration quite time consuming and costly. It became clear that such an apparatus could not be used in any systematic testing of large numbers of samples, and hence we sought an alternate method.

3) Experimental modifications. To avoid the difficulties of buoyancy effects just described, one must use very small drops and, if possible, place the shear field in a vertical plane and view the drop along the horizontal. In this case, the focal length between the drop and the microscope will be fixed throughout an experiment, assuming, of course, that the drop can be tracked in the vertical plane.

With these basic criteria, as well as the desire to have a low volume system, we decided to design and construct a microtube flow apparatus like that used by Mason and co-workers [23,24] in their suspension rheology work. The shear field is generated by vertical flow in a tube. To accurately approximate drop deformation in a locally uniform shear field, drop sizes considerably smaller than the tube diameter must be used. Then, if the radial position of the particle is known, and one assumes a parabolic profile, the local shear rate on the drop can be determined. For some time now, Mason and co-workers have used such methods interchangeably with Couette tests in studies of rigid particle and drop dynamics in shear fields.

Although the basic flow field is simple, the overall apparatus required for microtube tests is much more involved than the simple Couette system; this was the reason it was initially rejected in favor of the Couette system in our early tests. In Figure 2 we show a schematic diagram of the microtube apparatus which was recently constructed in this laboratory. In addition to the microtube chamber which holds the flow tube, the principal components are a precision micropump system and a 3-dimensional positioning stage. The micropump and the flow tube chamber are mounted on top of the stage with the tube located "under" the microscope (keep in mind that the tube is vertical). The stage is motorized for movement parallel to the axis of the

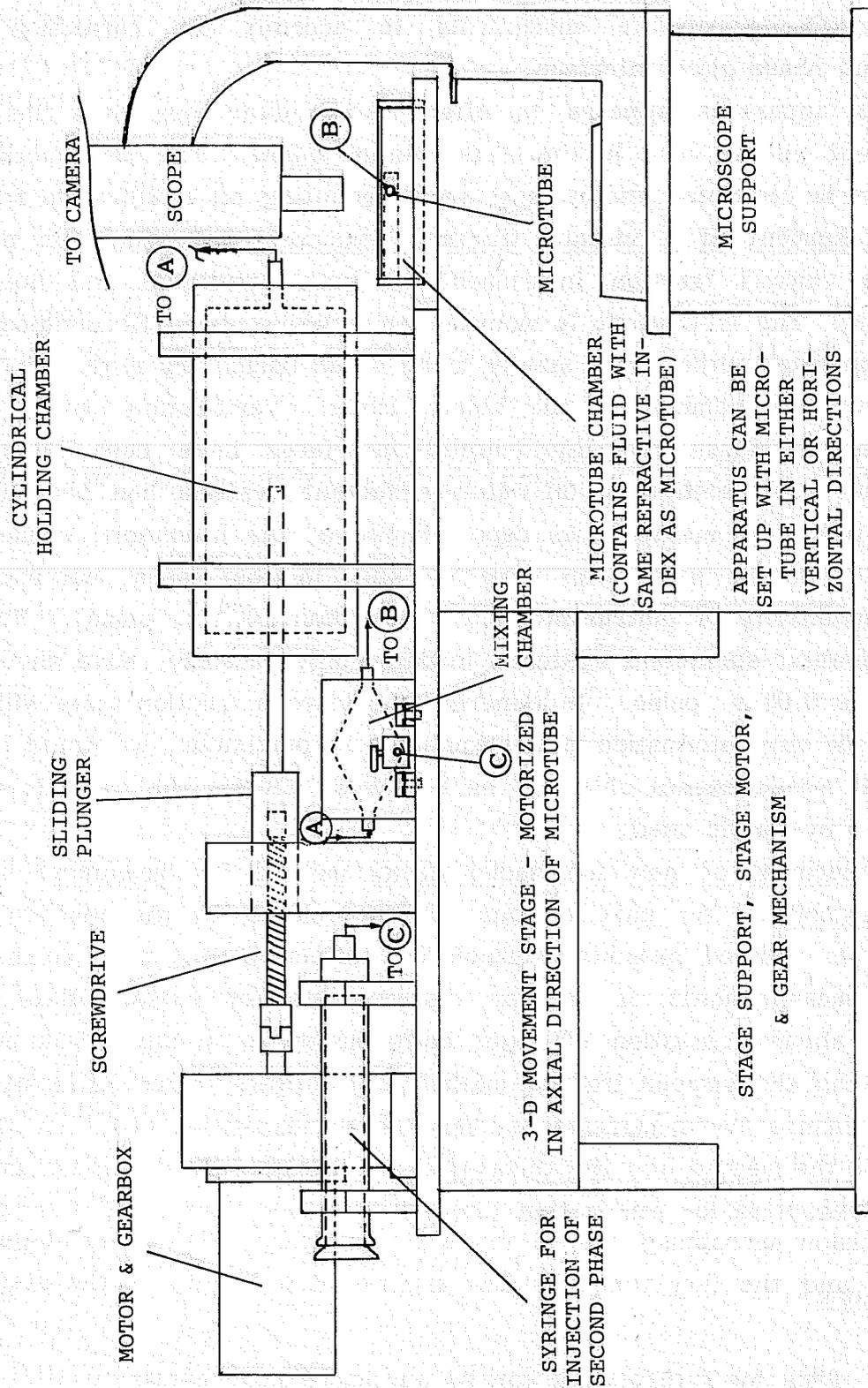


Figure 2. Schematic diagram of microtube flow apparatus

tube, and, hence, a drop can be held under the fixed microscope throughout an experiment by adjusting the stage speed to that of the drop, but in the opposite direction. The deformation and orientation is obtained from photographs with appropriate corrections to account for refraction at the continuous phase-glass interface.

This apparatus appears to offer many advantages over the Couette system and will be used in the tests planned below. The construction of the apparatus is complete, and it only needs mounting on a vibration free table.

4) Development of a viscous traction instrument. During this period we tested a viscous traction instrument on both gas-liquid and liquid-liquid interfaces. The instrument is mounted on a Weissenberg Rheogoniometer and can be operated either in a steady mode or an oscillatory mode; to date, our tests have been limited to the steady mode. Verification studies on both liquid-gas interfaces and liquid-liquid interfaces have been completed by Krieg [46], and testing of oil-water-surfactant systems has been underway for the past few months. As reported above, the interfacial viscosities for iso-octane systems have been very low and, in most cases, not measurable (below sensitivity of instrument, i.e., less than 10^{-4} s. poise). Tests with crude oil-water-surfactant systems, initiated only recently, have shown values as high as 0.05 s. poise. In general, the viscous traction tests will provide support for our deformation measurements. In particular, we would hope that consistent measurements of ϵ can be achieved between the methods when the same fluid system is used.

5) Development of new interfacial decay method for measuring interfacial shear viscosity. As part of our efforts related to the viscous traction method, we evolved possibly a simple but effective way of measuring ϵ . It involves measurements of angular displacements of surface fluid elements following abrupt cessation of rigid body motion in a cup. The method is simpler than the viscous traction method and appears to be sufficiently sensitive to measure low-to-moderate surface shear viscosities (10^{-4} -1 s. poise). Details of the method and the theoretical foundations are described in a paper recently submitted for publication [25].

Future Work

Our plans for future work can be summarized as follows:

- 1) Determination of interfacial viscosities for oil-water-surfactant systems

using the drop deformation and orientation tests in the microtube flow apparatus. In these tests we will be interested in testing systems with interfacial tensions in the range considered feasible for low tension flooding ($\sigma \sim 10^{-2}$ dynes/cm or lower). In our work, we plan to use the surfactants of the Sun Tech group. Screening tests are already underway to determine composition ranges to be considered. Since crude oils may exhibit significantly different dynamic interfacial properties than pure hydrocarbon "oils" such as iso-octane, we will initiate crude oil tests shortly after finishing the first series of iso-octane tests with a given surfactant system.

- 2) Verification measurements with viscous traction method. A few oil-water-surfactant systems will be tested with both the viscous traction method and the drop deformation-orientation method. The interfacial shear viscosities will be compared for verification of these independent methods. These samples will also be shared with the groups at Northwestern (J. C. Slattery) and IIT (D. T. Wasan). Hopefully, inter-laboratory verification will be possible. In the past we have carried on such comparisons with the group at Northwestern.
- 3) Extension of interfacial decay method to liquid-liquid systems. This should be a relatively straightforward theoretical exercise. We will simply alter the tangential stress boundary condition to include viscous effects from the top phase. Once this analysis is completed, we will carry out sensitivity calculations to determine proper operating conditions and geometry for the widest range of sensitive results. Following this, we will test the method in the laboratory on a liquid-gas system first, followed by one of the systems tested under (2) above.

Finally, we also plan to initiate experiments to measure the interfacial elasticity E_c . This quantity appears to be critically important to emulsion stability of crude oils [26-29], and should be important to the in situ displacement and coalescence phenomena associated with low tension flooding in porous media. We believe the pendant-drop retraction technique used by Reisberg and Doscher [6] offers several advantages over the Langmuir trough experiments, and, hence, will be used here. The basis of this technique will be an extension of the drop-weight method analysis of Pierson and Whitaker [30] to liquid-liquid systems.

ROLE OF DYNAMIC INTERFACIAL PROPERTIES IN OIL GANGLIA RECONNECTION AND DISPLACEMENT PROCESSES

Coalescence Studies

As noted previously, a necessary step in the formation of an oil bank is the reconnection of the mobilized ganglia. In the studies here, we are interested in such processes, and particularly, in the coalescence characteristics of oil-water-surfactant systems and the role played by the various interfacial and bulk phase effects.

The conventional view of the coalescence event between two droplets is that embodied in the film drainage model. This model assumes that the resistance to coalescence is related to the bulk and interfacial forces resisting the film drainage between the drops [30-35]. In Figure 3(a), we illustrate such a film drainage process; in 3(b) we show the typical time course of the film thickness δ . Initially, when the two drops are relatively far apart, δ changes very rapidly with time under the action of the coalescing force F . As the drop surfaces approach one another, the viscous and interfacial resistance forces associated with the film drainage increase and $d\delta/dt$ decreases. This continues to slow the rate of decrease of δ , as shown in 3(b), until a certain distance δ_c is reached, where either by hydrodynamic instabilities or molecular attraction forces, or both, the film suddenly collapses. If the molecular interactions are repelling, then $d\delta/dt \rightarrow 0$ and we can have a stable emulsion.

Now, a number of investigators have developed hydrodynamic models of the film drainage process. The works of Jones and Wilson [33], Reed et al. [34], Ivanov et al. [35, 36] and Barber and Hartland [37] represent some of the more recent contributions. The latter work is of particular importance to the studies here since dynamic interfacial properties are included in the analysis. Although Barber and Hartland present their results in integral form, one can analytically integrate their equations to obtain a relation between the coalescence time t_c and the applied force F , the effective contact radius R , the bulk viscosity of the film μ , the collapse distance δ_c , and the combination $\eta \equiv \kappa' + \varepsilon$ of the interfacial viscosity effects. The Barber and Hartland solution is represented graphically in Figure 4. Here we see that for a given force F , the coalescence time t_c is strongly dependent on contact

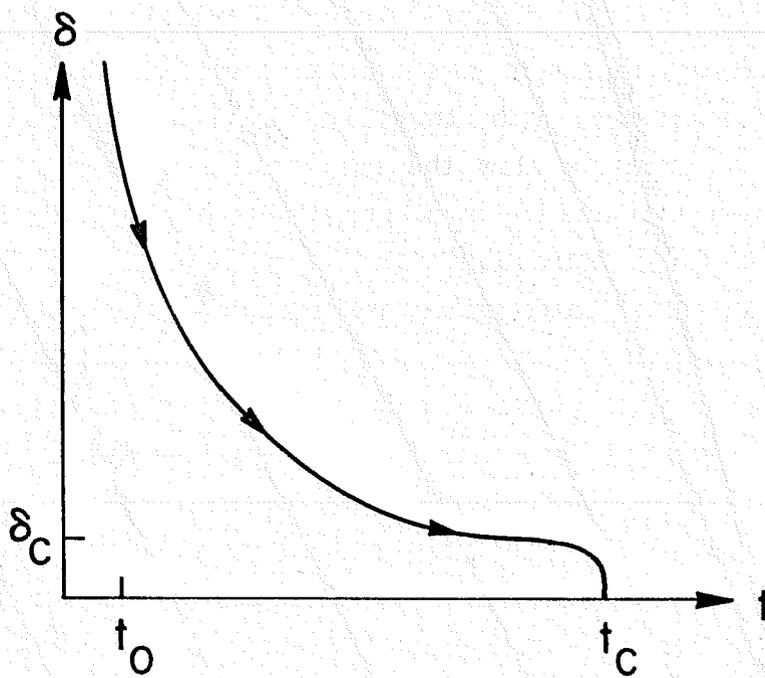
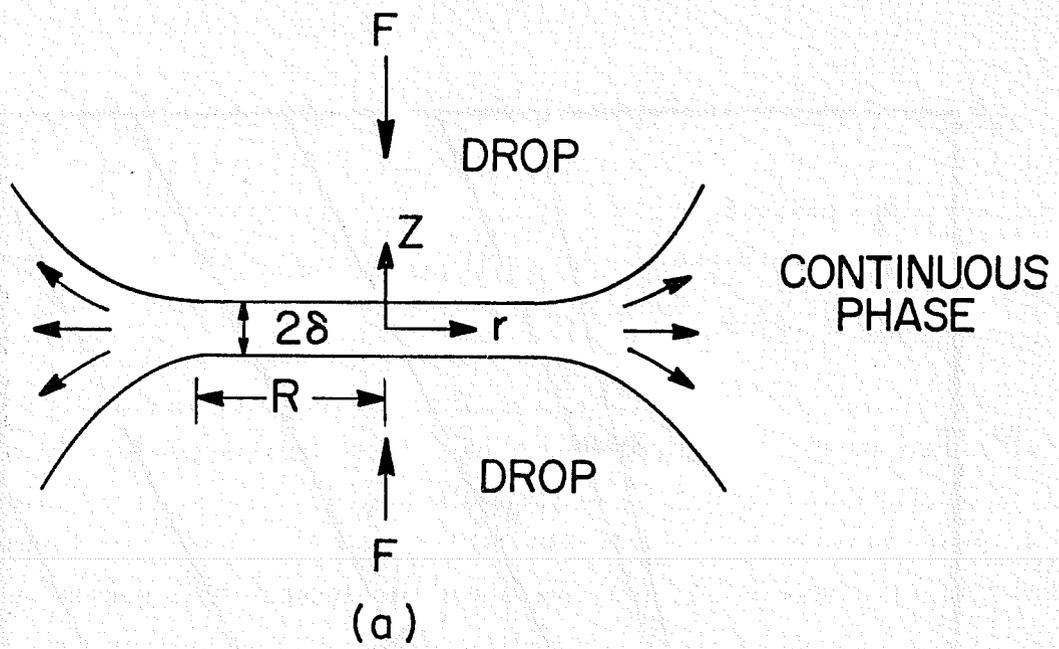


Figure 3. Film drainage model
of coalescence

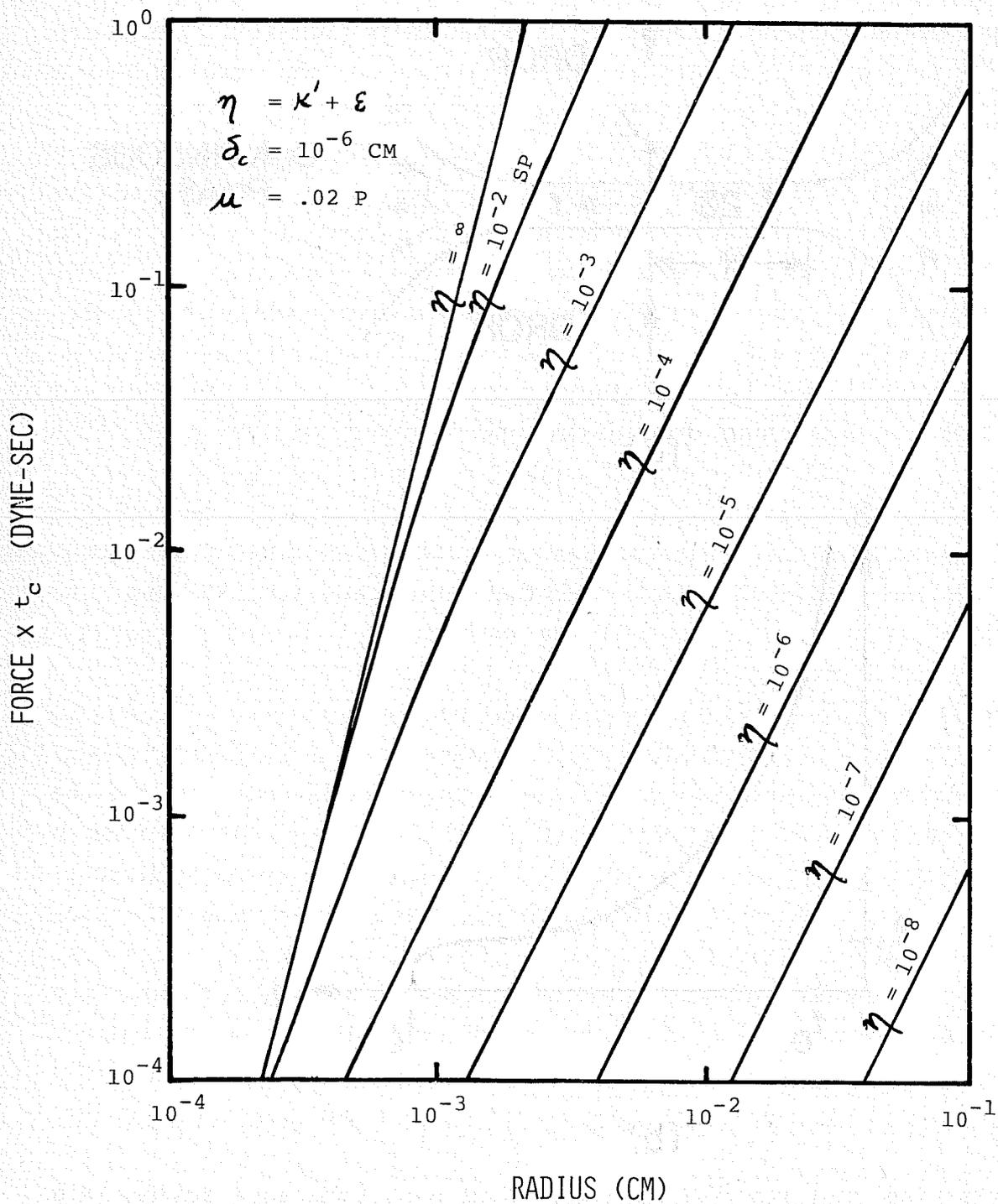


Figure 4. Predictions of Barber-Hartland theory.

radius R and the interfacial viscosity coefficient η . At large values of η , the film is rigid, and coalescence time is long (for a given R); at low values it is a mobile film, and the coalescence time is short. The interfacial tension enters the model through its effect on R .

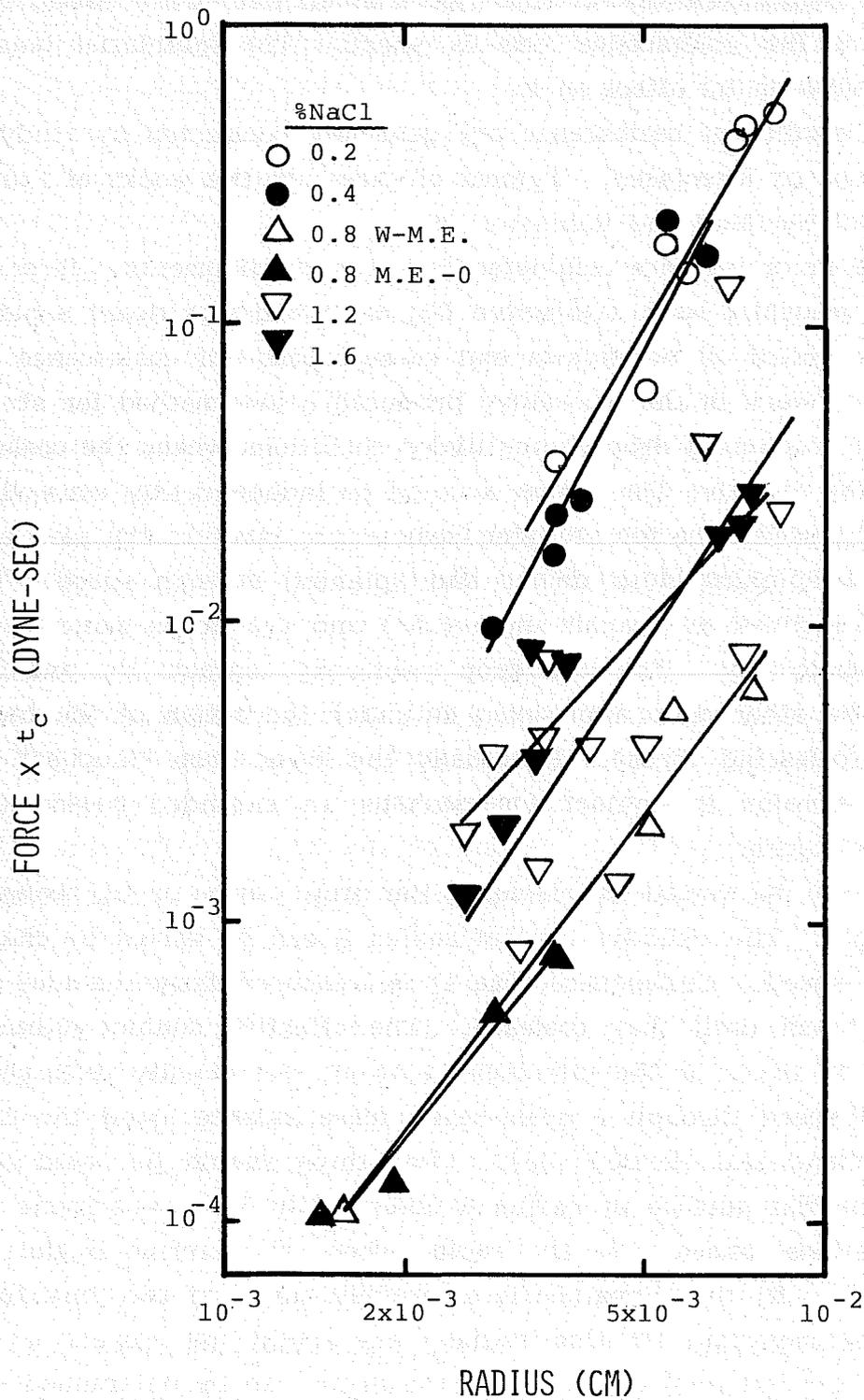
Experimental studies of coalescence are generally conducted by studying coalescence of drops at interfaces. Typical of these are the works of Burrill and Woods [38] and Hartland and Robinson [39].

Interest here in coalescence originated from two developments. First, in our porous media modeling work (Objective B), we noted significant negative consequences of residual oil breakdown and re-entrapment if coalescence did not occur. Second, work in the laboratory produced a new method for studying coalescence in a spinning drop device under conditions where the coalescing force F and the effective film radius R could be independently controlled.

The technique used here for studying coalescence involves the placement of two drops in a spinning drop device and spinning at high speed. The apparatus is then inclined at a small angle ($\sim 5^\circ$) and the drops move to the high end due to buoyancy. The lead drop eventually contacts the end wall and stops, and the other drop approaches it under the action of the buoyancy force (the coalescing force). Eventually the lower drop "touches" the upper drop and remains in contact for perhaps an extended period (t_c) before coalescence occurs.

The force F can be varied by changing the drop volume or by changing the inclination angle. The effective contact radius R can be varied by changing the rotational speed. Coalescence time t_c is measured from the time the drops appear to touch until they coalesce. The effective contact radius R can be predicted in terms of the interfacial tension, the density difference, and the rotational speed through a quasi-static force balance along the lines described by Hartland and Hartley [40]. (One thing should be noted here with respect to the flat surface of radius R observed in each experiment and the effect of rotational speed. In the region where the surface is flat (or nearly so), i.e., $r \leq R$, the curvature is essentially zero. If the centrifugal force effects were important in this region, one could not expect a flat surface.)

During the past year we have continued our coalescence studies with such an apparatus and have obtained coalescence data on several oil-water-surfactant systems. In Figure 5 we show data for an iso-octane/water/



44% ISO-OCTANE 44% WATER
 10% T-BUTANOL
 2% WITCO TRS 10-80

Figure 5. Coalescence results for an iso-octane/brine/surfactant system

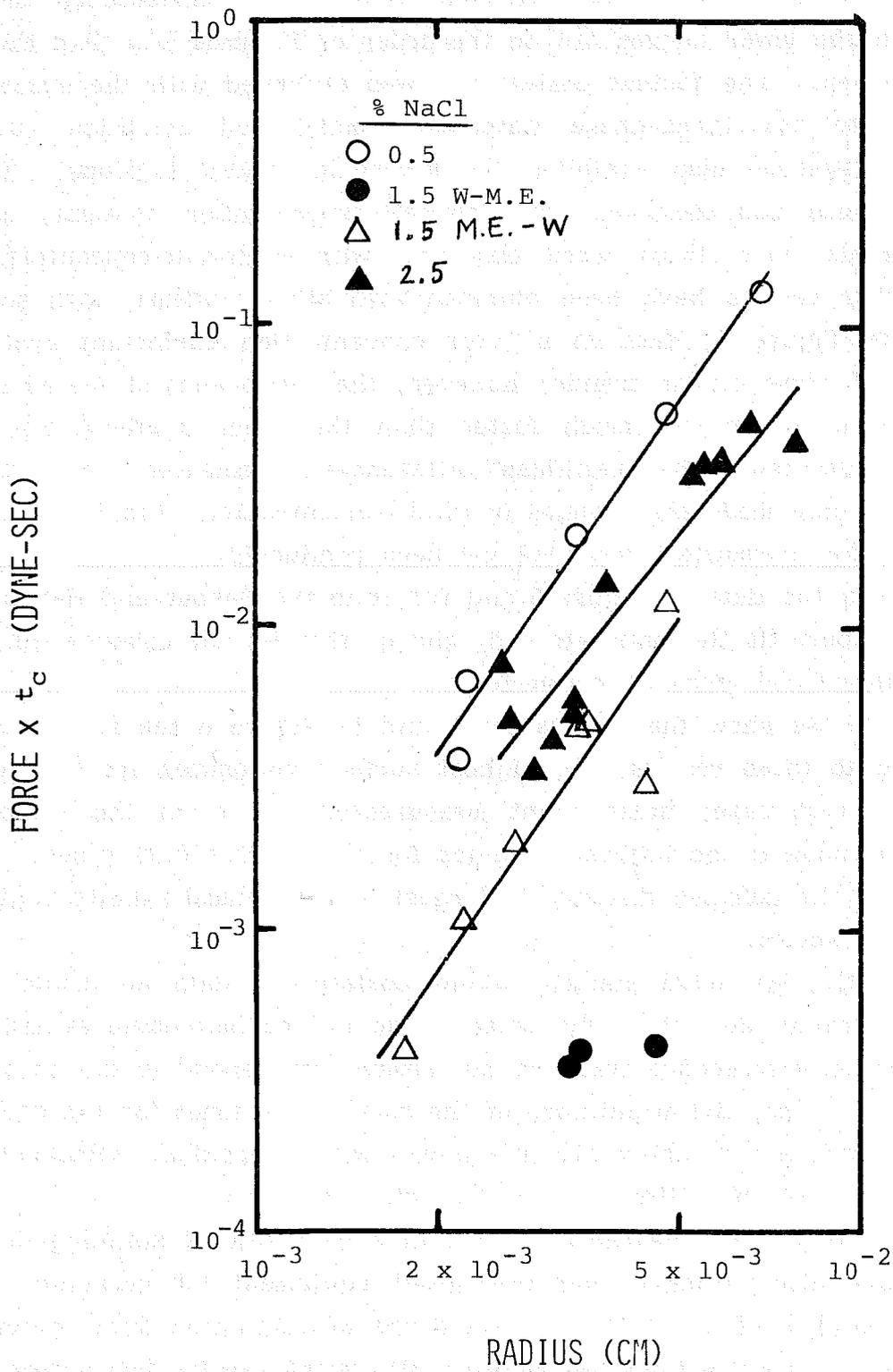
surfactant system at different salt concentrations. The coalescence times associated with the lower curves are on the order of 50 times less than those of the top curves. The fastest coalescence was observed with the systems corresponding to the three-phase water-microemulsion-oil condition (0.8% NaCl). These systems also exhibited the lowest interfacial tensions. The slowest coalescence was observed with low-salt-concentration systems, and intermediate coalescence times were observed with high-salt-concentration systems. Similar results have been obtained with other systems, with some exceptions. In Figure 6, data on a lower concentration surfactant system than in Figure 5 show similar trends; however, the coalescence of the microemulsion drops in water was much faster than the other systems. It is obvious from these results that significant differences in coalescence rates can be observed by only moderate changes in NaCl concentration. Studies of the effects of the other parameters have not yet been conducted.

If one takes the data in Figure 5 and fits it to the Barber and Hartland theory, we can best fit the parameters δ_c and η , that is, the collapse thickness and the interfacial viscosity parameter.

In Figure 7 we show the results for η and in Figure 8 the results for δ_c . According to these results, the highest surface viscosities are obtained in the NaCl = 1.2% case; independent measurements of ϵ on the viscous traction method showed the highest ϵ values for the NaCl = 0.8% cases. In Figure 8 we see the collapse distance is largest in the optimal salinity region for both systems shown.

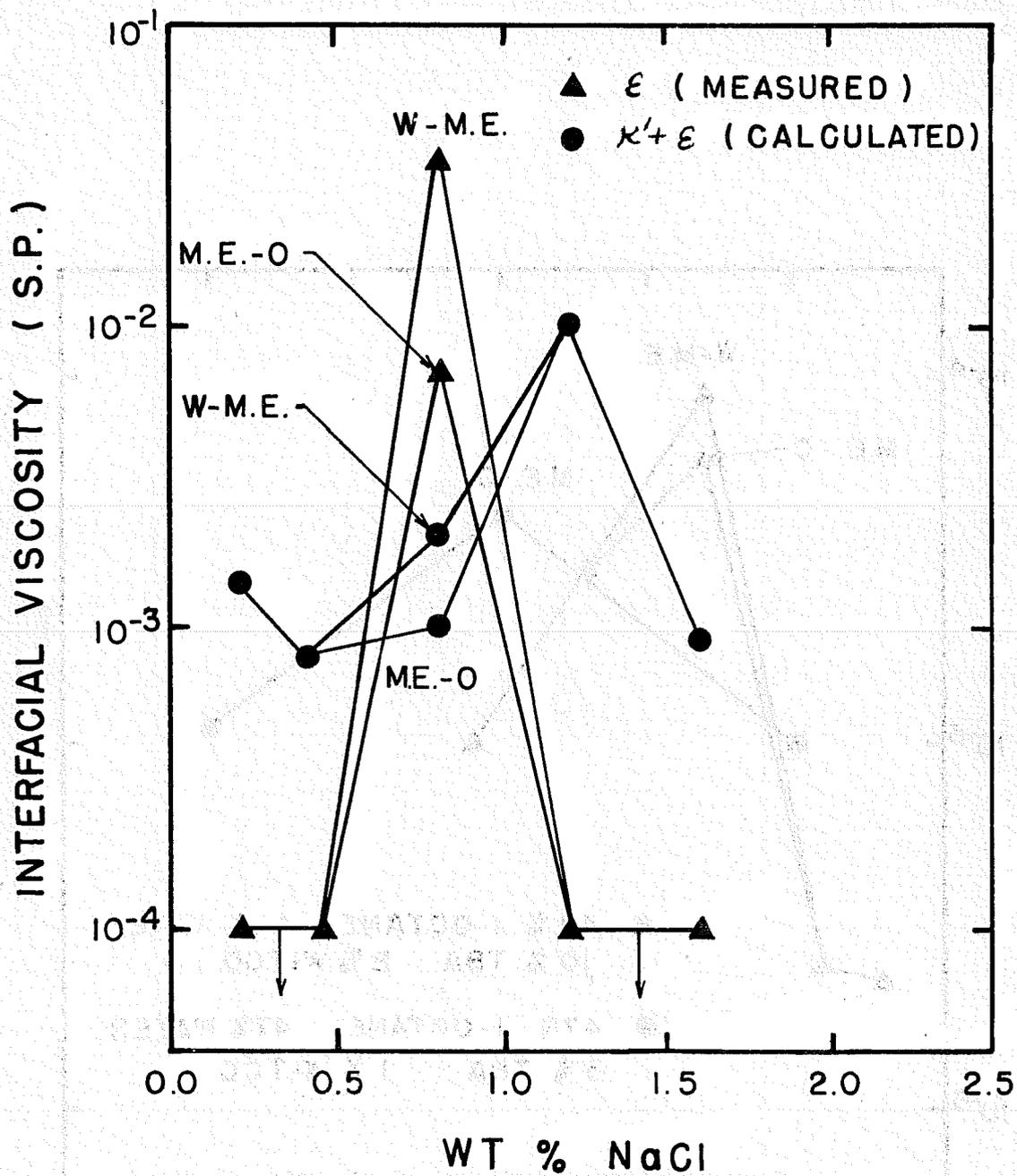
Only recently, we have started taking coalescence data on crude oil systems. The trends do not really match those of the iso-octane systems; that is, the lowest coalescence times do not always correspond to the optimal salinity systems. Also, the magnitudes of the coalescence times for the crude oils are at least one decade above similar systems with iso-octane. Obviously, crude oils are considerably different than iso-octane systems.

In addition to these coalescence studies in a conventional spinning drop device, we have also designed and purchased equipment for carrying out interferometry studies of the coalescence of drops in a spinning drop system. Using this system, the film thickness between the drops can be determined as a function of time. Through independent measurements of $\eta = \kappa' + \epsilon$ and δ , we can check the validity of the Barber-Hartland theory. Also, the mechanism of the film collapse can be studied, and this can provide a basis for more complete analyses of such processes.



47% ISO-OCTANE 47% WATER
 5% T-BUTANOL
 1% WITCO TRS 10-80

Figure 6. Coalescence results for an iso-octane-brine surfactant system



44 % 1-OCTANE 44 % WATER
 10 % T-BUTANOL
 2 % WITCO TRS 10-80

Figure 7. Comparison of measured ϵ values with $\kappa' + \epsilon$ values obtained indirectly from coalescence tests

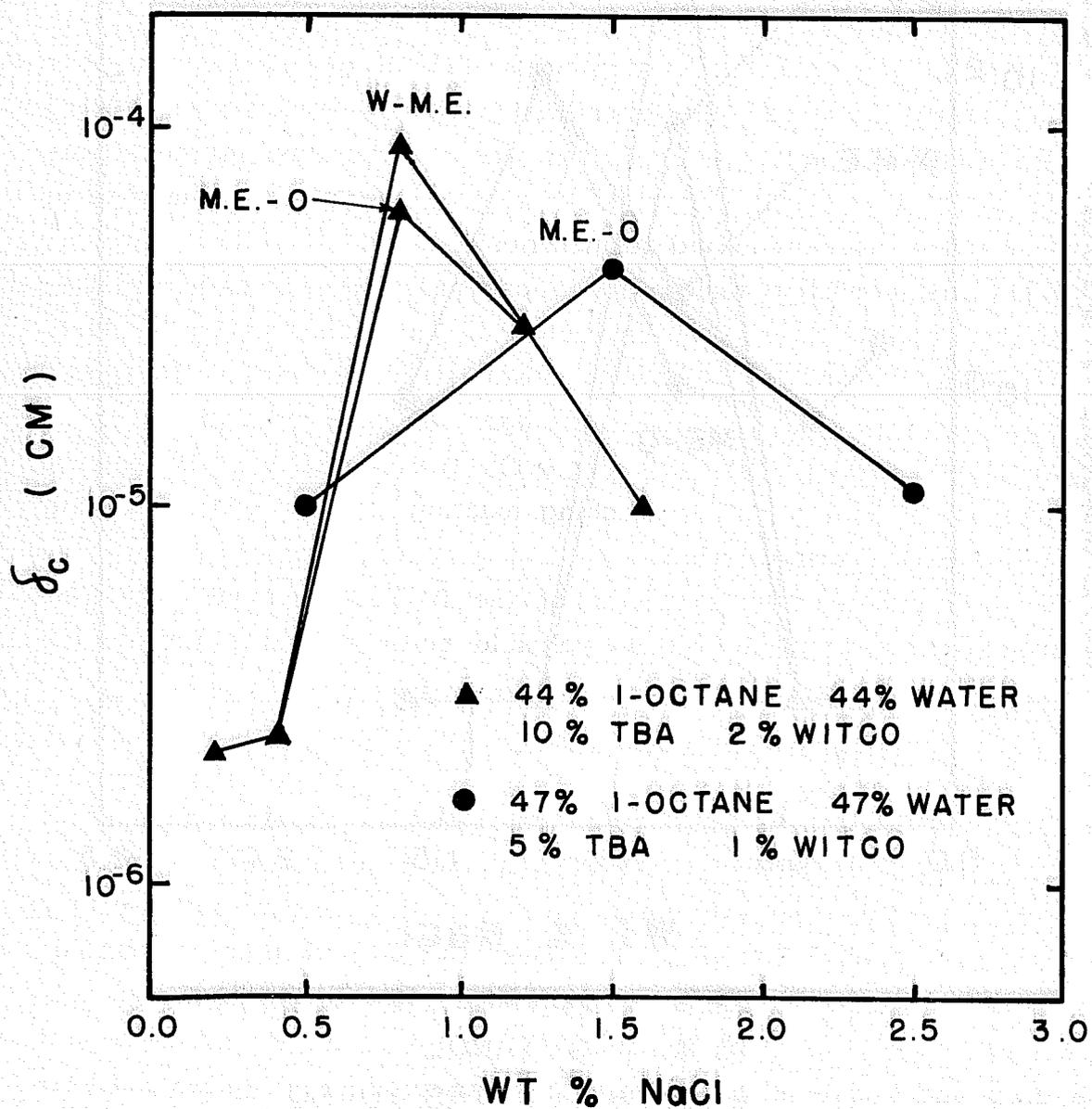


Figure 8. Critical collapse distance obtained from coalescence data and Barber & Hartland theory

Finally, on the theoretical side, a strategy has been developed for an extension of the Barber-Hartland theory to include the viscous effects of the drop phase. The preliminary results indicate the viscous effects of the drop are of secondary importance compared to film viscosity effects and interfacial effects.

Future Work

- 1) We will continue to study the coalescence behavior of oil-water-surfactant systems using the spinning drop coalescence method. We will coordinate the studies with similar studies of constituent effects previously described for interfacial viscosity measurements using the microtube flow apparatus. We will be interested in the effects of NaCl, surfactant, oil type, co-solvent, pH, and in the case of crude oils, asphaltene and resin content.
- 2) The interferometry coalescence apparatus will be constructed and data taken on a few well-characterized iso-octane systems. Tests on diluted crude oils will follow these iso-octane tests. The crude must be diluted so that sufficient light can pass through it. In all tests, we will measure $\delta = \delta(r, \theta, t)$, $R(\theta, t)$ and t_c . We will be particularly interested in checking existing theories and identifying collapse mechanisms.
- 3) We will complete the extension of the Barber-Hartland theory for viscous drops. This will be valuable because it will indicate the range of validity of the Barber-Hartland theory.

Displacement Tests

For some time now, we have been interested in the role of dynamic interfacial effects on the displacement mechanics of drops in small capillaries. To date, most of the work has focused on the displacement of iso-octane drops by water in 1 mm I.D. glass capillaries, and even though considerable effort has been expended to obtain reproducible results, the efforts to date have not been successful. We have conducted tests under both constant pressure drop and constant displacement rate conditions. Typical observations in the constant pressure drop experiments were: (1) mobilization at some applied pressure which could not be reproduced in followup experiments. (2) the movement of the drop at a non-uniform velocity along the tube, in some cases accelerating, then decelerating, and even stopping.

In an attempt to obtain more consistent data, we upgraded our cleaning methods, eventually evolving to a technique of placing the capillaries in an oven at elevated temperatures, passing oxygen through them and essentially burning clean the surface. We also placed the capillaries in a lathe and attempted to smooth the capillary walls by rotation and heating. These efforts improved the displacement observations somewhat, but consistent and reproducible data still could not be obtained.

We further carried out several tests under constant displacement conditions using the microtube apparatus. In these tests the drop interface was not uniform. In particular, the contact line at the wall was jagged, indicating either wall roughness effects or adsorbed impurities on the wall. Also, the movement of the contact line was not continuous and smooth, but somewhat episodic, even though the volumetric displacement rate was uniform.

In view of these difficulties, we are abandoning, at least temporarily, tests with aqueous systems. We have now switched to immiscible organic systems and will attempt to carry out constant pressure drop and constant displacement rate tests on pure systems first, followed by systems with surfactants. Although these will not be typical of the fluid systems encountered in surfactant flooding processes, they may allow fundamental observations relating to the role of dynamic interfacial effects in capillary displacement. Tests to date indicate that reproducible results are possible with such organic systems.

OIL GANGLIA POPULATION DYNAMICS DURING IMMISCIBLE DISPLACEMENT

Even though considerable effort has been devoted by several investigators to the study of the conditions under which a single oil ganglion can get mobilized, no attempt has been made, prior to the present project, to theoretically describe the fate of an oil ganglion, once mobilized. However, the fate of a mobilized oil ganglion and, much more importantly, the collective fate of a population of oil ganglia engulfed by a chemical flood, are problems of fundamental significance in understanding the formation of an oil bank and elucidating the mechanisms through which significant amounts of oil remain entrapped. Successful oil bank formation depends on the outcome of the competition between the process of oil ganglia deterioration through breakup and stranding on one hand, and the process of oil ganglia collision and coalescence on the other.

A problem related to that of oil bank formation and having, perhaps, even greater significance is that of attrition through shedding of large oil blobs from the trailing edge of the moving bank. Such blobs find themselves immersed in a deteriorated and probably incompetent part of the chemical flood, and, as they move, they continue breaking down into smaller ganglia, which gradually get stranded. Hence, in addition to the part of the oil-in-place that fails to be mobilized initially, a significant part of the mobilized oil is left behind by the moving oil bank in the form of a trail of stranded ganglia.

In order to describe mathematically the collective fate of oil ganglia populations, we have developed the following strategy:

- i. Formulate a porous media model which is suitable for the stochastic simulation of the fate of solitary oil ganglia (mobilization, breakup, stranding) as well as for the study of the dynamics of large populations of oil ganglia.
- ii. Develop a method to calculate probabilities for the mobilization, breakup and stranding of solitary oil ganglia.
- iii. Determine an expression for the average velocities of oil ganglia of different sizes.
- iv. Determine axial and lateral ganglion dispersion coefficients.
- v. Determine the probability of coalescence given a collision between two ganglia.

- vi. Develop ganglia population balances.
- vii. Integrate the ganglia population balances (the zeroth and first moments may suffice).
- viii. Produce charts showing the domains of conditions favorable and unfavorable to oil bank formation.

As discussed in the next section, steps (i), (ii), (iv) and (vi) have been completed for the case of unconsolidated granular porous media. Work is currently in progress on the remaining steps. Also, the generalization of this work to consolidated porous media is planned.

Work Accomplished To Date

Progress in this line of investigation was reported in Payatakes, Flumerfelt, and Ng [1-3]. A comprehensive summary of the most important results is given in two recent papers:

Payatakes, A. C., K. M. Ng and R. W. Flumerfelt, "Oil Ganglia Dynamics During Immiscible Displacement. Model Formulation," AICHE J. (submitted for publication), 1979.

Ng, K. M. and A. C. Payatakes, "Stochastic Simulation of the Motion, Breakup and Stranding of Oil-Ganglia in Water-Wet Granular Porous Media During Immiscible Displacement," AICHE J. (submitted for publication), 1979.

These papers can be obtained directly from the authors and can be consulted for details.

Here we simply list the main tasks already completed.

- A new model for unconsolidated granular porous media was formulated, which is suitable for the calculation of absolute and relative permeabilities, stochastic simulation of the fate of solitary oil ganglia and study of the dynamics of large ganglia populations.
- A new mobilization-breakup criterion was developed which takes into account the size, shape and orientation of the oil ganglion, the local topology of the porous medium, the contact angle, and the capillary number.
- A method for the stochastic simulation of the mobilization, breakup and stranding of solitary oil ganglia was developed.

- Hundreds of computer-aided stochastic realizations were performed for solitary ganglia of all sizes of interest moving in a 100 x 200 sandpack. These realizations show clearly that a solitary ganglion gets slenderized as it moves, and that either it gets restranded whole after a few rheons, or that it first breaks into two daughter ganglia, which eventually get stranded.
- A method was developed that enables calculation of the probability of mobilization, the probability of breakup per rheon and the probability of stranding per rheon. Such probabilities were calculated for a 100 x 200 sandpack and oil ganglia ranging in size from one to fifty-one pores, and were plotted versus capillary number. These probabilities are necessary for the prediction of the dynamics of oil bank formation and/or for attrition.
- The stranding coefficient, the breakup coefficient, and the breakup-mode probability were calculated, also for a 100 x 200 sandpack and various ganglia sizes, and were plotted versus capillary number.
- A system of two coupled integrodifferential equations were formulated which constitute ganglia-population balances; the first was for mobilized ganglia and the second for stranded ones. Expressions for the collision-coalescence kernels of these equations were also derived. Solution of these equations will delineate the conditions under which the original ganglia organize into fewer and larger ones through collision-coalescence (in which case we have favorable bank formation conditions), or rather they disintegrate into more numerous and smaller ones that rapidly become stranded (in which case we have conditions that are adverse to bank formation).

Future Work

Future activities will be focused on:

- 1) Experimental validation of the (already developed) immobilization-breakup criterion. Tests in random bead packs are planned.
- 2) Experimental determination of the average migration velocity of oil-ganglia and of the rheon-time distribution as functions of ganglion size, porous medium geometry and flood conditions. Development of dimensionless correlations based on the experimental data.

- 3) Solution of the (already developed) ganglia population balance equations and preparation of charts showing the domains of conditions favorable to oil bank formation and the domains of conditions unfavorable to bank formation but favorable to bank attrition.
- 4) Generalization of the (already developed) model for unconsolidated granular porous media to make it applicable to consolidated granular porous media.

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SUMMARY OF PROJECT ACTIVITIES - 1978-79

Personnel

Faculty: R. W. Flumerfelt (Professor, Chemical Engineering)
A. C. Payatakes (Associate Professor, Chemical Engineering)

Graduate Students: A. Catalano (MS, 1979)
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S. Lam (MS, 1979)
K. Ng (PhD, 1980)
S. Rapin (MS, 1980)
J. Woodham (MS, 1979)

Undergraduate: D. Carter (undergraduate research project, summer, 1978)
C. Blaney (lab technician)

Publications

Payatakes, A. C., Flumerfelt, R. W., and K. M. Ng, "Oil Ganglia Dynamics during Immiscible Displacement. Effects of Interfacial Properties," Proceedings, 4th DOE Symposium on Enhanced Oil and Gas Recovery, pp. B-5/1 to 25, Tulsa, Oklahoma, August, 1978.

Publications Submitted*

Flumerfelt, R. W., "Effects of Dynamic Interfacial Properties on Drop Deformation and Orientation in Shear and Extensional Flow Fields," submitted to J. Colloid Interface Sci. (1979).

Phillips, W., Graves, R., and R. W. Flumerfelt, "Effects of Dynamic Interfacial Properties on Drop Dynamics in Shear Fields: Role of Dynamic Interfacial Properties," submitted to J. Colloid Interface Sci. (1979).

Krieg, R., and R. W. Flumerfelt, "A New Method for Surface Shear Viscosity Measurements: Decay of Surface Motions at a Rotated Gas-Liquid Interface," submitted to J. Colloid Interface Sci. (1979).

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Payatakes, A. C., Ng, K. M., and R. W. Flumerfelt, "Oil Ganglia Dynamics During Immiscible Displacement," submitted to AIChE J. (1979).

*Copies can be obtained from principal investigators (RWF or ACP).

RESEARCH PRESENTATIONS

Flumerfelt, R. W., "Drop Dynamics in Dilute Suspensions: Dynamic Interfacial Effects," ACS Annual Meeting, Surface Chemistry Division, Anaheim, California, March, 1978.

Flumerfelt, R. W., Krieg, R., Tong, C-H, and A. Catalono, "Measurement of Dynamic Interfacial Properties of Oil-Water-Surfactant Systems and Their Effects on Droplet-Droplet Coalescence," 49th Annual Meeting, Society of Rheology, Houston, Texas, October, 1978.

Payatakes, A. C., Flumerfelt, R. W., and K. M. Ng, "On the Dynamics of Oil-Ganglia Populations During Immiscible Displacement," AIChE 84th National Meeting, Atlanta, Georgia, February, 1978.

Ng, K. M., and A. C. Payatakes, "On the Mobilization and Fate of Oil Ganglia during Immiscible Displacement," 49th Annual Meeting, Society of Rheology, Houston, Texas, October, 1978.

OTHER ACTIVITIES

We have established a weekly seminar program in which students, faculty, and industrial researchers present recent work relating to enhanced oil recovery. This has been quite successful, with participation of a number of people from local industry as well as faculty from Rice University. We plan to expand these activities during the coming year, hopefully with financial support from the University of Houston Energy Laboratory. This program can become a forum for local industrial-university interaction on EOR problems.

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