In "Surface Phenomena in Enhanced Oil Recovery", editor, D.O. Shah, Plenum Press, New York, NY. pp. 327-375, 1981.

POROUS MEDIA RHEOLOGY OF EMULSIONS IN TERTIARY OIL RECOVERY

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Emulsions containing 5 wt % TRS 10-410, 3 wt % isobutanol, sodium chloride (X %), water and equal volume of dodecane oil were prepared by sonication and by hand-shaking. The coalescence behavior of emulsions was studied for hand-shaken as well as sonicated systems. In general, sonicated emulsions required a longer time for phase separation as compared to hand-shaken systems. It was observed that for both the cases, the coalescence rate at room temperature (25°C) was maximum at the optimal salinity (1.5% NaCl) while interfacial tension was minimum at this salinity.

For the flow of emulsions through a sand pack at room temperature (25°C) the emulsions at most of the salinities studied exhibited a non-Newtonian behavior. However, at and near the optimal salinity the flow behavior was Newtonian. Moreover, the apparent viscosity of the emulsions in the porous media was minimum at the optimal salinity, hence it is proposed that ultra low interfacial tension causes minimum resistance to fluid flow and thus aids in the process of maximum oil recovery obtained at this optimal salinity.

Porous media studies of sonicated emulsions in a EM-Gel packed bed at 35°C formed with different aqueous to oil phase ratios for different salt concentrations indicate that pressure drop across the bed increases with an increase in the amount of the dispersed

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phase. Thus, for water-external macroemulsions the pressure drop increases with an increase in the amount of oil, while for oil-external macroemulsions pressure drop increases with an increase in the amount of water.

Sonicated emulsion results at 35°C as a function of phase ratio and salt concentration further show that the behavior of these emulsions in the porous media is different from those at 25°C. Even three phase systems give relatively more stable emulsions and possess non-Newtonian behavior. Hysteresis effect shown by some emulsions in porous media experiments is highlighted. The nature of emulsions produced by sonication and by the shearing of liquids in the porous media is contrasted. Extensive physical property data for these emulsions are also given. The applicability of Darcy's law for the present situation is discussed.

The results of our earlier investigation using spin-labelling technique to understand the structural aspects involved in the various emulsions, support the theory that water-external macroemulsions exist below optimal salinities and oil-external types exist beyond optimal salinity. In addition it was found that microemulsions coexisted with macroemulsions and were of the same type in the sonicated emulsions. These findings are further complemented by electrical conductance and bulk viscosity data.

INTRODUCTION

In tertiary oil recovery process, similar to primary and secondary recovery processes, one encounters problems associated with the formation of emulsions. Evidently such emulsions may either impede or accelerate the recovery depending on their physicochemical characteristics under given conditions. For example, if the formation of emulsion is considered adverse in operating the recovery scheme then selective methods of demulsification should be invoked.

A review of the literature shows very little mentioning of flow of emulsions through porous media. Some interesting observations favoring the presence of macroemulsion in the oil recovery process have been reported by McAuliffe (1). The ease with which emulsions flow at high pressure gradients was proposed by McAuliffe to be an advantage in the field applications because in a radial flow system the highest pressure decrease per unit distance occurs near the well-bore.

The unfavorable aspect of having an emulsion arises outside the reservoir conditions. Although it is well known that macroemulsions are thermodynamically unstable, the presence of multiple

surfactants in the flood can effectively prolong the emulsion stability to time periods of the order of weeks or months. The formation of such relatively stable emulsions has been identified by Boneau and Clampitt (2).

Lissant (3) in a recent review indicated that the occurrence of emulsion is a natural and all pervasive phenomenon in petroleum production and emulsions are to be avoided if possible. He further reported that a considerable amount of literature on the development of techniques for resolving emulsions can be found and that this technology should be taken into consideration when emulsification is deliberately employed to achieve additional oil recovery.

It appears from these investigations that we have two opposing effects in having macroemulsions in the oil recovery process--one a possibly favorable situation in the reservoir and the other an adverse effect off-the reservoir. The obvious questions to be posed are: (1) Can a compromise for having the emulsion considering the two effects in terms of its efficiency, be reached? (2) For a given surfactant formulation and conditions, how would one go about assessing emulsion formation and separation? (3) What is the influence of oil-external, water-external and middle phase microemulsions on the formation of macroemulsions and emulsion phase separation? (4) With an impure surfactant system such as TRS 10-410, can we characterize the macroemulsion containing oil, cosolvent and brine? (5) If a relatively stable macroemulsion is produced can one fundamentally investigate its flow behavior in a porous system with respect to pressure drop, permeability, shear degradation, droplet population, etc.?

With all these factors in mind, we have attempted to carry out the emulsions aspect of the investigations at the University of Florida Improved Oil Recovery Research Program (4,5). The emulsion systems contain TRS 10-410, isobutanol, sodium chloride, dodecane and water. Extensive physical property data and microstructural studies of the aqueous surfactant formulations have been already reported by Vijayan et al. (6). Also, the structural aspects of the emulsions containing the same species with aqueous to oil ratio of 1:1 as well as various physical property data as a function of salt concentration have been reported by Vijayan et al. (7). A detailed study of the middle phases formed by the same surfactant formulation with dodecane oil with respect to microstructural changes and microemulsion (swollen micelle) phase inversion has been reported by Ramachandran et al. (8).

With this background knowledge of the behavior of the aqueous surfactant formulations and 1:1, aqueous : oil emulsions and, middle phases as a function of sodium chloride content, the objectives of the present investigation are:

(1) to experimentally measure the physical properties of relatively stable emulsions of a specific surfactant formulation consisting of TRS 10-410 + isobutanol (5:3% W/W), sodium chloride (X%) + water and dodecane oil (Y%).

(2) to investigate the flow behavior of these emulsions in an unconsolidated sand pack and in an unconsolidated porous bed containing EM-Gel packing.

(3) to obtain the phase separation characteristics of various sonicated and hand-shaken emulsions by batch settling tests, and

(4) to correlate physical property data and structural state of emulsions with phase separation data, pressure drop results, shear rate effects and permeability factors.

The concentration of brine and aqueous to oil ratio are the variable parameters considered throughout the investigation.

EXPERIMENTAL

Chemicals: The surfactant formulation consisted of fixed amounts of the surfactant TRS 10-410, a petroleum sulfonate (5 wt %) and isobutanol (3 wt %) in brine solutions of different sodium chloride concentrations up to 8.0 wt %. The oil used was dodecane. Double distilled water with conductivity less than 2 μS/cm was used throughout the experiments. Dodecane oil was of technical grade (95 mole %) supplied by Phillips Petroleum Company (Lot N-919).

The petroleum sulfonate TRS 10-410 (~ 60% active) was obtained from Witco Chemical Company. Isobutanol (IBA) and sodium chloride were of high purity grade (> 99%) from Chemical Sample Company and Fisher Scientific, respectively.

Porous media: The following two porous media were employed in the present study. (1) A sand packed bed (400 mesh), (0.25 inch diameter and 2 inches long) with column made of stainless steel, and (2) a second porous media system with column made of stainless steel (0.25 inch diameter and 6 inches long and EM-Gel SI 2500Å packing material with particle size 0.063-0.125 mm). Mean pore diameter measured with a mercury porosimeter gave a value of 2800Å. The material was obtained from Merck, Cat. No. 9364, batch no. YE 94, 3949803.

Packing mode: dry packing
Porous media state: Unconsolidated porous bed

Porous media (1) was exclusively used for emulsions containing equal volumetric amounts of oil and aqueous phases and salt levels from 0 to 8.0 wt %.

Preparation of solutions: Aqueous solutions were prepared by dissolving 5% (W/W) of TRS 10-410 and 3% (W/W) isobutanol together with constant stirring. Desired concentration of sodium chloride in water was prepared separately and then known amounts of the surfactant mixture and the brine solution were mixed volumetrically. It should be noted that while the concentrations of surfactant and alcohol are expressed in percent weight based on total weight of aqueous phase, the concentration of sodium chloride is based on the total weight minus the weight of surfactant and alcohol.

Experimental set-up and procedure: Macroemulsions were produced by constant sonication for a period of about forty-five minutes in a thermostated bath at desired temperatures. Kinematic viscosity and specific conductance data of emulsions were obtained using standard Cannon-Fenske viscometer and conductivity meter, respectively. Bulk density and Screen factors of emulsions and equilibrated phases were determined by standard specific gravity bottles and screen viscometer, respectively. The interfacial tension values of oil/aqueous systems were measured by spinning drop technique. The details of measurement procedures are described elsewhere (4,5).

Porous media experiments: Flow experiments in sand-packed beds were carried out using 1:1, aqueous : oil emulsions at 25°C for salt concentrations of 0 to 8 wt %. Porous media experiments in EM-Gel-packed columns were done at 35°C for emulsions produced by several aqueous to oil ratios (4:1, 2:1, 1:1, 1:2, 1:4) and different salt concentrations varying from 1 to 3.5 wt %.

Procedure: Appropriate aqueous-oil systems were taken in glass bottles with a capacity of 150 ml and were placed in a thermostated bath. (The experimental set-up is shown in Figure 1.) Sonication was effected by an ultrasonic vibrator. Simultaneously, constant stirring was maintained by a magnetic stirrer system. The emulsion thus formed, was pumped from the bottle by a Constametric 1 HPLC Pump (Milton Roy Co., Serial No. 7804-03). The flow rate was accurately controlled by an in-built potentiometer setting. The pressure drop (against atmosphere) was measured using three pressure transducers (for higher accuracy in measurement) depending on the range of their calibration. Calibrations of 0-50 psi range, 0-100 psi range and 0-500 psi range were used. For a given emulsion, pressure drop was measured as a function of flow rate and the emulsion was recycled continuously.

During the experiment, five different columns were used so that the pressure drop of water, which was used as a standard for judging the condition of the regenerated bed, remained within reasonable limits of the pressure drop obtained for fresh beds. The procedure to fill the columns with the porous material was followed consistently.

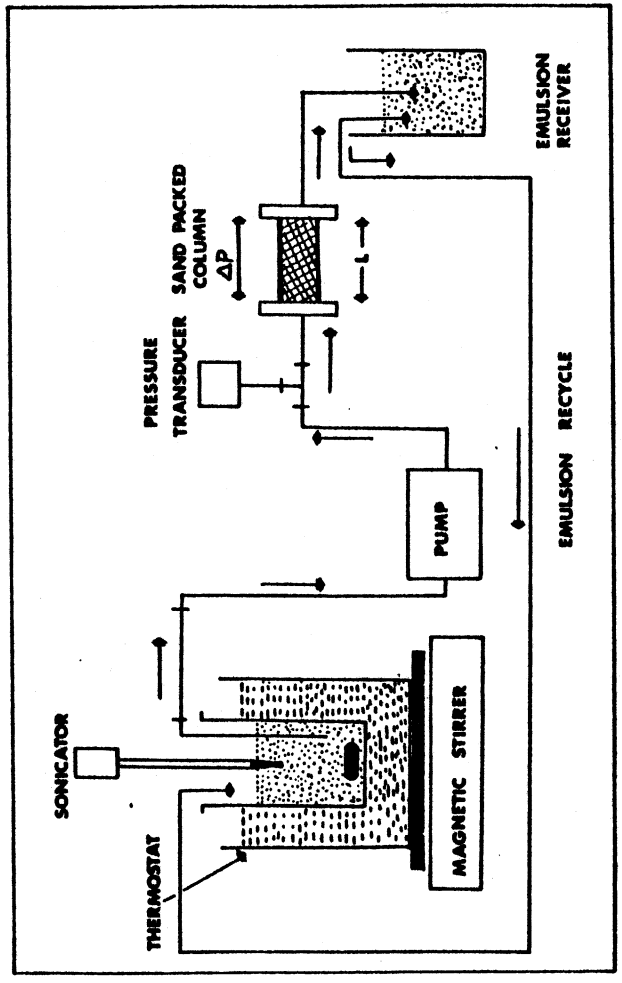

Fig. 1. Schematic flow diagram of laboratory emulsion flow through porous media studies.

It is obvious that the bed characteristics alter slightly once an emulsion is pumped through the bed. Regeneration was attempted by flushing the bed thoroughly with acetone and distilled water. In order to account for the variations in the bed behavior, if any, the following procedure was used:

Pressure drop of water (ΔP_{WM}) was measured and plotted as a function of flow rate for the regenerated bed. Then the pressure drop of the emulsion (ΔP_{EM}) was measured; and the values at the particular flow rate were normalized by dividing them by the ΔP_{WM} values, obtained from the experimental plot and at the corresponding flow rate (i.e. the ratio $\Delta P_{EM}/\Delta P_{WM}$ was thus obtained.) A generalized pressure drop (ΔP_{WG}) curve for water obtained by taking an average of about 30 calibrations was used to multiply the above mentioned ratio. This gave the normalized pressure drop of the emulsion (ΔP_E), that is, $\Delta P_E = [\frac{\Delta P_{EM}}{\Delta P_{WM}}](\Delta P_{WG})$.

Figure 2 is used as the generalized curve of the pressure drop of water (ΔP_{WG}) in the 6 inch long porous bed. Figure 3 illustrates typical pressure drop versus flow rate curves for water flowing through a 2 inch long sand-packed column after passage of various emulsions.

Our contention is that by using the above method, any permeability changes taking place due to the flow of the emulsions, can be accounted and therefore a meaningful comparison of the pressure drop results of different systems can be achieved.

Batch Settling Experiments for Hand-Shaken and Sonicated Emulsions for Oil to Aqueous Phase Volume Ratios of 1:1 and 2:1

Appropriate volumes of the aqueous formulation and dodecane oil were taken in 50 ml mixing cylinders. For hand-shaken experiments, the cylinders were hand-shaken for one minute and then the time required for complete separation was followed by noting the volume change of separated phase with time. Similar experiments were also carried out using sonicated emulsions at constant sonic power input of 30 watts for a period of 5 minutes.

The objective in these experiments was to collect separation-rate data for the various emulsions as a function of sodium chloride concentration. As the time taken for complete separation of sonicated emulsions containing low (less than 1 wt %) and high (greater than 2%) salt concentrations was in the order of days, we restricted our measurements to time taken for 50% phase separation.

Reproducibility check was made by using different batches of the same formulation. It was estimated that the data are reproducible within ± 5%. It should be emphasized that our primary aim

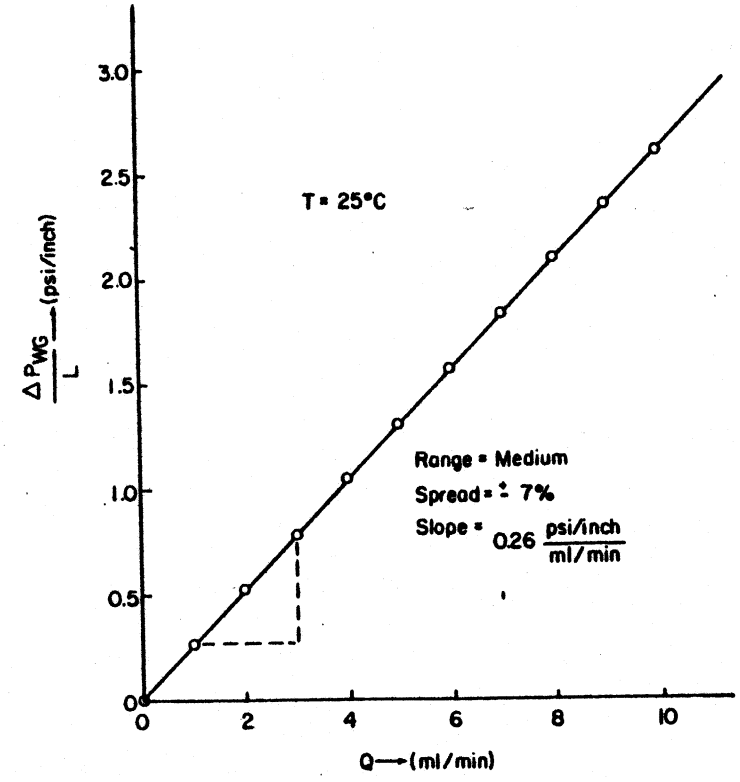

Fig. 2. Generalized curve for the pressure drop of water with flow rate.

was not to obtain accurate phase separation data, but to understand the relative ease with which the emulsions separate for several salt concentrations. Phase separation experiments were all carried out at room temperature (23 ± 1°C).

RESULTS AND DISCUSSION

1. Physical Properties

Density, viscosity and interfacial tension data of the equilibrated phases corresponding to an aqueous to oil ratio of 1:1 are presented in Table 1. Table 2 is the summary of the number of equilibrium phases present at 35°C for different aqueous to oil ratios and sodium chloride concentrations. It should be noted that the 1:1 system having 2% NaCl at 35°C represents a three phase system. However, at 25°C the same system gave only two phases. Upon prolonged storage (of the order of weeks) at 25°C, this system

Table 1. Physical property data at 30°C and property group controlling phase separation for conditions of negligible double layer (repulsive) and van der Waal (attractive) forces

NaCl Concn. (wt %)	Aqueous : Oil = 1 : 1						
	ρ_{aq} (g/ml)	ρ_{oil} (g/ml)	μ_{aq} (cp)	μ_{oil} (cp)	σ_i (dyne/cm)	$\frac{\sigma_i^2}{\mu_{aq} x \Delta\rho}$	$\frac{\sigma_i^2}{\mu_{oil} x \Delta\rho}$
0	0.9833	0.7410	1.26	1.2	0.422	57	60
0.5	0.9851	0.7410	1.21	1.24	0.105	3.7	3.6
1.0	0.9729	0.7422	2.33	1.26	0.0178	0.058	0.109
1.2	0.9612	0.7434	6.86	1.25	0.0056	0.002	0.011
1.5*	1.0018[1]	0.7417[1]	0.89	1.24	0.0008[2]	0.00028	0.0002
2.0*	1.0490[1]	0.7518[1]	0.96	--	0.0097[2]	0.033	--
3.5	1.0174	0.7664	0.84	2.77	0.083	3.26	0.99
6.0	1.0362	0.7581	0.83	1.56	0.243	25.7	13.6
8.0	1.0490	0.7664	0.93	1.72	0.39	57.8	31.3

*These systems have three equilibrium phases

1) For systems showing three phases ($\Delta\rho$) refers to maximum density difference in system.
2) Interfacial tension values refer to the lowest value in the three phase system. Here it is the value at the middle phase/oil interface.

Table 2. Equilibrium number of phases at 35°C for different aqueous to oil ratios and sodium chloride concentrations

NaCl Concn. (wt %)	Aqueous : Oil				
	4 : 1	2 : 1	1 : 1	1 : 2	1 : 4
1.0	2*	2	2	2	2
1.3	3*	3	3	2	2
1.4	3	3	3	3	2
1.5	3	3	3	3	3
1.6	3	3	3	3	3
1.8	3	3	3	3	3
2.0	3	3	3	3	3

*Numbers 2 and 3 indicate that the system has two and three equilibrium phases, respectively.

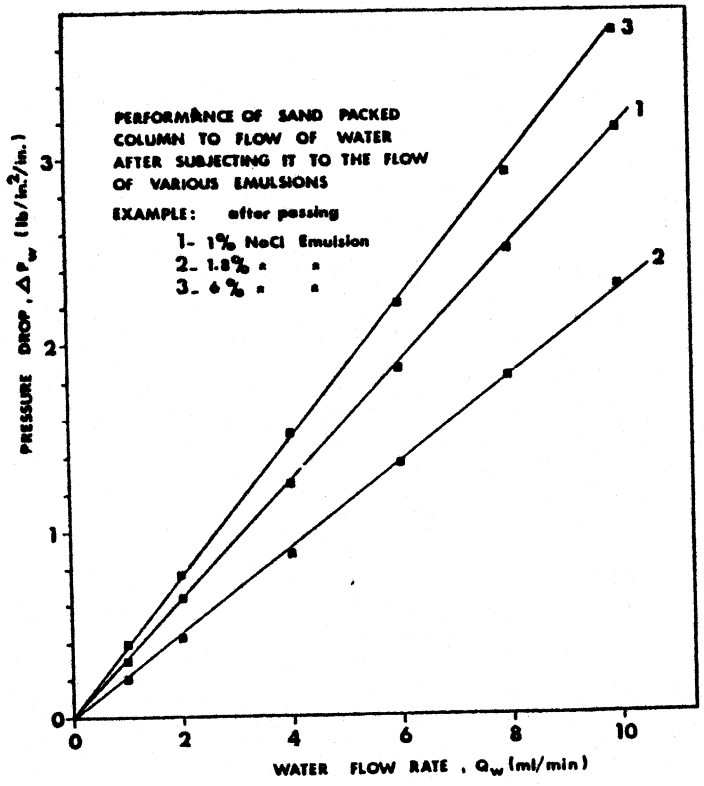

Fig. 3. Pressure drop vs. flow rate curves for water flowing through sand-packed column (1/4" diameter & 2" inch long) under various column conditions.

gradually produced three phases. Electrical conductivity and kinematic viscosity data of the 1:1 emulsions as a function of sodium chloride concentration are given in Figure 4. Extensive data of bulk density, absolute viscosity and electrical conductivity of the emulsions for various aqueous to oil ratios and sodium chloride concentrations are presented in Tables 3, 4 and 5, respectively.

a) Temperature effects: Figure 4 shows that electrical conductivity values of 1:1 emulsions are about 2000 μS/cm lower than those reported in Table 5 at low salinities (< 1.6 wt %) and similarly lower by about 400 μS/cm at 2% NaCl. Allowing for experimental errors, the differences in these two sets of data arise because of the 10°C difference in the temperature of measurements. Temperature effects can be further illustrated by considering the optimal salinity concentration, ease of formation of emulsion and equilibrium number of phases. Recent phase equilibria studies (8) have indicated that even 3.5% NaCl system with aqueous to oil ratio 1:1, separates out into three phases at room temperature. (Note

Table 3. Bulk density in g/ml of the sonicated emulsions at 35°C

NaCl Concn. (wt %)	Aqueous : Oil				
	4 : 1	2 : 1	1 : 1	1 : 2	1 : 4
1.0	0.9549	0.9150	0.8659	0.8292	-
1.5	0.9512	0.9147	0.8652	0.8253	-
1.6	0.9525	0.9183	0.8699	0.8262	-
2.0	-	-	-	0.8190	0.7824
3.5	0.9620	0.9229	0.8762	0.8299	0.7926

Table 4. Absolute viscosity (cp) of sonicated emulsions at 35°C

NaCl Concn. (wt %)	Aqueous : Oil				
	4 : 1	2 : 1	1 : 1	1 : 2	1 : 4
1.0	2	3	20.8	70.5	-
1.5	8.2	3.5	8.7	12	-
1.6	7.3	5.2	7.7	13.6	-
2.0	-	-	12.8	14.6	46.5
3.5	138	36	9.2	3.8	2.3

Table 5. *Specific electrical conductivity (μS/cm) of the sonicated macroemulsions at 35°C

NaCl Concn. (wt %)	Aqueous : Oil				
	4 : 1	2 : 1	1 : 1	1 : 2	1 : 4
1.0	13700	11300	8300	4700	< 1 μS/cm
1.3	18000	12600	8400	4900	"
1.4	18200	14000	8800	4700	"
1.5	18700	15000	9000	5500	"
1.6	19700	16000	10000	6100	"
1.8	590	740	530	485	"
2.0	400	430	620	700	"
3.5	500	15	< 1	< 1	< 1

*For values greater than 5000 μS/cm error is about 10%. For values less than 1000 μS/cm error is considerably greater. However, the order of magnitudes are highly reproducible in both cases.

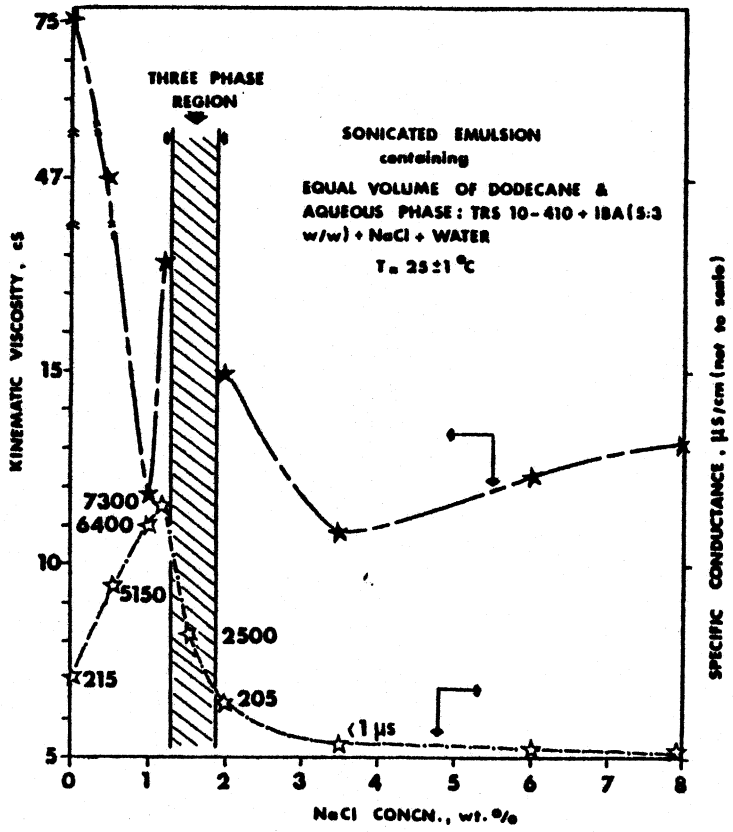

Fig. 4. Variation of kinematic viscosity and specific conductance of sonicated emulsions (aqueous : oil = 1:1) with NaCl concentration.

hat till now it was believed that the 1:1 system separates into wo phases at room temperature (25°C) for NaCl concentration reater than 1.9% at room temperature upon prolonged standing for eriods of the order of three to four weeks.) However, in recent xperiments we have found that the time necessary for the formation f three phases in these systems can be accelerated from 'weeks' o 'hours' by increasing the temperature from 25 to 45°C. Once a hree-phase was formed, lowering the temperature back to 25°C did ot alter the number of phases. When making sonicated emulsion at .5% NaCl with aqueous:oil, 1:1 we found that relatively stable mulsions could be produced at 35°C by prolonged sonication (about ne hour). However, sonication of the system at 25°C did not give ny emulsion at all. Evidently this experiment reveals the tempera- ure sensitivity of the emulsions. In the later discussions of ressure drop results of emulsions at 25°C and 35°C, we will fur- her elaborate the temperature effects. In the context of reservoir

temperature conditions where one would expect temperature variations up to 60-70°C, it can be expected that the problems associated with the formation of emulsions are unavoidable.

b) Effect of phase ratio and addition of salt: Interpretation of electrical conductivity and viscosity results (Figure 4) reported in Reference (7) together with microstructural studies using spin-labels for 1:1 emulsions at 25°C seem to favor the coexistence of water-external microemulsions (swollen micelles) and macroemulsions (O/W type) below the optimal salinity (~ 1.5% NaCl). However, above the optimal salinity, the results favor the coexistence of oil-external microemulsions and W/O type macroemulsions. Viscosity and conductivity results at 35°C given in Tables 4 and 5 as a function of aqueous to oil phase ratio and salt concentration show two distinct behavior with a transition occurring around 2 wt % NaCl. At and below 2 wt %, viscosity increases as aqueous to oil ratio decreases. Above this concentration, viscosity decreases drastically up to aqueous : oil ratio of 1:1 and thereafter decreases gradually. Emulsions containing 1% NaCl show an opposite trend, that is, viscosity gradually increases up to aqueous : oil ratio of 2:1 and suddenly increases thereafter. If we consider the viscosity variation as a function of salt concentration it appears that viscosity values of emulsions with aqueous to oil ratios of 1:4, 1:2 and 1:1 decreased with increase in salt concentration up to 1.6 wt %, gradually increases up to 2 wt % and decreases thereafter. As opposed to this, viscosity values of 2:1 and 4:1 emulsions increase gradually up to about 1.5 wt % NaCl and after passing through a local optimum at around 1.5 wt % NaCl, increase abruptly for further increase in salt concentrations. Electrical conductivity results of emulsions as a function of sodium chloride concentration (Table 5) at 35°C follow essentially the pattern shown in Figure 4 for 1:1 emulsions at 25°C. The only difference is that the salinity at which a maximum in the conductivity occurs is shifted from 1.2% (Figure 4) to 1.6% NaCl in Table 5 for all phase ratios. In terms of the variation of conductivity with decrease in aqueous to oil ratio, it can be readily seen that up to 1.6% NaCl and above 2%, conductivity values abruptly decrease when aqueous to oil ratio is decreased. A transition appears to exist in the 1.8 - 2.0% NaCl region. Regarding the state of emulsion with respect to the effect of addition of salt it is evident that up to 1.6% NaCl the emulsions are of water-in-oil type for all phase ratios studied. Above 2% NaCl, a decrease in conductivity results show the presence of oil-in-water type emulsions for all phase ratios. The state of emulsion in the transition region (2.0% > [NaCl] > 1.6%) is not clearly understood presently.

Although the presence of higher volume percent of aqueous phase is expected to produce oil-in-water emulsions, such a conclusion is not obvious in the present situation because of the interfering effect of sodium chloride. The viscosity and electrical conductance behavior of 4:1 (aqueous:oil) and 2:1 emulsions present

some interesting problems: The magnitude and the relative increase in the viscosity values with the addition of sodium chloride tend to favor the existence of oil-in-water emulsions. However, the conductivity values do not seem to support this deduction. With this uncertainty, in the absence of other relevant data, it can be speculated that the abrupt increase in the viscosity values could at best be the result of a drastic reduction in the emulsion droplet size.

2. Batch Settling Tests

a) Hand-shaken emulsions of 1:1 aqueous:oil system at 25°C: Typical batch settling curves for the emulsions at 25°C as a function of concentration, are shown in Figure 5. Four major differences in the emulsion behavior with respect to salt concentration were observed. There were two types of emulsions where the first phase boundary leading to phase separation was formed after a certain time. We have designated this time as the "initial time taken for the formation of an observable phase boundary" (ITFOPB). The four types are:

I. Gradual phase separation with time with ITFOPB of the order of 5 to 15 minutes.

II. Gradual phase separation with ITFOPB of the order of 1 to 3 hours.

III. Gradual phase separation leading to "creaming" of emulsion.

IV. Rapid phase separation.

Sodium chloride concentrations in the emulsions falling under the above types are:

Type I. [NaCl] = 1.2% [ITFOPB = 10 min.],
2% [ITFOPB = 5 min.], 3.5% [ITFOPB = 15 min.],
6% [ITFOPB = 5 min.],

Type II. [NaCl] = 1% [ITFOPB = 3 hrs.],
8% [ITFOPB = 1 hr.].

Type III. [NaCl] = 0 and 0.5%

Type IV. [NaCl] = 1.5%

With Type I emulsions, the volume versus time curves (Figure 5) are S-shaped. In the case of Type III emulsions it should be emphasized that although the time taken for 50% phase separation is lower than that of the emulsion containing 1% NaCl, in fact, "creaming" of these emulsions takes place approximately after 50% phase separation. As observed in the systems without isobutanol (see ref. 4), "creaming" gives rise to a "denser white texture"

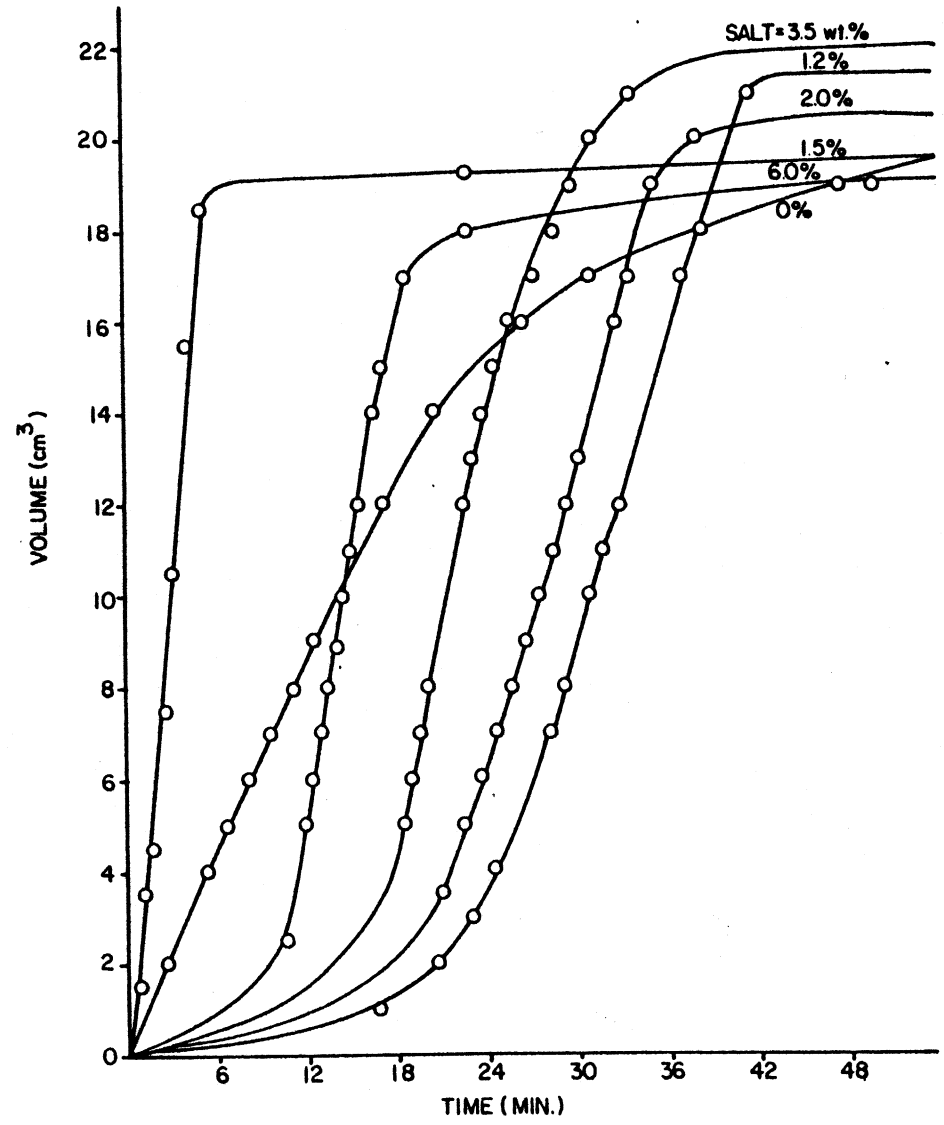

Fig. 5. Batch settling curves for TRS 10-410 (5%) + IBA (3%) + NaCl (varying wt %) + equal volume of dodecane.

near the phase boundary and also gives a greater stability to the emulsion in the batch settling test. Taking this effect into consideration the total time taken for complete phase separation of these emulsions would be very large.

Characteristic Phase Separation Behavior of Emulsions at Optimal Salinity

Type IV system yields three phases after complete phase separation. That is, when the emulsion is being separated, movement of two boundaries can be observed. The results are shown in Figure 6. It is evident from the figure that both the boundaries move at almost identical rates.

Recalling the observation (Table 1) concerning the occurrence of low and almost the same interfacial tension values between the middle phase/oil and the middle phase/aqueous phase systems, we were interested in the study of the phase separation behavior of these two phase systems. Therefore, three different combinations of "two phase systems" out of one three phase system were made by selectively deleting the third phase (Figure 6). Macroemulsions were produced as described in the experimental section.

It is interesting to note that the phase separation behavior of all of the three combinations is nearly the same. The behavior of the oil/middle phase emulsion is similar to that of the three phase system. Likewise, the two emulsion systems constituting oil/aqueous and middle phase/aqueous phase appear to behave identically within the experimental error.

Macroscopically, the important observation is the occurrence of rapid separation of the emulsion at optimal salinity in comparison with that of other emulsions. This effect is best illustrated in Figures 6 and 7. When one considers the time taken for 50% phase separation, the time at which an abrupt change in slope of the volume versus time curve occurs and the reciprocal separation rate with NaCl concentrations as criteria, three pronounced anomalies are obvious:

1) a maximum at 1% NaCl
2) a pronounced minimum at 1.5% NaCl and
3) a local minimum at 6% NaCl

Alternatively, if the total time taken for complete separation of these emulsions is considered, then we are left with the anomalies (2) and (3). Anomaly (1) drops out because of creaming effects.

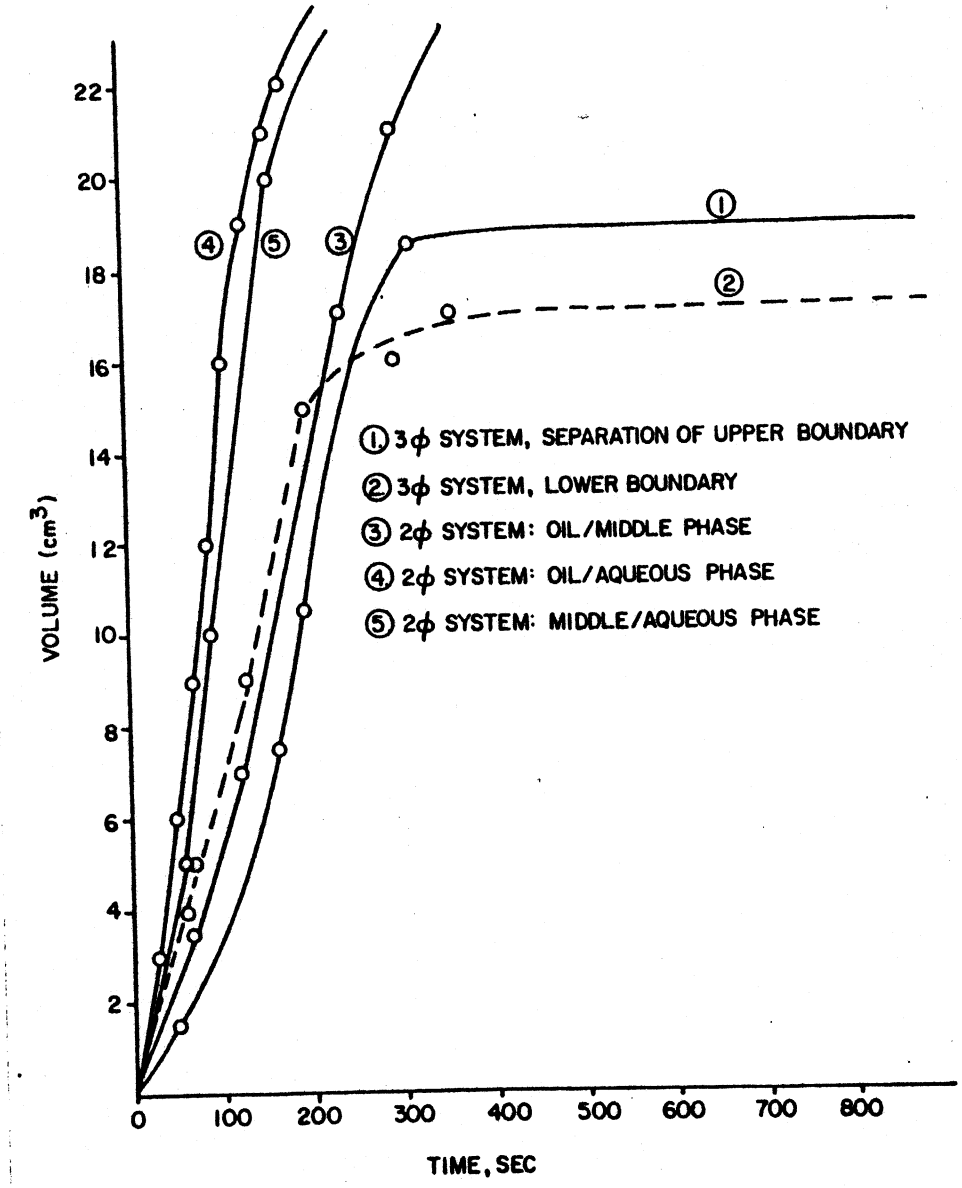

Fig. 6. Batch settling curves for 1.5% NaCl + TRS 10-410 (5%) + IBA (3%) three phase system with dodecane.

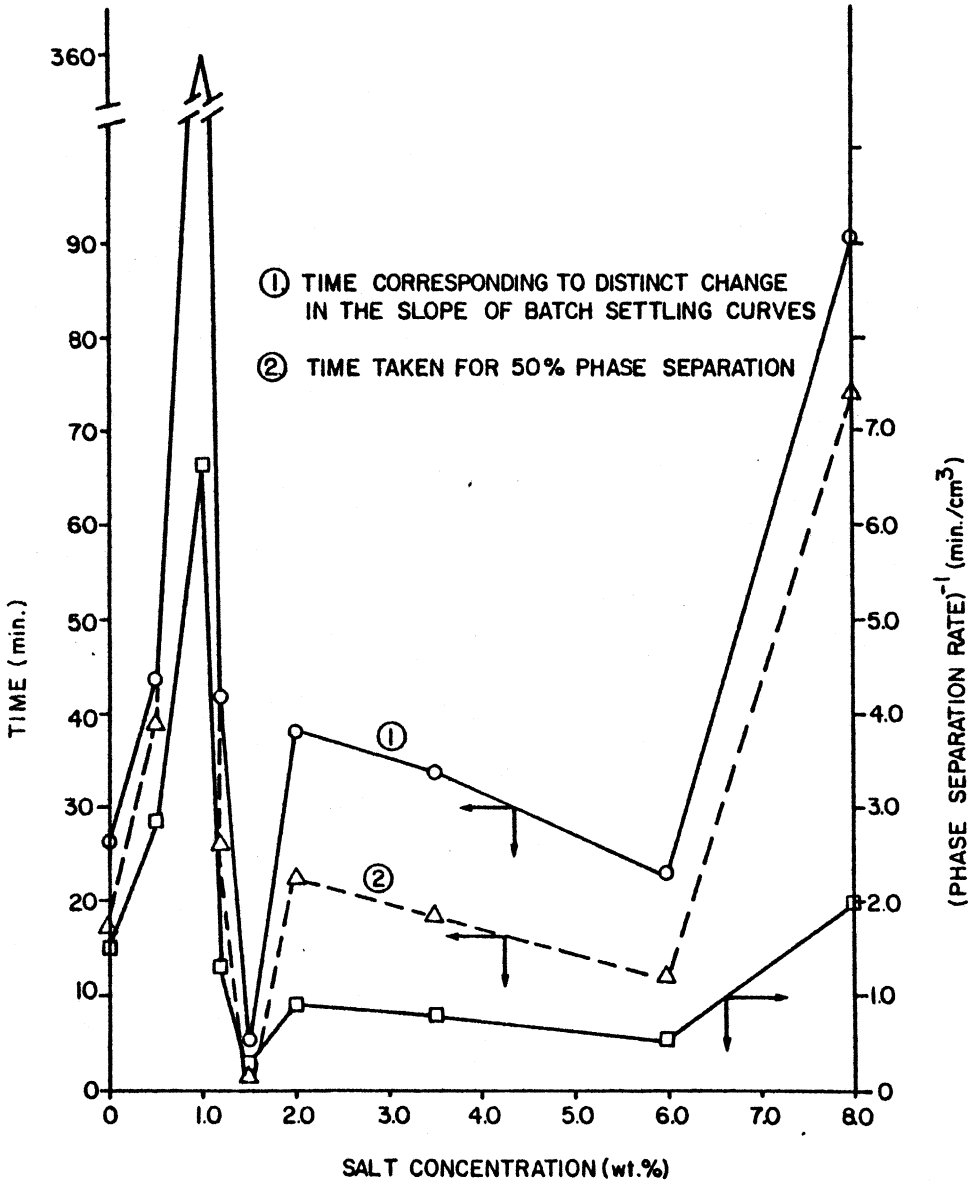

Fig. 7. Comparison of phase separation data

Drop stability: It is well known that the phase separation of the emulsions is controlled by the factors which influence the coalescence of drops. Therefore, we will now attempt to apply the developed Theory of Coalescence to the present situation.

Although the stability of emulsions containing micron-size droplets has been studied using a variety of emulsions in the past no unified and quantitative approach based on the physico-chemical properties of the system has been achieved. Obviously, this lack of understanding can be attributed to the complexity of the systems which invariably contain several species. A substantial contribution to the factors affecting emulsion stability has been made by Boyd et al. (9) using Spans or Tweens with Nujol and water. Some aspects of energy barriers associated with emulsion stability have been considered by several authors. The details can be found in the reference, Davies and Rideal (10). We will consider the electrical barrier-effects encountered with the oil-water and water-oil emulsion systems in a later section.

For the prediction of emulsion stability conditions, it is necessary to have some criteria in terms of the measurable quantities. Evidently, the role of equilibrium physical properties of the system would give some insight into the understanding of the operative mechanisms causing stability. Although a large amount of literature exists depicting this aspect, no satisfactory generalization can be made presently.

For illustrative purposes, we will now consider the role of interfacial tension on the stability of emulsions. A majority of researchers [Bickerman (11)] agreed that since emulsions possess very high interfacial area when the interfacial tension is reduced one expects an increased emulsion stability. Adamson (12) stated, "interfacial tension criterion is unassailable. It is also relatively useless except for qualitative arguments."

Yasukatsu Tamai et al. (13) showed that both the oil separation curve and the interfacial tension (σ_i) curve have a minimum at the same value of HLB. In the case of blended emulsifiers, they did not observe any marked minimum and, at the same time the rate curves also showed no minimum. They indicated that emulsion stability is indeed ruled by many factors but interfacial tension should be one of them and appears to be a useful measure of getting a stable emulsion. They suggested that low tension means energetically a stable interface and consequently may represent a stable structure of the adsorbed emulsifier at the interface.

Davis et al. (14) studied the stability of fluorocarbon emulsions. They reported that although coalescence times are expected to decrease with increased interfacial tension their results for the perfluorinated oils did not support any such trend.

Having realized the complexity of micrometer-droplet systems and the lack of reported literature dealing with the modeling of such systems we thought it would be interesting to see as to how the fluid properties would influence liquid/liquid dispersions containing larger drops of the order of 1 mm diameter or greater. It is interesting to note that a considerable amount of information is available with regards to the fluid dynamic behavior of droplets. In view of the many similarities that exist between micrometer and millimeter size droplets we believe that the "film drainage" concept developed for millimeter droplets can be equally applied to the case of micron droplet dispersions.

In the past, investigations involving the phenomenon of coalescence have been largely concerned with the study of single droplets resting on plane liquid/liquid interfaces. The main objective was to ascertain the influence of various physical parameters on this process. In the earlier works, experiments were directed mainly towards measuring the rest-time of drops. Although rest-time is a measure characterizing the drop residence and hence the coalescence behavior of the drop at a liquid/liquid interface, the direct factor which controls the coalescence step has been considered to be of hydrodynamic origin, namely "film thinning". Much attention was focused on this problem with the result that investigations were extended so that instead of measuring the rest-time, the variations of film thickness during thinning were determined. Extensive details of this process for a number of systems have been reported by many researchers, for example, Jeffreys and Davies (15), Woods and Burrill (16), Vijayan and Ponter (17,18).

It should be emphasized here that all of the earlier-developed models and experiments have been limited to systems containing low surfactant concentrations (below the CMC) and for droplet sizes of about 1 mm diameter or greater. We would like to restate some of the major assumptions in these models and will use them as the basis for extending the models to micron-size dense dispersions (or emulsions) containing high concentrations of one or more surfactants and electrolytes.

The major assumptions are:

(1) The effects due to electrical double-layer repulsion forces, electroviscous effects and the physical presence of adsorbed film are neglected.

(2) Effects due to attractive forces of molecular origin are assumed to be negligible.

(3) All external body forces are absent except for buoyancy (or gravity) force.

(4) Among surface forces, only surface (or interfacial) tension contribution is included. Other probable effects arising from surface rheological parameters are neglected.

Following the suggestions of various authors (19), we will now examine the influence of viscosity ratio of phases, density difference and interfacial tension values.

Drop size and density difference between phases: It is known that the size of drops and the difference in density between the oil and water phases determine the force which a drop exerts on an interface. The greater the force pushing a drop against an interface, the shorter the lifetime of the drop. Generally, large differences in density give rise to deformation of the drop. Thus the drop tends to flatten and the area of the draining film is increased. But at the same time the hydrostatic force causing drainage does not increase proportionately. In fact it was confirmed by many earlier workers that the rest-time increased with increase in the density difference between the phases.

Viscosity ratio of the phases: An increase in the viscosity of the continuous phase relative to the drop phase increases the rest-time as would be expected because the resistance to drainage of the film is increased.

Interfacial tension: A high interfacial tension results in the drop resisting deformation so that the area of the drainage film will tend to decrease as the interfacial tension increases. Thus coalescence time tends to decrease with increase in the interfacial tension. However, increase in interfacial tension also tends to inhibit the flow of film itself. Thus, here again the physical property produces two opposing effects. In general, however, coalescence time decreases with increase in interfacial tension.

Application of the theory of coalescence to the observed phase separation anomalies: For the "even mode of drainage" of the liquid film separating the drop from another drop or from an interface, several models have predicted a physical property group as the controlling group in addition to functions characterizing the drop dimensions and the rupture film thickness.

As a first approximation let us now assume (1) the average drop diameter in the emulsions to be a constant and (2) the magnitude of rupture film thickness to be a constant throughout the NaCl concentration range. Based on these assumptions let us see whether this physical property group ($\sigma_i^2/\mu_c\Delta\rho$) would adequately explain the anomalous phase separation behavior at 1.5% and 6% NaCl concentrations. This group was evaluated using the physical property data given in Table 1. The results are presented in Figure 8. It is

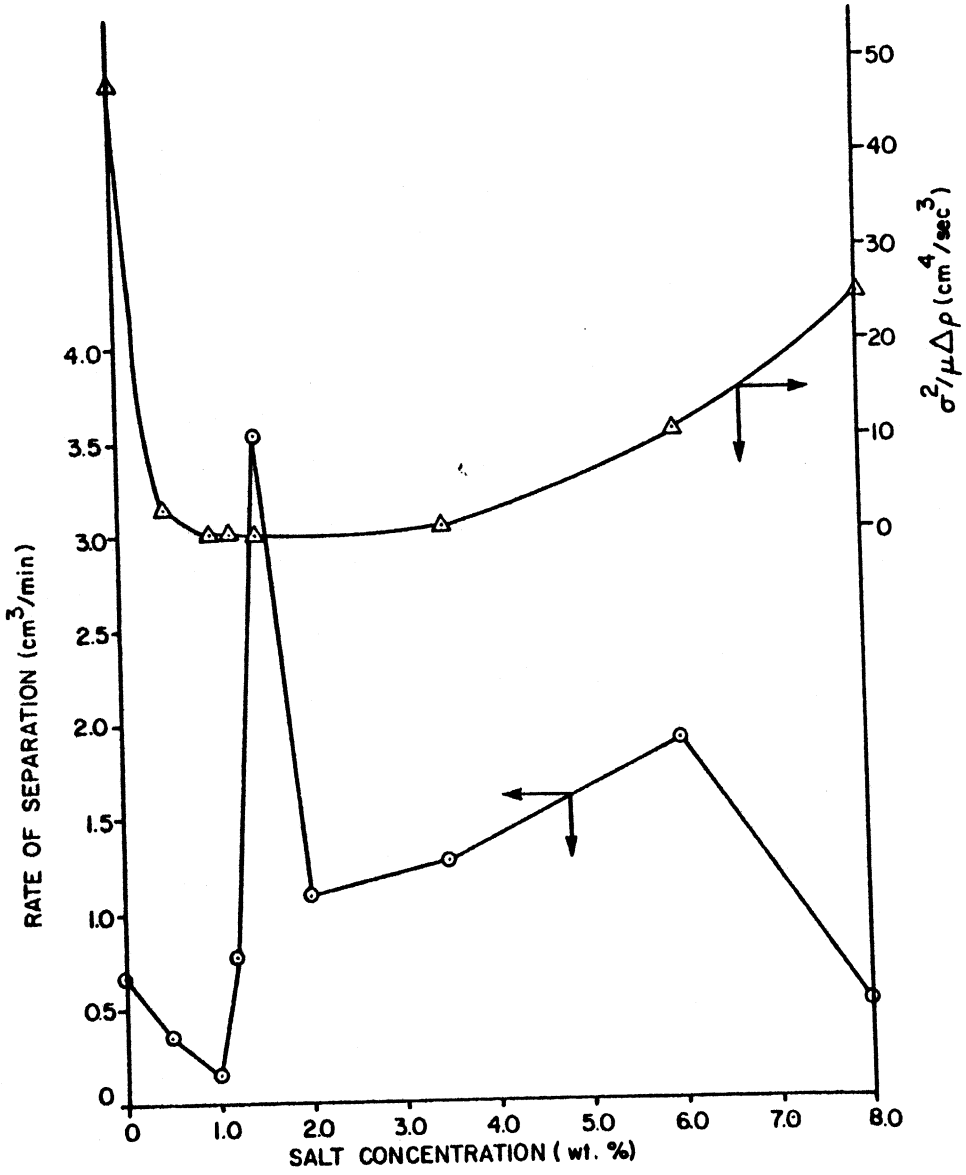

Fig. 8. Rate of separation in batch settling experiment for TRS 10-410 (5%) + IBA (3%) + NaCl (varying from 0% to 8.0%).

evident from the figure that the variation of this group with increase in NaCl concentration does not reveal a parallel behavior with the phase separation curve. Instead, we get a minimum for $(\sigma_i^2/\mu_c\Delta\rho)$ at 1.5% NaCl compared to a maximum in the phase separation rate. In the case of 6% NaCl system, although the phase separation curve shows a local minimum no such trend is found in the physical property group. It is obvious that the low values of interfacial tension in these systems play a dominant role in determining the magnitude of the physical property group as compared to the effect of either bulk viscosity or density difference variations.

When it was realized that the equilibrium physical property group just considered was not sufficient to explain the observed phase separation anomaly, one is left with the following questions:

(1) Are the assumptions in the coalescence modeling realistic?

(2) For concentrated mixed surfactant system such as the one under investigation, would it be possible to apply the models developed primarily for "even film" drainage mode?

In an earlier investigation Vijayan and Woods (20) studied the stability of oil (benzene) drops at oil oil/water interface containing mixed surfactants (sodium dodecyl sulfate and dodecanol) around and below the critical micelle concentration. They measured both coalescence times and film drainage rates using interferometer-cinematography. For the range of concentration studied, they found uneven film drainage modes which finally lead the drops to coalescence. Also, anomalous coalescence time behavior was found at some concentration of the surfactant. (Note the comparison between this observation with the anomaly at 1.5% NaCl concentration in the current study.)

For uneven draining films, Liem and Woods (21) extended the even film drainage model and proposed a new expression for the coalescence time, t, given by

$$t = \frac{\phi\eta_G^2}{16}\left[\frac{\mu_c\Delta\rho\, g}{\sigma_i^2}\right] b^5 \left[\frac{1}{h^2} - \frac{1}{h_0^2}\right] \qquad (1)$$

where

ϕ = a surface mobility parameter defined as

$$= \frac{4 - 2n_M}{1 + n_M}$$

n_M = number of moving surfaces which can take fractional values suggesting a local mobility in the interface.

n_G = dimensionless geometrical parameter that relates the radius of curvature of the film to the radius of curvature of the undeformed drop of radius b.

It is interesting to note that this model basically contains the same physical property group as the other models but now has, in addition, a "surface mobility parameter". (If the drop and the planar interfaces are relatively motionless, then $n_M \simeq 0$.) The use of the model (eqn. 1) to study mixed-surfactant system by Vijayan and Woods (20) partially explained some of the coalescence time anomalies.

Furthermore, the evaluation of the quantity ϕ (or n_M) is tedious and needs extensive film thinning rate data.

In spite of the partial success in the application of the model one is left with some ambiguities as to the magnitude and to the physics and chemistry of the parameter, n_M. A more fundamental problem would be to understand the factors which would directly influence the mobility of surfaces. Evidently factors such as attractive and repulsive forces of molecular origin between surfaces, and the mechanical properties of the liquid film separating the surfaces have to be understood. Quantitative experimental measurements of these parameters are not readily available.

b) Sonicated emulsions: effects of phase ratio and salt concentration at 25°C: Similar to hand-shaken emulsion studies discussed in section (2a), three sonicated systems containing 2:1, 1:1 and 1:2 aqueous to oil ratios were investigated as a function of salt concentration. From extensive data of volume separated versus time, results expressed as time taken for 50% separation as a function of sodium chloride concentrations were obtained. Typical results are shown in Figures 9 and 10 for 2:1 and 1:1 systems, respectively.

From the results obtained using the three phase ratios, it can be seen that the general tendency of these emulsions has been to give fastest separation at 1.5% NaCl, and also give comparable separation at 1.2% NaCl. For all the phase ratios studied, separation of 0% and 0.5% NaCl emulsions was not measured because these emulsions were very stable (of the order of days) when sonicated. Emulsions with 1:2 aqueous to oil ratio provide the most stable emulsions at several salt concentrations. In this case, separation of 6% and 8% NaCl in addition to 0% and 0.5% was not measured because of the large times associated with the separation process (of the order of days).

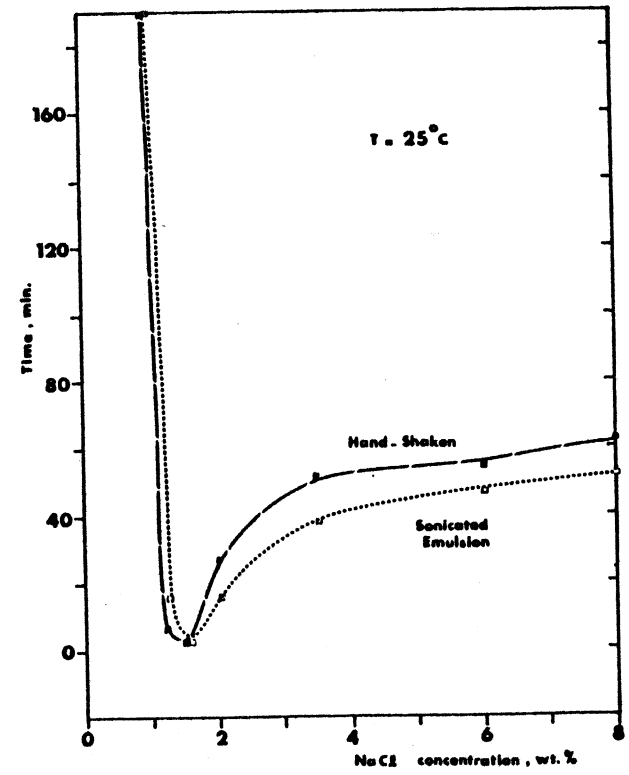

Fig. 9. Time taken for 50% phase separation for 2:1 sonicated and hand-shaken emulsions versus sodium chloride concentration.

Note on 1:1 emulsions: When constructing the settling curves for these systems an interesting observation was recorded. For all salt concentrations, with the exception of 1% and 8% NaCl, all the emulsions showed a gradual phase separation behavior with time. However, the emulsions containing 1% and 8% NaCl revealed a large initial lag before any visible separation commenced. This initial time taken for the formation of an observable phase boundary (ITFOPB) is of the order of hours. Furthermore, a comparison of the macroscopic structures of these emulsions by scanning electron microscopy (7) surprisingly reveal similar polyhedral structures. The physico-chemical aspect of the presence of polyhedral structures in relation to the initial stagnation period (at least for visual observations) is an important consideration in the area of emulsions. Obviously the next step is to see the microscopic changes taking place during the macroscopic stagnation period.

Separation behavior of emulsions: hand-shaken versus sonicated systems: For the different aqueous to oil ratio systems considered presently, the general trend in the settling curves (volume of phase separated versus time) remains essentially the

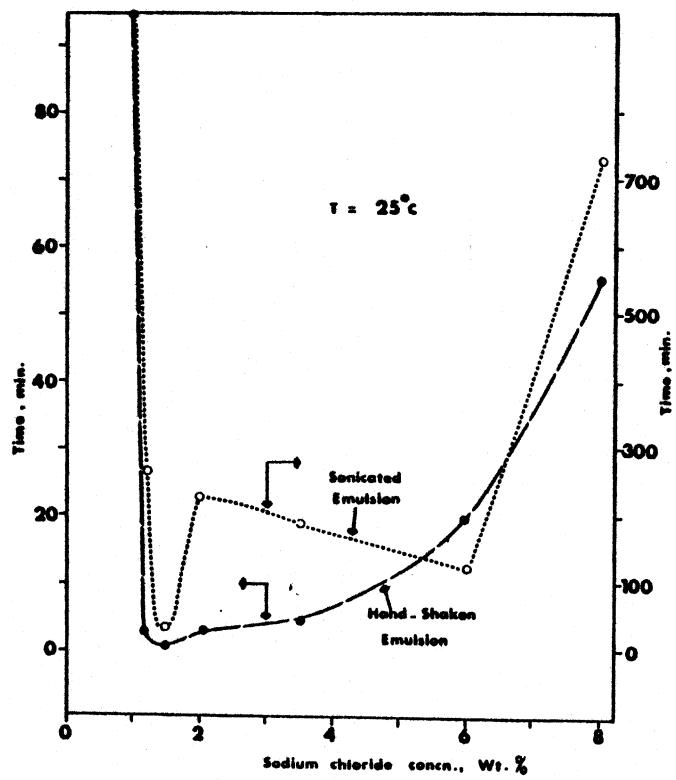

Fig. 10. Time taken for 50% phase separation for 1:1 sonicated and hand-shaken emulsions versus sodium chloride concentration.

same for the hand-shaken and the sonicated emulsions for a given aqueous to oil ratio but differs slightly from one ratio to the other. However, a comparison of the time taken for 50% separation does show appreciable differences in the separation behavior between the two modes of emulsion production. This difference is pronounced in the case of 1:1 emulsion system. The 2:1 emulsion system does not reveal any such differences between the hand-shaken and sonication modes.

Globally speaking, one can reason out the difference in the behavior of hand-shaken and sonicated emulsions in terms of the production of stable drop sizes. One would expect the sonicated emulsions to provide a stable equilibrium drop population. In the case of 2:1 emulsions, it is surprising as to why a difference in the separation behavior, in spite of the two modes of emulsion-making used, is not observed. Probably the power input by the hand-shaking mode is sufficient to produce equilibrium drop population.

3. Flow Through Porous Media Studies in Unconsolidated Sand-Packed Beds at 25°C

a) Water: Pressure drop results in the sand-packed bed using water (see apparatus, Figure 1) for several flow rates and different column conditions are presented in Figure 3. It can be seen from the figure that the pressure drop values increase linearly with flow rate passing through origin. That is, the flow curves demonstrate evidently Newtonian behavior as expected. Small variations in the expanded pressure drop diagram arise from small changes occurring as the result of passing other fluids and emulsions. Obviously it is an anticipated effect. Nevertheless, it is small compared to the overall increase in the pressure drop values associated with aqueous solutions and macroemulsions.

b) Aqueous solutions of TRS 10-410: isobutanol (5:3% w/w) containing sodium chloride (0 to 2 wt %): Pressure drops produced by the flow of aqueous solutions for several NaCl concentrations and flow rates are given in Figures 11 and 12. Aqueous solutions with NaCl concentration 0%, 0.5%, 1% and 1.2% follow Newtonian type flow behavior over the flow rates investigated. At low shear rates (less than 2 ml/min. flow rate) aqueous solutions containing 1.5% and 1.8% NaCl demonstrate a non-linear pressure drop-flow rate relation. However, at higher shear rates the ΔP-Q relation appears to be linear. It has been demonstrated from molecular order parameter studies (5,6) and physical property data (see for example, bulk viscosity, Figure 12) that maximum structural effect and liquid crystalline behavior are revealed by these solutions. On this basis, it is not surprising to observe a non-Newtonian type of behavior at low shear rates. At high shear rates it is possible that this structural effect is destroyed, in a relative sense, and the pressure drop increases proportionally with flow rate. Aqueous solution containing 2% NaCl seems to lie in between ΔP and Q still persists but the intensity is considerably reduced. At flow rates higher than 2 ml/min., we have essentially a Newtonian type fluid behavior.

The study of flow of aqueous solutions through unconsolidated sand bed thus demonstrates the influence of structural aspects of surfactant formulation on pressure drop values at low shear rate flows.

c) Sonicated macroemulsions consisting of aqueous phase (5:3% w/w TRS 10-410: IBA) + NaCl (X%) and dodecane oil (oil: aqueous = 1:1 w/w): Pressure drop data with flow rate for sonicated macroemulsions as a function of sodium chloride concentration is given in Figure 13. Here, as discussed in the earlier section, we have both two phases and three phases under equilibrium conditions. That is, the macroemulsions upon standing give rise to equilibrated clear phases which could be two or three phases

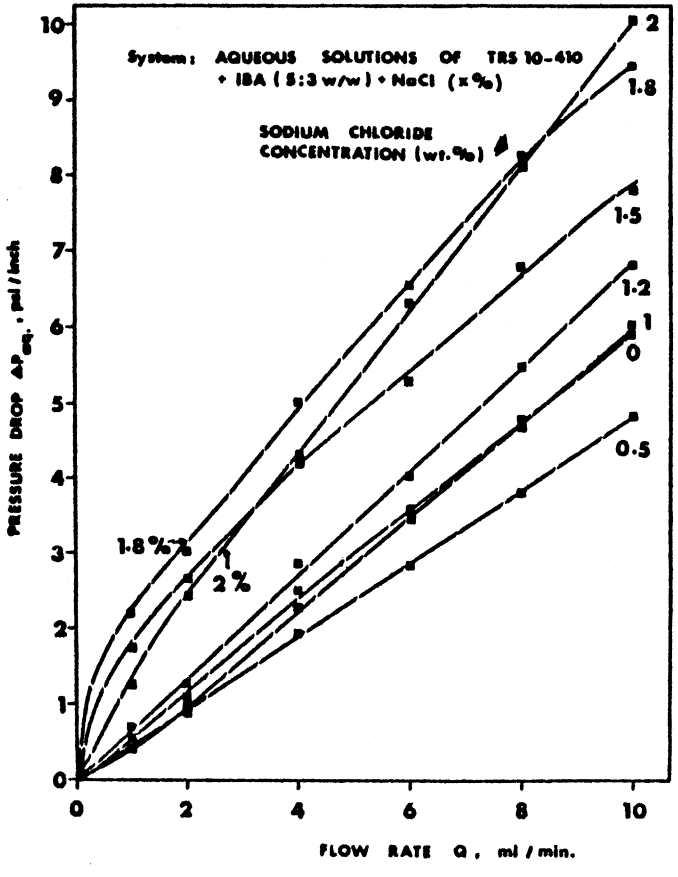

Fig. 11. Pressure drop versus flow rate curves for aqueous surfactant formulations flowing through a sand pack as a function of sodium chloride concentration.

depending on the salt concentration. In particular, we have two salt concentrations, 1.5 and 1.8 wt %, where three phases are produced whilst other concentrations (0, 0.5, 1, 1.2, 2, 6, 8 wt %) give two phases. Unlike aqueous phase pressure drop behavior, macroemulsions containing 0%, 0.5%, 1%, 1.2%, 2% and greater salt levels show non-linear ΔP-Q relation at low flow rates. This effect is more pronounced for 0 and 0.5 wt % NaCl emulsions. Again at high flow rates, similar to aqueous solution behavior, proportional variation in ΔP values with emulsion flow rate is observed. The very high pressure drop values of 0% and 0.5% emulsions can be readily attributed to their viscosity values (see Figure 4). The kinematic viscosity of these emulsions are 75 cS and 47 cS, respectively. With the exception of 1.5% and 1.8% NaCl emulsion, the kinematic viscosity of all other emulsions fall in the range 12 to 17 cS. Being very unstable, viscosities of 1.5% and 1.8% NaCl

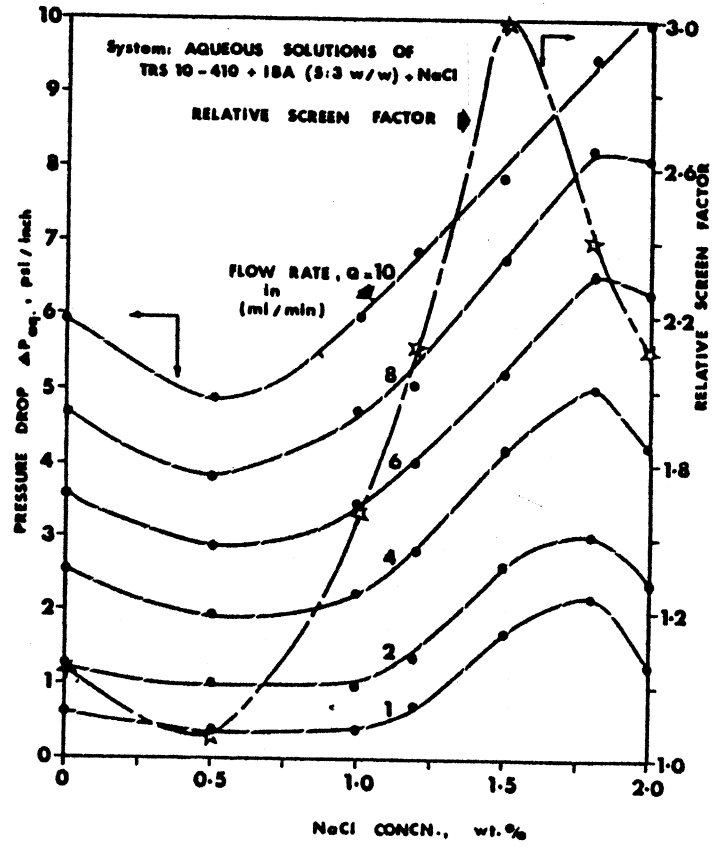

Fig. 12. Pressure drop and screen factor vs. sodium chloride concentration for aqueous solution of TRS 10-410 + IBA (5:3 w/w) + NaCl (X%).

emulsions could not be measured. (See Experimental section.) It is interesting to note that while equilibrium two phase systems with dodecane oil forming macroemulsions show higher pressure drops for a given flow rate and non-Newtonian type (probably pseudoplastic) of behavior at low shear rates (less than 2 ml/min.), three phase systems with dodecane oil forming macroemulsions exhibi very low pressure drops and a perfectly Newtonian type of behavior. This reasoning can be deducted directly by a comparison of water pressure drop in the porous media (see Figure 3). One obvious reason is that the effective viscosity of these emulsions is very low, of the order of a few centipoise.

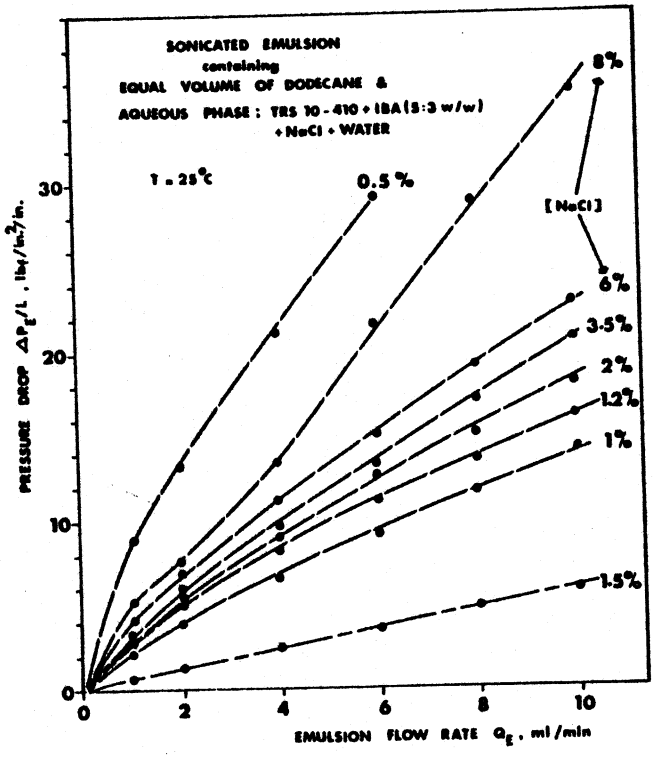

Fig. 13. Pressure drop values of sonicated emulsions in a sand packed column as a function of flow rate and NaCl concentration.

Effect of Addition of Sodium Chloride to Aqueous Surfactant Formulation Containing TRS 10-410 + IBA (5:3% w/w) on Pressure Drop in a Sand-Packed Bed and on Screen Factor

Figure 12 depicts that the $(\Delta P)_{aq}$ (aqueous phase pressure drop) remains steady up to 1% NaCl, gradually increases reaching a maximum at about 1.8% NaCl and then decreases. At higher flow rates (between 2 to 8 ml/min.) $(\Delta P)_{aq}$ decreases from 0% NaCl reaching a minimum at 0.5% NaCl and then increases up to 1.8% NaCl and again decreases. At 10 ml/min. flow, $(\Delta P)_{aq}$ - minimum is more pronounced at 0.5% NaCl but at the same time the maximum in $(\Delta P)_E$ occurring at 1.8% NaCl with low flow rates disappears. For all NaCl concentrations, increasing the flow rate increases the pressure drop. When the relative screen factor values of these solutions are superimposed, two optima are found to occur—a minimum at 0.5% NaCl and a maximum at 1.5% NaCl. It is interesting to see that both screen factor results and pressure drop results reveal a minimum at 0.5% NaCl. However, the maximum screen factor occurring at 1.5% NaCl does not correspond to the maximum in the pressure drop results. It is probable that a correspondence for maxima between the screen factor and $(\Delta P)_{aq}$ might have occurred at much lower flow rates (less than 1 ml/min.). Microstructure studies also indicate structural changes at these concentrations (5,6). Among the aqueous solutions, it has been found that 0.5% NaCl solutions form the most clear solution and remain so upon prolonged standing.

The important outcome of this study is that under the conditions of experimentation, the occurrence of a maximum in bulk viscosity and in screen factor at a certain NaCl concentration does not correspond with the pressure drop results. Except for this disagreement, the variations in the screen factor and viscosity are faithfully followed by pressure drop values in the flow rate range of 4 to 8 ml/min.

d) Comparison of emulsion pressure drop in a sand-packed bed with batch settling separation data and emulsion viscosities: Figure 14 shows the agreement between $(\Delta P_E/\Delta P_W)$ [ratio of pressure drop of emulsion to that of water] and the time taken for 50% separation of the emulsion. The pronounced minima in these two factors occurring at 1.5% NaCl is worth noting. The significance here is that at this temperature, the formation of stable emulsions at 1.5% NaCl was not possible and this may be the reason why the pressure drop as well as the emulsion stability is very low. Viscosity data of the emulsions again show a similar trend. An increase in the emulsion viscosity at 1.2% NaCl from 1% NaCl system (12 cS to 18 cS) is reflected directly on the pressure drop values. However, this effect is not revealed by the phase separation results. It should be emphasized that all these measurements were taken at 25 ± 1°C. Later measurements in our laboratory indicated that by increasing the temperature to 35°C and by prolonging the sonication for periods of hours, it was possible to form relatively stable emulsions at 1.5% NaCl. This effect together with the oil to aqueous phase ratio effect on the physical properties of emulsions and pressure drop in a 6 inch column are discussed in the following section.

4. Flow of Sonicated Emulsions in a 0.25 Inch Diameter, 6 Inch Long EM-Gel Packed Unconsolidated Bed at 35°C

a) Pressure drop as a function of phase ratio and salt concentration: The pressure drop results of the systems, described in Table 2, across the 6 inch bed as a function of salt concentration and aqueous to oil ratios, are presented in Figures 15-20 and in Table 6. In particular, the pressure drop results for the three phase systems are somewhat different from that of the results for the flow of macroemulsions through a sand-packed column at 25°C

Table 6. Pressure drop of sonicated emulsions ($\Delta P_E/L$ in psi/inch) flowing at Q = 4 (ml/min) across the bed at 35°C

NaCl Concn. (wt %)	Aqueous : Oil				
	4 : 1	2 : 1	1 : 1	1 : 2	1 : 4
1.0	3.4	4.3	11.4	19.3	31.6
1.3	6.6	7.0	7.3	9.9	11.3
1.4	6.0	5.7	6.3	10.7	14.8
1.5	4.3	7.0	8.6	11.4	11.2
1.6	7.1	6.1	9.0	12.7	14.5
1.8	4.0	4.4	10.1	13.3	12.8
2.0	14.8	6.5	3.9	14.4	23.3
3.5	48	18.4	8.5	4	2.7
Mean for 1.3 to 1.8%	5.6	6	8.3	11.6	12.9

Mean for 1.3% to 1.8% salt concentrations has a maximum spread = ± 25%.

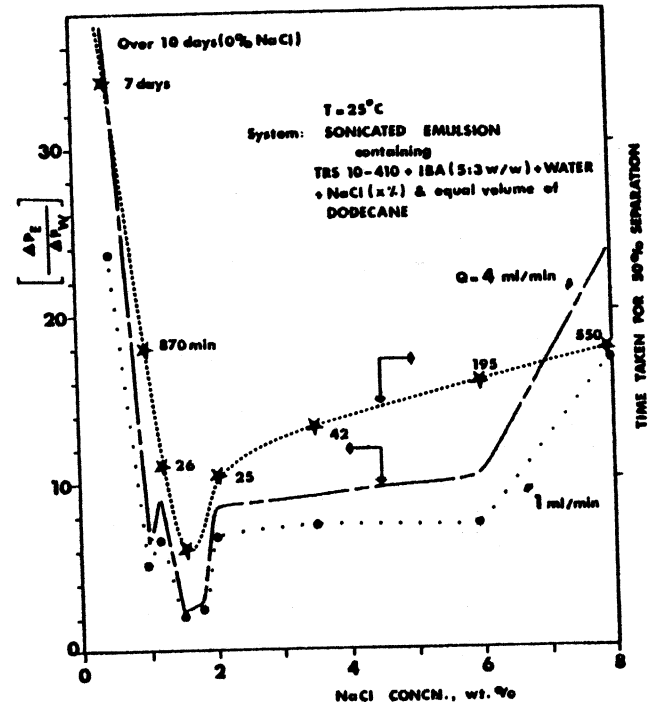

Fig. 14. Ratio of pressure drop of emulsion to water in a sand pack and phase separation data plotted against NaCl concentration.

(see section 3) where a Newtonian type of characteristic linear plot was obtained between ($\Delta P_E/L$) and Q for 1:1 emulsions containing 1.5% and 1.8% sodium chloride. However, the results shown in Figures 16-18 do not entirely reveal Newtonian type of behavior. It should be noted that our recent observations (8) indicate that even 3.5% salt concentration system with aqueous to oil ratio of 1:1 separate out into three phases upon standing at room temperature (~ 25°C) for a few weeks. Evidently this system did not reveal any Newtonian type behavior in the sand-pack experiments at 25°C where this system presumably gave only two phases at the experimental conditions. Therefore, it is incorrect to conclude that three phase systems exhibit, in general, Newtonian type characteristics.

Interestingly, results of the system containing 1.5% salt and 1:1 aqueous to oil ratio (Figure 16) do not show a Newtonian type behavior (especially at low shear rates). The reason being that we could form a relatively stable emulsion this time as opposed to the previous attempt (~ 35°C as opposed to 25°C in the sand-pack experiments). The higher temperature operation thus seems to have

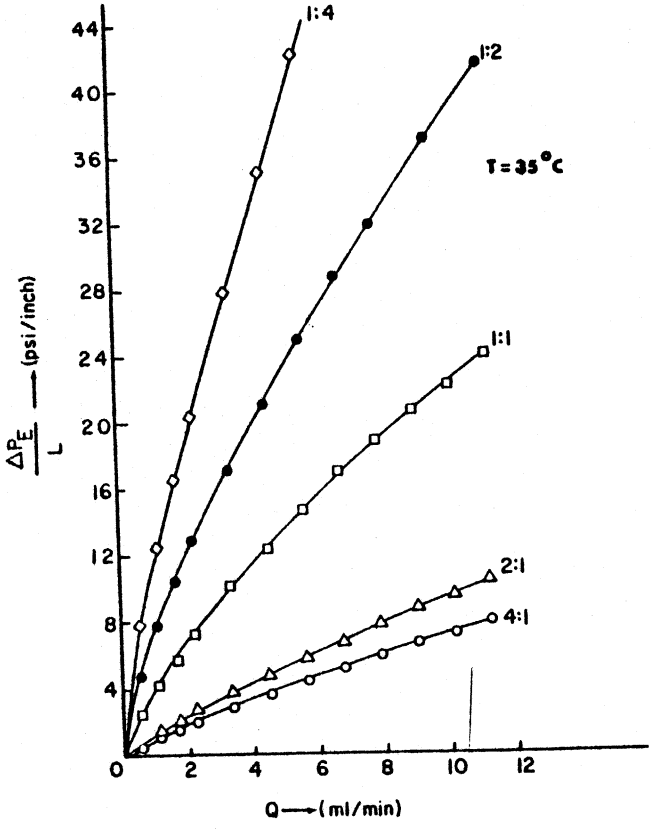

Fig. 15. Pressure drop variation with flow rate for 1% salt emulsion system as a function of aqueous to oil ratio.

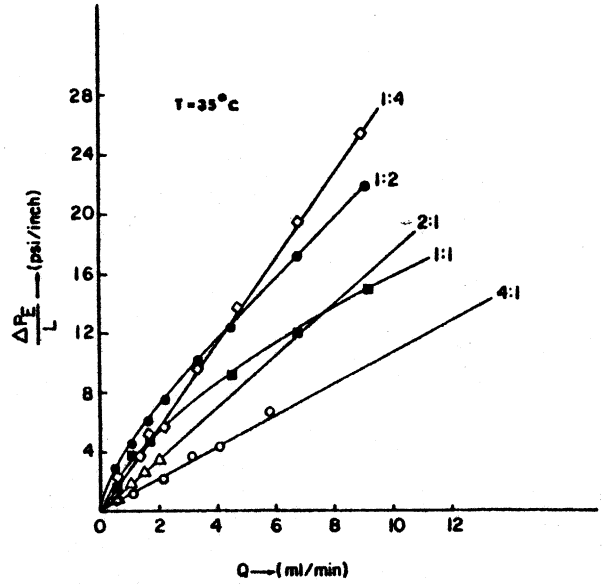

Fig. 16. Pressure drop variation with flow rate for 1.5% salt emulsion system at different aqueous to oil ratios.

made this profound difference in the state of the emulsion. Therefore, it may be concluded that higher temperatures and continuous sonication for about one to two hours can lead to the formation of relatively stable emulsions.

In general, most of the 1:4 aqueous to oil ratio systems did not produce stable emulsions even after prolonged sonication (~ three hours). However, by passing these systems, well-mixed, through the porous bed at very high flow rates, relatively stable emulsions were obtained. This observation leads us to conclude that sonication alone is not capable of producing emulsions in 'certain' systems while mere shearing at high flow rates is capable of emulsifying such systems.

The 2% NaCl system with aqueous to oil phase ratio of 2:1 showed hysteresis phenomena as shown in Figure 17. With emulsion systems having other phase ratios very long time period (of the order of five to six hours) was required for achieving steady state in the pressure drop values at a particular flow rate. Once steady state conditions were reached at higher flow rates, the time taken for the attainment of steady state at lower flow rates was considerably reduced (about 15 minutes). This system again reveals non-Newtonian type characteristics. It appears that 2% NaCl systems show a transition state with respect to pressure drop values. Comparison of ($\Delta P_{E/L}$) values for different salt concentration at

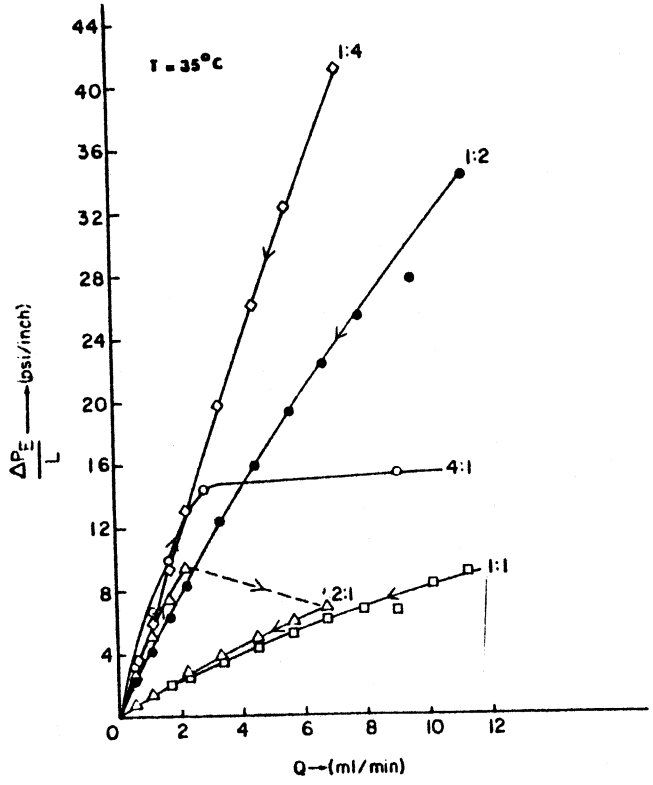

Fig. 17. Pressure drop variation with flow rate for 2% salt emulsion system at different aqueous to oil ratios.

particular aqueous to oil ratios (Figure 19) shows that (a) for 4:1 and 2:1 systems pressure drop increases considerably beyond 2% NaCl, (b) for 1:2 and 1:4 systems pressure drop decreases beyond 2% NaCl and (c) for 1:1 systems, although the changes in the pressure drop with salt concentration are not significant, a discontinuity with an optimum at 2% NaCl can be seen. In general, the discontinuities present in the vicinity of 2% NaCl region correspond with the discontinuous changes as revealed by the conductivity data in Table 5.

Comparison of the pressure drop values as a function of aqueous to oil ratios at particular salt concentrations (Figure 20) shows that: (a) $(\Delta P_{E/L})$ increases almost exponentially with phase ratio for 1% NaCl systems, (b) $(\Delta P_{E/L})$ decreases exponentially with phase ratio in the case of 3.5% NaCl systems, (c) for 2% NaCl systems $(\Delta P_{E/L})$ decreases with phase ratio, going through a minimum at aqueous to oil ratio = 1:1 and increases abruptly thereafter, (d) for emulsion systems containing salt concentration in the range of 1.3 to 1.8 wt %, $(\Delta P_{E/L})$ increases gradually but linearly with

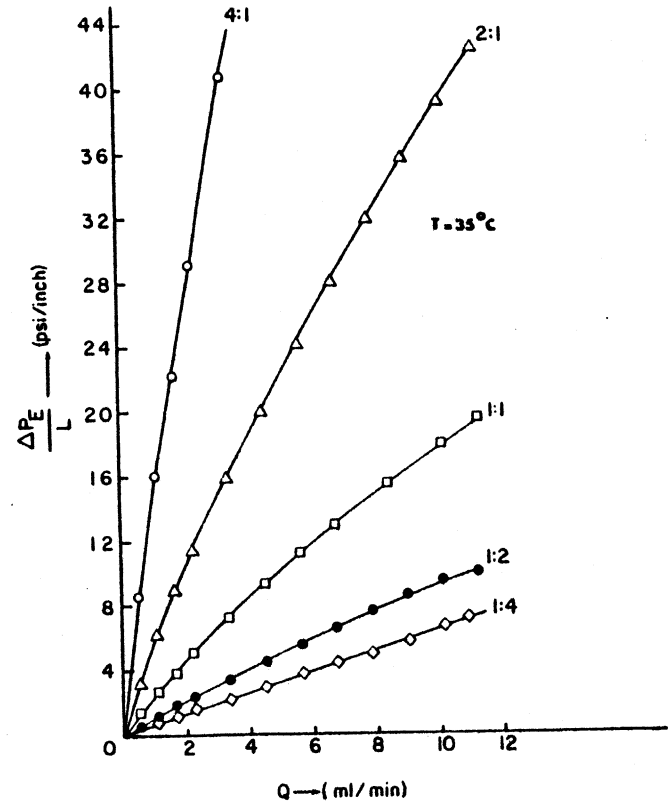

Fig. 18. Pressure drop variation with flow rate for 3.5% salt emulsion system at different aqueous to oil ratios.

phase ratio. For prediction purposes, various pressure drop results in the region are grouped together at a given flow rate. The curve shown in Figure 20 is estimated to be accurate within ± 30%. It should be noted that although Figures 19 and 20 illustrate the behavior of emulsions at Q = 4 ml/min., the interpretations presented above remain essentially unaltered for other flow rates as well.

The electrical conductivity results discussed in section 1 have shown that the macroemulsions seem to exsit as W/o type below 1.8% NaCl and as O/W type above 1.8% NaCl for all aqueous to oil phase ratios. This result together with the pressure drop data thus suggest that pressure drop associated with the flow of macroemulsions increase with the increase in the amount of the dispersed phase irrespective of whether it is oil or aqueous phase. It is suggested that the anomalous behavior at 2% NaCl could only be attributed to 'optimal salinity' effects. Rheological data for this composition and for those compositions in the transition region

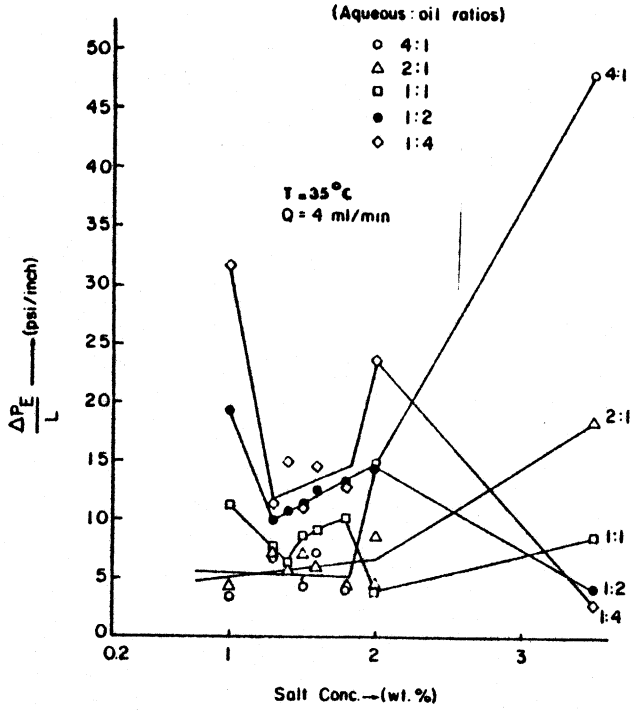

Fig. 19. Pressure drop variation with salt concentration of sonicated emulsions for different aqueous to oil ratios at 4 ml/min. flow rate.

indicate that the discontinuity must be due to structural changes present within the fluid which is in good agreement with our microstructural results published elsewhere (8). Similar transition states associated with phase inversion and structural properties as reflected by rheological properties of some microemulsion systems, have been studied by Dreher et al. (22). Their flow experiments using microemulsions (swollen micelles) showed that oil-external microemulsions exhibit Newtonian flow behavior whilst systems in those composition range that are in the oil-external to water-external transition region, exhibit non-Newtonian behavior. Our results for the transition region appear to corroborate these findings. In aqueous systems (Figure 11) the birefringent characteristics (liquid crystalline) of 1.2% - 2% NaCl systems evidently show non-Newtonian flow behavior of pseudoplastic type characteristics.

b) Applicability of Darcy's law: For steady laminar viscous flow in horizontal beds, Darcy's law is:

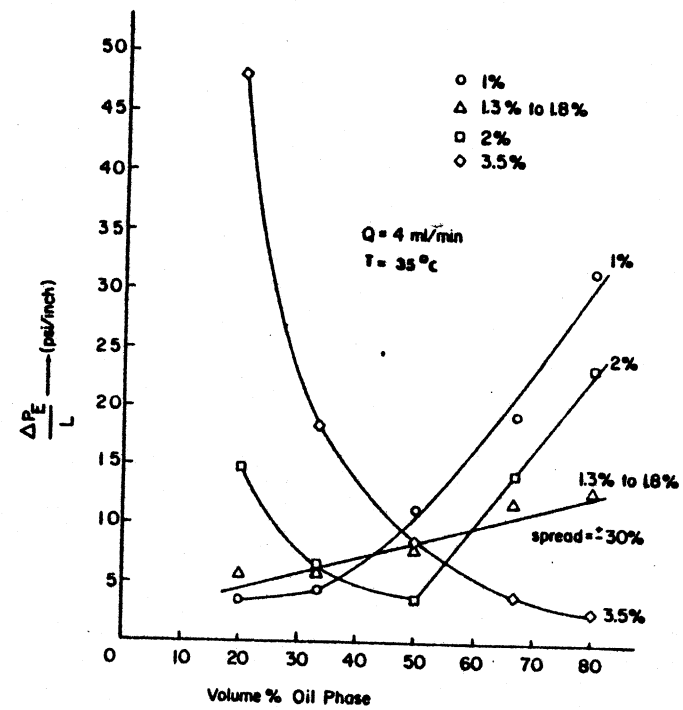

Fig. 20. Variation of pressure drop with percent volume of oil phase for different salt concentrations at 4 ml/min. flow rate.

$$Q = -\frac{KA\ \Delta P}{\mu L} \qquad (2)$$

where the permeability K is determined by the structure of the porous material and has the unit: 'Darcy' (d) [1 darcy = 1 (cm^3/s). 1 (cp)/1 (cm^2). 1 (atm/cm)]. The transition from laminar to turbulent flow occurs, say in sands and sandstones, gradually in the range of Reynolds number from 1 to 10. The Reynolds number is defined as

$$Re = \frac{Q \cdot \rho \cdot \delta}{\mu \cdot A \cdot \phi} \qquad (3)$$

where δ and ϕ are the sand-grain diameter and porosity of the bed respectively. Since porous systems possess a distribution of pore sizes, the transition from laminar to turbulent flow is not abrupt at a critical Reynolds number as in the case for flow through pipes.

To verify the applicability of eqn. (2), it is possible to calculate the maximum Reynolds number from eqn. (3) that could have been encountered in the present investigation. Substituting values

for the parameters in eqn. (3) except for the porosity [δ = 0.063 - 0.125 mm, A = 0.317 cm^2, μ = 0.95 cp (lowest value), ρ = 1.0 g/cm^3 (maximum value), Q = 11.3 ml/min. (maximum value)], we have Re_{max} = 0.78/ϕ. If a percentage porosity as low as 10% is substituted, it would only give a maximum Reynolds number of 7.8 which is well within the range of 1 to 10 for the transition from laminar to turbulent flow in sands and sandstones. Although the porous media used in the present study are composed of different materials, the order of magnitude of the maximum Reynolds number is quite within reasonable limits, should be sufficient for the applicability of Darcy's law. It should be noted that the viscosities of emulsions are, in most cases, much higher than that of water. Consequently, Reynolds numbers would go even below 1. This condition would rule out the possibility of a change from laminar to turbulent flow in the present studies.

c) Permeability and viscosity considerations: In the absence of reliable viscometric data (relating viscosity as a function of shear rate) for the emulsion systems under study, an attempt is made presently to calculate the ratio of permeability to viscosity parameter of the emulsions in the porous bed using Darcy's law. The calculated values are presented in Table 7 for three aqueous to oil ratios, four different salt concentrations and five flow rates. With increase of emulsion flow rate, the (k/μ) ratio increases for salt concentrations less than 2% for 1:1 and 1:4 emulsions. At and above 2% NaCl, the ratio remains essentially constant as the flow rate is increased. For 4:1 emulsion system, with NaCl concentrations of 2% and higher the ratio increases with the flow rate. These observations appear to reveal the existence of a 'transition region' in the phase ratio. More likely the transition point is expected to lie in between 2:1 and 1:1 emulsions.

The determination of absolute permeability values as a function of shear rate, salt concentration and phase ratio, poses some problems because of the complex interaction of the parameters. Although permeability is the property of the porous medium, it has been recognized by investigators (see for example, 23 and 24) that the nature of the fluid in terms of its wetting characteristics with the packing material, would equally contribute to permeability effects. Therefore, a strict evaluation of this quantity from Darcy's law requires extensive viscosity-shear rate data from independent viscometric measurements. Our data from low and constant shear rate experiments (Table 4) although indicate variations with respect to phase ratio and salt concentration (paralleling the observed pressure drop values) are not sufficient to be able to give realistic values of permeability. Order of magnitude calculations show that K can vary anywhere from 5 to 16 darcy. It should be noted that the flow of water through the same porous system gives an average permeability of 7 darcy. If the fluid is assumed to be Newtonian, then it is possible to use the water permeability

to evaluate the 'apparent viscosity' of the various emulsion systems from the calculated (k/μ) values in Table 7. Evidently, this approach is not entirely correct for the present situation. However, this basis can be useful to understand the relative behavior of the various systems. From such a calculation it can be seen that: (a) for 4:1 emulsions having 2% and 3.5% NaCl, μ_a decreases as the flow rate is increased while μ_a of 1% and 1.5% NaCl emulsions remain constant at about 3-3.5 cp. (b) Apparent viscosity values of 1%-2% emulsions with 2:1 aqueous to oil ratio are essentially independent of flow rate. However, the 3.5% NaCl emulsion shows a decrease in μ_a with an increase in flow rate. (c) Both 1:1 and 1:4 emulsions behave identically. Here, for 1% and 1.5% NaCl, μ_a decreases with flow rate and for 2% and 3.5% NaCl the apparent viscosity values are independent of flow rate.

The observations presented above evidently show that by increasing the oil phase volume, a phenomenological change occurs around 2:1 aqueous to oil ratio in the apparent viscosity values as a function of sodium chloride concentration. For lack of viscometric data, further analysis of the rheological behavior of the emulsions is not carried out.

In summary, the authors wish to point out that all of the results reported in this investigation of emulsion behavior under various conditions show evidently the complexity of the problem. Simplified correlations are difficult to propose at this stage. Nevertheless, this investigation highlights a number of pertinent problems caused by the presence of emulsion in tertiary oil recovery systems. This is only the beginning and obviously more detailed studies are inevitable relating microstructure of micellar systems with macrostructure of emulsions and their physical and rheological properties before analyzing their fluid dynamic behavior in porous media.

CONCLUSIONS

1. Discontinuities in electrical conductivity values demonstrate the existence of a phase inversion process in macroemulsions. For 1:1 (aqueous:oil) emulsions at 25°C, phase inversion of O/W to W/O occurs around optimal salinity (1.5% NaCl).

2. For a given phase ratio, the phase inversion process parallels the observed (ref. 7) phase inversion in microemulsions (swollen micelles) by electron spin resonance studies.

3. Emulsions containing optimal salinity concentration of sodium chloride are very unstable at 25°C. By increasing the temperature to 35°C, relatively stable emulsions can be formed by sonication.

4. Increasing the system temperature favors the production of

Table 7. Values of the ratio of permeability to viscosity (k/μ) from Darcy's equation using experimental emulsion pressure drop and flow rate data at 35°C

Flow rate, Q (ml/min)	(k/μ) in (cm³/sec)/(cm²·atm/cm)																	
	aq:oil = 4:1				aq:oil = 1:1						aq:oil = 1:4							
	Salt concn. (wt %)				Salt concn. (wt %)						Salt concn. (wt %)							
	1	1.5	2	3.5	1	1.5	2	3.5	1	1.5	2	3.5	1	1.5	2	3.5	1	1.5	2	3.5
0.5	2.9	1.9	0.3	0.11	0.5	0.5	1.96	0.98	0.12	0.33	0.33	1.96	0.12	0.33	0.33	1.96	0.12	0.33	0.33	1.96
2.0	2.5	1.9	0.3	0.13	0.6	0.8	1.96	0.82	0.19	0.56	0.36	3.9	0.19	0.56	0.36	3.9	0.19	0.56	0.36	3.9
4.0	2.3	1.8	0.5	0.16	0.7	0.9	2.02	0.92	0.24	0.7	0.34	2.9	0.24	0.7	0.34	2.9	0.24	0.7	0.34	2.9
6.0	2.5	1.8	0.8	-	0.84	1.05	2.4	1.0	0.26	0.7	0.35	3.1	0.26	0.7	0.35	3.1	0.26	0.7	0.35	3.1
10.0	2.8	1.8	1.3	-	0.93	1.24	2.3	1.1	-	0.7	-	3.3	-	0.7	-	3.3	-	0.7	-	3.3

3-phases (otherwise 2-phase systems at low temperatures). Once three phases are produced reverting to room temperatures makes the phase change irreversible.

5. Discontinuities in emulsion viscosity values reconfirm the phase inversion process as revealed by electrical conductivity results.

6. At 25°C, hand-shaken as well as sonicated 1:1 emulsions at optimal salinity exhibited maximum phase separation rate.

7. Phase separation results for hand-shaken and sonicated emulsions with aqueous to oil ratios of 1:1 and 2:1 as a function of sodium chloride concentration follow very closely to each other although the time taken for separation of sonicated emulsions are much higher than that of hand-shaken emulsions.

8. Application of the simplified theory of coalescence (developed for millimeter-droplets and for relatively high interfacial tension values) to micron-droplet system (present case) having ultra low interfacial tension values, has not been successful.

9. For low shear rate experiments in sand packs for the flow of aqueous surfactant formulations containing 1.5% NaCl and more, a non-linear pressure drop-flow rate relation exists. Other formulations having less than 1.5% NaCl, ΔP-Q plots show linearity. High shear rate experiments reveal linear variations in ΔP and Q.

10. Non-linear behavior of aqueous formulations containing 1.5-2.0% NaCl at low shear rates, is attributed to liquid crystalline nature of these phases. Screen factor measurements further corroborate these findings.

11. Flow of sonicated emulsions in sand packs at 25°C having equilibrium 3-phases, produce low pressure drops. Also, they possess Newtonian type flow behavior. However, 1:1 emulsions with 0-1.2% NaCl give high viscosities and consequently high pressure drops. Reasons for this behavior are attributed in terms of emulsion droplet size and structure.

12. Results of the flow of aqueous surfactant formulations in sand packs together with the physical property data demonstrate that the occurrence of a maximum in bulk viscosity and in screen factor at 1.8% NaCl, does not correspond to the pressure drop results. Otherwise, pressure drop values, in general, follow the bulk viscosity and screen factor variations.

13. Emulsion pressure drop results as a function of NaCl concentration in sand pack experiments follow closely the separation rate results from batch settling tests at 25°C with a pronounced minimu at 1.5% NaCl.

14. Emulsion flow in a EM-Gel packed bed at 35°C as a function of phase ratio and salt concentration demonstrates the presence of a transition region in the vicinity of 2% NaCl. This, in turn,

corresponds to the discontinuous change as revealed by the conductivity data.

15. Pressure drop results of emulsions containing 1.3 to 1.8% NaCl in a EM-Gel packed bed reveal a linear variation with phase ratio.

16. In general, flow experiments in EM-Gel packed beds show that pressure drop of emulsions increase with the increase in the amount of dispersed phase, irrespective of whether it is oil or aqueous phase. The anomalous behavior at 2% NaCl is attributed to optimal salinity effects.

17. Reynolds number calculations rule out the possibility of a change from laminar to turbulent flow in the present studies. The shear rate magnitudes and flow regime favor the applicability of Darcy's law.

18. The average permeability of EM-Gel packed beds using water is 7 darcy and the emulsion systems give permeabilities in the range of 5 to 16 darcy.

19. In the absence of reliable viscometric data, the apparent viscosity values (evaluated using Darcy's law with the permeability of water) show a discontinuity around aqueous to oil ratio of 2:1. For several salt concentrations and phase ratios, the apparent viscosity variation with emulsion flow rate is essentially constant.

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NOMENCLATURE

A	cross-sectional area of porous bed, cm^2
B	a constant with dimension of reciprocal length squared which is characteristic of the pore geometry. B is also proportional to the specific surface
g	acceleration due to gravity
h	liquid film thickness at any time t (eqn. 1)
h_o	initial liquid film thickness (eqn. 1)
K	permeability ($= \phi/B$), a constant characteristic of the medium, darcy [1 darcy = $(cm^3/s) \cdot cp/cm^2 \cdot (atm/cm)$]
L	length of porous bed
P	pressure, psi
ΔP_E	pressure drop across porous bed by the flow of emulsion, psi

ΔP_W	pressure drop of water across porous bed, psi
Q	volumetric flow rate of fluid, ml/min
ρ	bulk density, g/cm^3
$\Delta\rho$	density difference between aqueous and oil phases, g/cm^3
μ_a	apparent viscosity, cp
$\mu_{aq.}$	aqueous phase viscosity, cp
μ_{oil}	oil phase viscosity, cp
μ_c	continuous phase viscosity, cp
ϕ	porosity of bed
σ_i	interfacial tension, dyne/cm

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