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Coalescence of Water-in-Shale Oil Emulsions

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Abstract

The coalescence and interfacial behavior of water-in-shale oil emulsions in the presence of chemical additives was studied using photomicrographic analysis. Both the coalescence and flocculation rate constants were determined as a function of the demulsifier concentration. The coalescence rates increased and the interfacial viscosity decreased with an increase in the temperature. These changes are due to the decrease in bulk and interfacial viscosities with increase in temperature, higher temperatures facilitating better film drainage and hence better coalescence rates. The overall coalescence rate goes through a maximum as the speed of agitation is increased. This maximum may be explained by the mechanism of flocculation and redispersion. The presence of solids was seen to significantly increase the stability of these emulsions.

INTRODUCTION

Oil shale is one of the most abundant sources of synthetic fuel in the world. The United States has oil shale reserves equivalent to 7 trillion barrels of oil (*1*). While relatively small quantities of shale oil are being produced today, the changing scenario of world petroleum supply and demand may make it a very viable commercial source of fuel. Projects under development project shale oil production to reach 574,000 bbl/d by 1992.

In this paper we discuss our study of the stability of water-in-shale oil emulsions. These emulsions appear during the processing of oil shale. The stability of such emulsions has been attributed to the presence of asphaltene molecules in shale oil. These asphaltene molecules penetrate the oil–water interface giving it great mechanical strength (*2*). Although the asphaltene or

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resin concentration in shale oil is low, its presence is responsible for the dark color and viscosity of the oil. The emulsion stabilization is also enhanced by the high content of nitrogen polycyclics in the asphaltenes (*3*). Often the emulsions are additionally stabilized by solid particles which are dispersed in the oil during retorting of oil shale.

The stability of oil-in-water emulsions has been studied by a large number of investigators (*4–9*). Water-in-crude oil emulsions have also been studied by many researchers (*10, 11*) but the specific study of shale oil emulsions has not been undertaken by many investigators. Shale oil is different from crude oil in many respects. Table 1 is a summary of some of the properties of shale oil and some crude oils (*1*). Shale oil in general is low in sulfur and high in nitrogen, and has a high pour point. Also, raw shale oil can contain up to 3% solids. Cottingham et al. (*12*) analyzed the stability of shale oil-water emulsions using pentane insolubles and solubles to stabilize the interfaces. Their study revealed that the addition of the pentane-soluble portion (extracted from the shale oil) to the emulsion caused the separation of the aqueous and oil phases within a few minutes. Addition of both the pentane solubles and insolubles, however, caused greater stability of the emulsions: the phases did not separate even after a few hours.

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In our study we investigated the effects of demulsifier concentration, temperature, speed of agitation, and mode of demulsifier addition and solids concentration on the coalescence behavior of water-in-shale oil emulsions.

EXPERIMENTAL

The shale oil from Rundle, Australia was supplied to us by Exxon R&E Co. and has a viscosity of 0.032 poise and a density of 0.856 g/cm^3. The

TABLE 1
Comparison of Raw Shale Oil and Conventional Petroleum Properties (*1*)

	Gravity (°API)	Sulfur (wt%)	Nitrogen (wt%)	Pour point (°F)
Raw shale oils:				
Surface retorting	20	0.7	2.0	70 to 90
Modified *in-situ* retorting	25	0.6	1.30	50
Petroleum crudes:				
Alaskan North Slope	27.5	1.0	0.04[a]	30
PADD 4 low-sulfur	39	0.2	0.003[a]	7
PADD 4 high-sulfur	26	2.3	0.01[a]	0
California (heavy)	19 to 24	1 to 2	0.1 to 0.3[a]	−5 to 90

[a] Nitrogen contents for petroleum crudes on 525 to 1000°F cuts.

demulsifier system used was a blend of Breaxit-126 and Corexit-420 (Exxon) in the ratio of 4:1. Corexit-420 is a blend of ester surfactant and aryl sulfonic acid in mixed aromatic solvents. Breaxit-126 is a mixture of oxyalkylated phenolic resins in glycol ether and aromatic solvents. A mixture with 1.5% of Span-60 and Tween-60 with an HLB of 5.7 was dissolved in the oil phase to act as an emulsifier. The emulsion was prepared by passing the aqueous and oil phases through a laboratory homogenizer. A 10% water-in-oil emulsion was used for all of our experiments. The homogenizer nozzle was adjusted to produce droplets with a mean volume diameter of ~30 μm. The demulsifier was added after homogenization and the emulsion was mildly shaken to disperse the demulsifier droplets. Throughout the experiment the emulsion was mildly stirred in the vertical plane to eliminate the phenomenon of gravity settling of the droplets.

The photomicrographic technique was employed to study the coalescence behavior of the emulsions. A sample of the emulsion was placed in a Howard cell and photographed through a Nikon microscope with a magnification of 100×. The microscope has a maximum magnification of 1000× and is equipped with interference phase contrast, polarizing light, and slow and fast speed cinematographic equipment. The first photographs were taken 10 s after the sample had been emulsified. Additional photographs were taken at different times throughout the experiment. The size distribution of the droplets was determined using a Zeiss MOP image analyzer.

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RESULTS AND DISCUSSIONS

We studied the effect of demulsifier concentration, temperature, mode of demulsifier addition, and speed of agitation on the coalescence behavior of water-in-shale oil emulsions.

Demulsifier Concentration

The interfacial properties and coalescence phenomena were studied with the demulsifier concentration varying from 300 to 1000 ppm. Figure 1 shows a semilogarithmic plot of the number of droplets per unit volume of the aqueous phase as a function of time with the demulsifier concentration as the parameter. The plot of the system containing no demulsifier is a straight line showing that the kinetics of coalescence is first order and can be represented by

$$N = N_0 \exp(-Kt) \tag{1}$$

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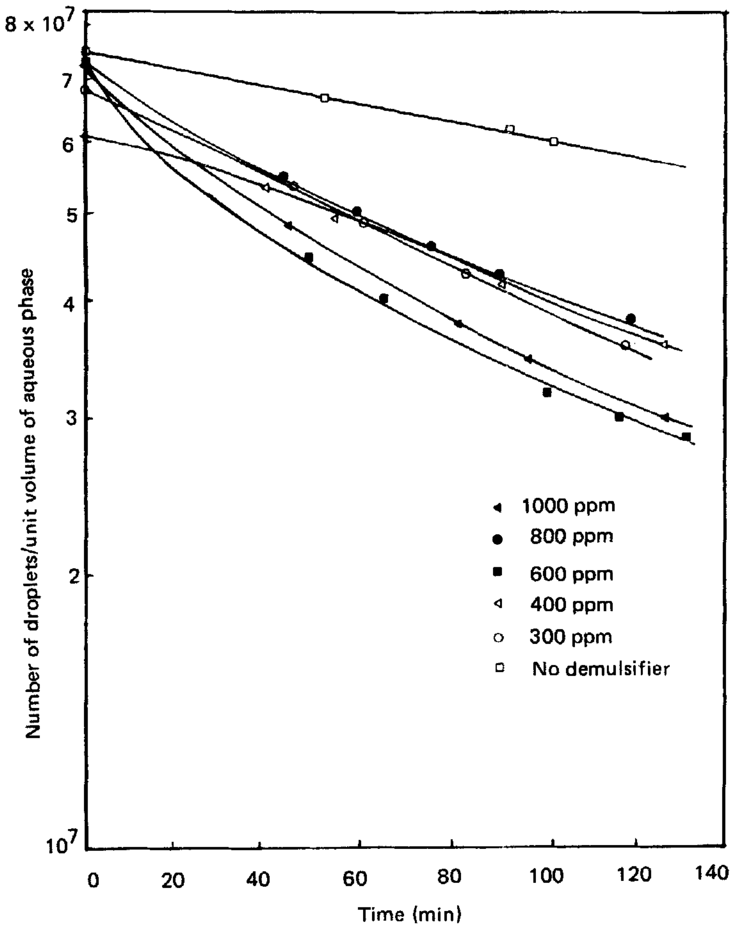

FIG. 1. Coalescence behavior of water-in-oil emulsion with demulsifier concentration as a parameter.

where N = number of droplets per unit volume of aqueous phase at time t
N_0 = number of droplets per unit volume of aqueous phase at initial time
K = coalescence rate constant (s^{-1})
t = time (s)

The plots of the systems containing demulsifier, however, are not linear, implying that these systems cannot be represented by a simple first-order coalescence rate expression. Hence a more general rate expression con-

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taining the coalescence and flocculation rate constants was used to analyze the experimental data. This expression is

$$N = \frac{N_0}{(1 + aN_0t)} + \frac{aN_0^2t}{(1 + aN_0t)^2}\left\{\frac{aN_0}{K} + \left(1 - \frac{aN_0}{K}\right)e^{-Kt}\right\} \tag{2}$$

where a = flocculation rate constant.

The above expression (*13*) was derived by treating flocculation and coalescence as consecutive steps of the coagulation process. The parameters a and K were obtained by fitting the coalescence data to Eq. (2) using a nonlinear least square regression analysis fit.

Figure 2 shows the variation of the coalescence rate constant K with the concentration of demulsifier. The rate of coalescence increases with increasing concentration of demulsifier. Figure 3 shows the effect of demulsifier concentration on the flocculation rate constant. The flocculation rate constant decreases with increasing concentration of demulsifier. At low concentrations of demulsifier there is not enough demulsifier to reach the droplet interface and hence coalescence is slow. In addition, the presence of the nonionic Span-60 and Tween-60 molecules at the interface does not hinder droplet agglomeration. Thus flocculation is high at low demulsifier concentrations.

When the demulsifier concentration is high, it breaks the emulsifier coating at the interface and facilitates rapid coalescence. The surfactant Corexit-420 is anionic in nature; hence droplets with adsorbed demulsifier layers repel each other, thus leading to a low rate of flocculation. Once this repulsion is overcome, coalescence is rapid.

The initial slopes of the plots of $\log N$ vs time are tabulated in Table 2. The initial slope is a measure of the rate of decrease of disperse phase droplets and is therefore a direct measure of the overall coalescence rate. From Table 2 we find that the emulsion system containing 600 ppm of demulsifier has the greatest value of the initial slope and therefore this is the optimum concentration of demulsifier for the 10% water-in-oil emulsion samples. This system is flocculation rate controlling.

The interfacial viscosity of the water–oil interface containing the chemical additives was measured using a viscous traction deep channel surface viscometer (*14*). The interfacial tension was measured using a spinning drop tensiometer. Figure 4 is a plot of the shear viscosity vs the demulsifier concentration. The shear viscosity decreases with increasing concentration of demulsifier and attains a constant value of about 0.02 surface poise at 600

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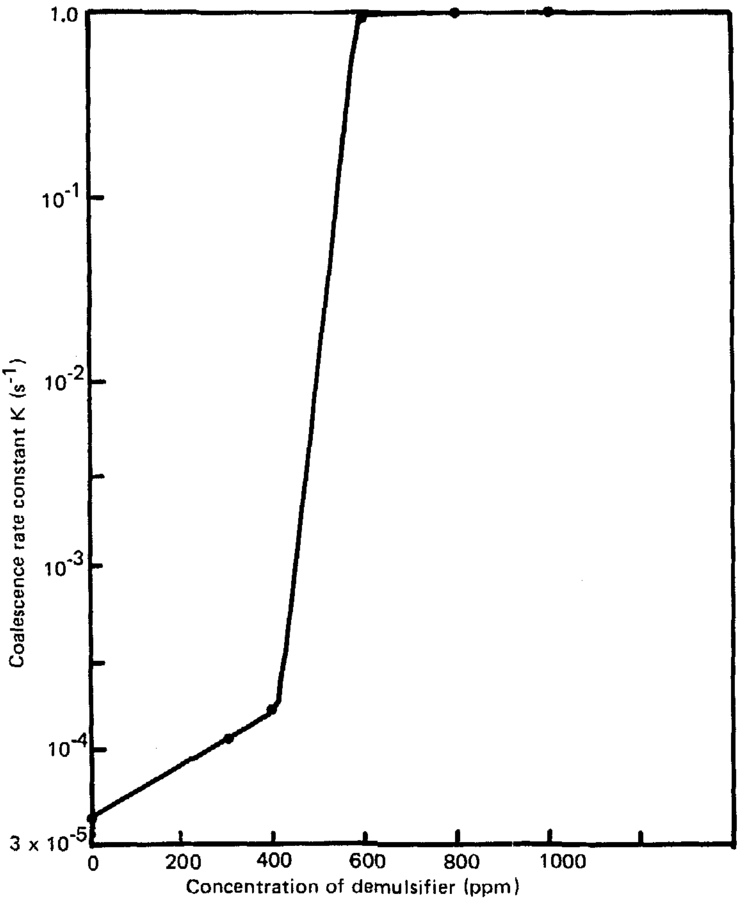

FIG. 2. Variation of the coalescence rate constant with demulsifier concentration.

ppm. The coalescence rate constant also decreases with increasing interfacial viscosity (Fig. 5). A low value of shear viscosity implies that the process of film drainage is facilitated (*15*). It can be seen that at a demulsifier concentration of about 600 ppm, the coalescence rate is highest and the interfacial viscosity is lowest. Hence this concentration of demulsifier is optimum for the specific system we studied. Figure 5 also shows the variation of the interfacial tension with the demulsifier concentration. There appears to be no trend between interfacial tension and demulsifier concentration. This observation is in agreement with similar results obtained by Wasan et al. (*4*).

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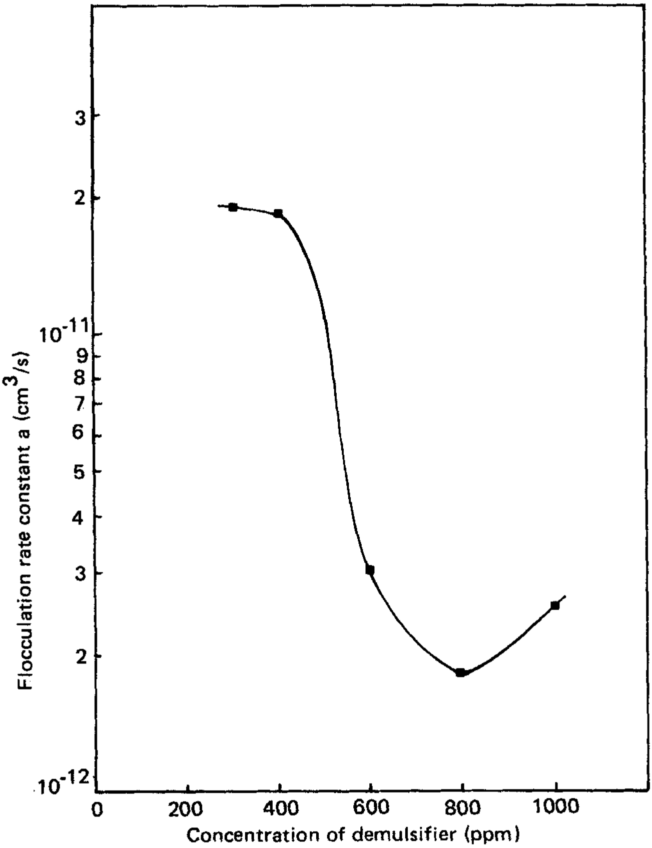

FIG. 3. Variation of the flocculation rate constant with demulsifier concentration.

Temperature

A 10% water-in-oil emulsion, stabilized by 1.5% of Span-60/Tween-60 of HLB 5.7 and containing 600 ppm of the demulsifier blend, was studied as a function of temperature. The entire system was placed in a water bath in which the temperature could be maintained to ±1°C of the desired temperature. We calculated the coalescence and flocculation rate constants at temperatures ranging from 25 to 65°C by fitting the coalescence data to Eq. (2).

Figure 6 is a semilog plot of the number of droplets per unit volume of the aqueous phase vs time. Table 3 gives the initial slopes of the plots in Fig. 6 at

TABLE 2
Variation of the Initial Coalescence Rate Constant with the Demulsifier Concentration

No.	ppm demulsifier	Initial coalescence rate constant
1	no demulsifier	3.55×10^{-5}
2	300 ppm	6.11×10^{-5}
3	400 ppm	5.84×10^{-5}
4	600 ppm	1.91×10^{-4}
5	800 ppm	1.09×10^{-4}
6	1000 ppm	1.53×10^{-4}

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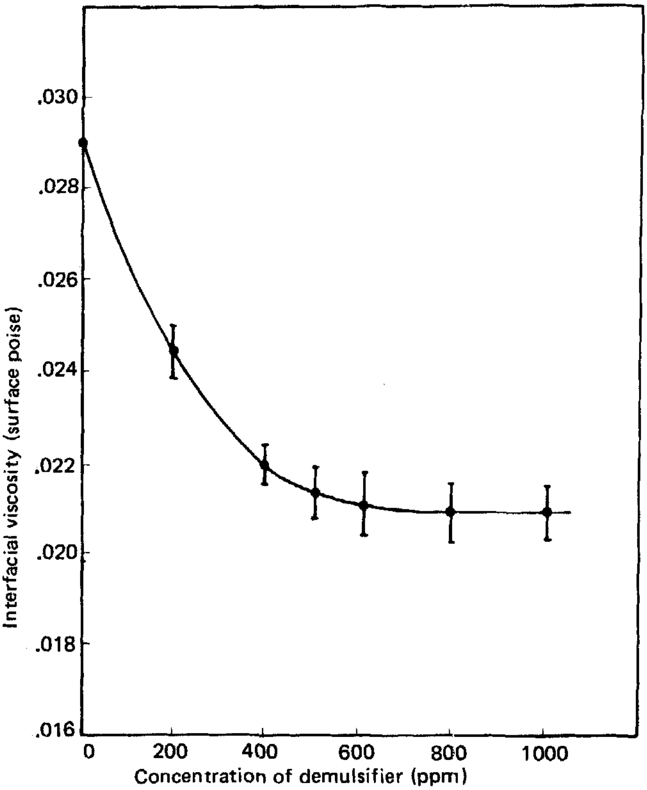

FIG. 4. Variation of interfacial viscosity with demulsifier concentration.

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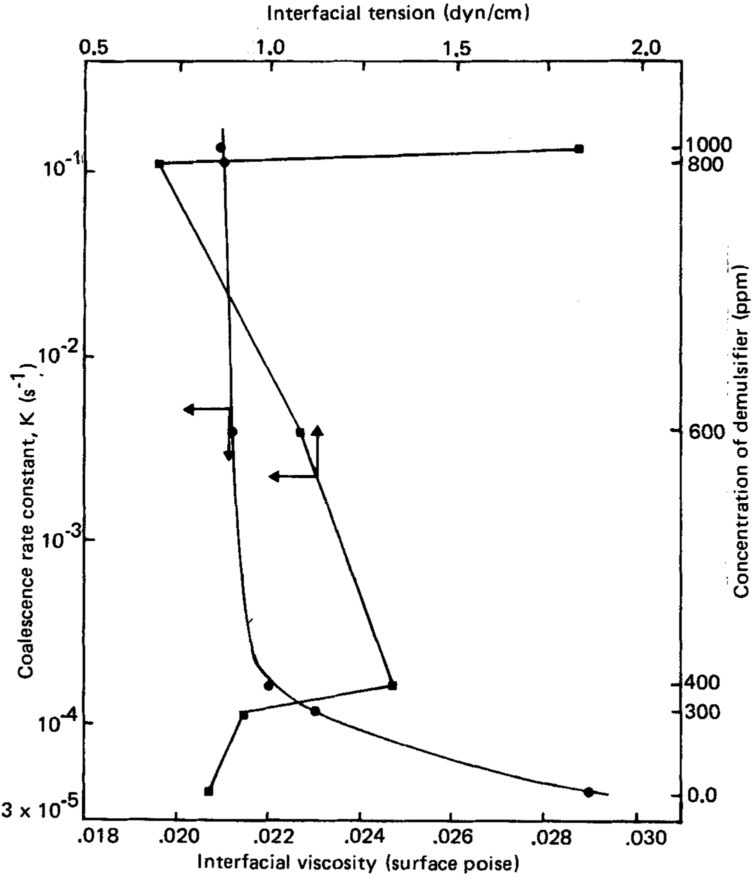

FIG. 5. Change of interfacial viscosity and interfacial tension with the concentration of demulsifier and coalescent rate constant $\underline{K}$.

different temperatures. The initial slopes increase with increasing temperature, showing an improved rate of coalescence with a rise in temperature. Figure 7 is a plot of the flocculation rate constant vs the reciprocal of the temperature. This plot is a straight line, indicating that the flocculation rate constant has an "Arrhenius-type" dependence on temperature. A similar observation has been made by Vold et al. (*16*) for ultracentrifugal demulsification. The slope of the plot if 6.86 kcal/gmol, which is the apparent activation energy of flocculation.

Figure 8 shows the variation of interfacial viscosity with temperature. The interfacial viscosity decreases with increasing temperature. This trend is in

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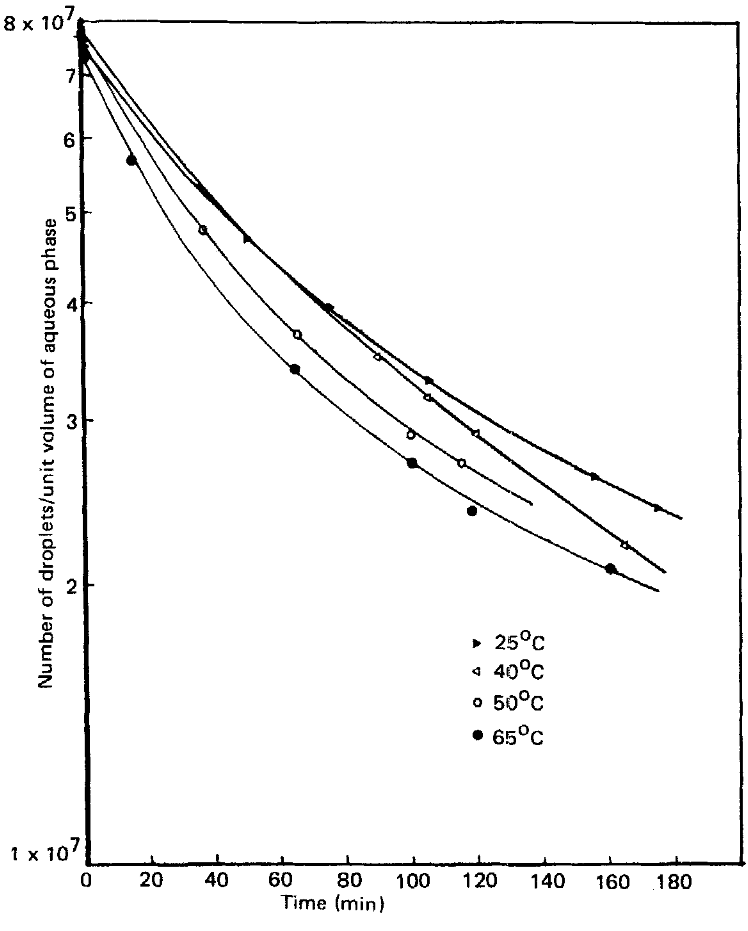

FIG. 6. Coalescence behavior at different temperatures.

TABLE 3

Variation of the Initial Coalescence Rate with Temperature

Temperature (°C)	Initial slope (s^{-1})
25	1.67×10^{-4}
40	1.87×10^{-4}
50	2.25×10^{-4}
65	2.76×10^{-4}

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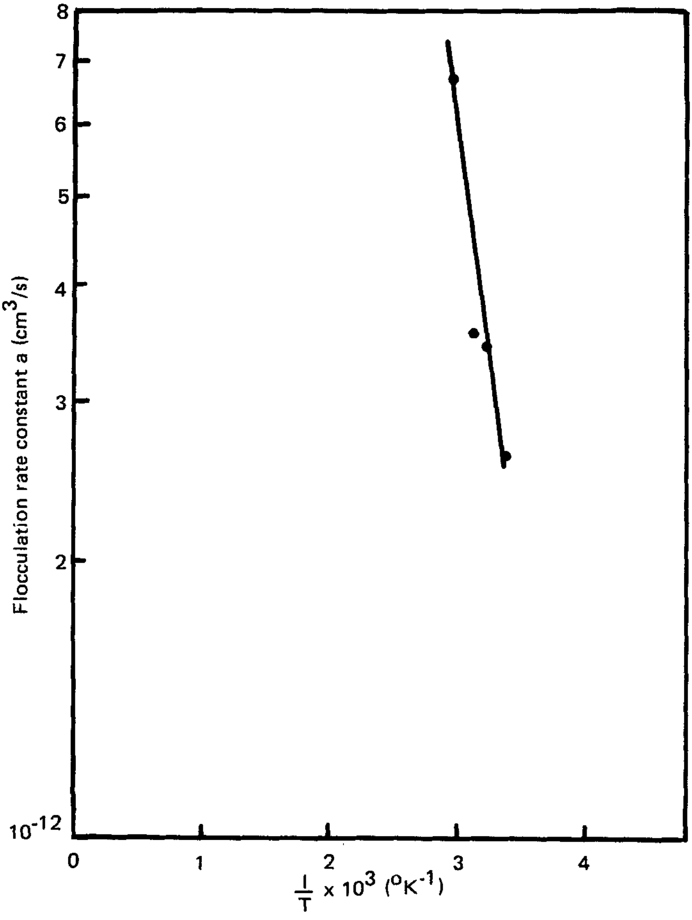

FIG. 7. Effect of temperature on the flocculation rate constant.

agreement with the coalescence behavior since an increase in temperature lowers the viscosity of the two phases, thereby facilitating the film drainage between the emulsion droplets.

Mode of Addition of Demulsifier

We compared the flocculation behavior of two systems, one in which the demulsifier was added prior to homogenization (System A) and the other in which the demulsifier was added after homogenization (System B). Both

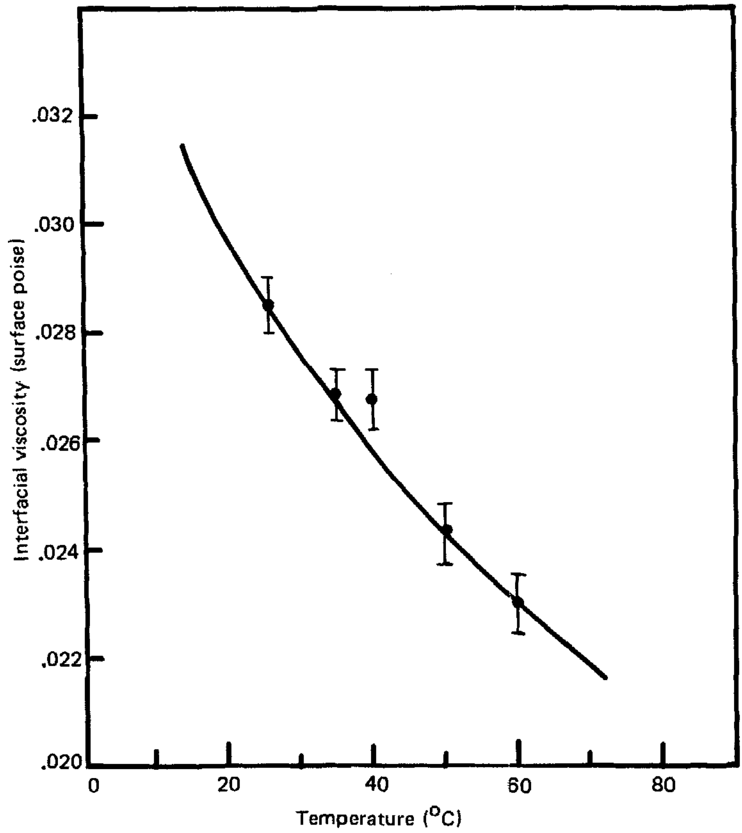

FIG. 8. Effect of temperature on the interfacial viscosity.

Systems A and B contained a 10% water-in-oil emulsion stabilized by a 1.5% concentration of Span-60/Tween-60 and both were maintained at 50°C. A 600 ppm of the demulsifier blend was added to System A before homogenization of the phases and to System B after the phases were homogenized. Figure 9 shows the initial drop size distribution of both the systems. The curve for System A is shifted toward larger droplet sizes as compared to System B. This means that System A exhibits a better coalescence rate than System B. This observation is reasonable since the addition of demulsifier prior to homogenization permits a better dispersion of the demulsifier molecules and hence a better effectiveness of the demulsifier. In comparison, the demulsifier molecules in System B are only dispersed by

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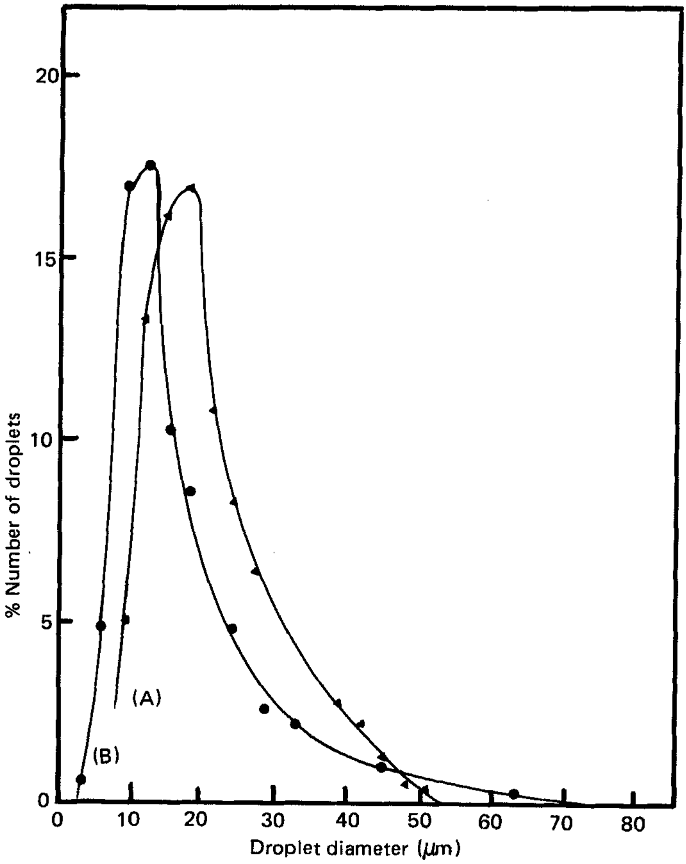

FIG. 9. Drop size distribution for System A (▲) where the demulsifier is added before homogenization and System B (●) where the demulsifier is added after homogenization.

diffusion aided by mild agitation. Table 4 gives the flocculation rate constants and the initial slopes for both systems.

Agitation

A 600 ppm of the demulsifier blend was added to a 10% w/o emulsion stabilized by 1.5% of Span-60/Tween-60 and the system was maintained at 50°C. The emulsion system was agitated at speeds varying from 30 to 140 rpm. Figure 10 is a plot of log N vs time with the agitation speed as a parameter. Table 5 lists the initial slopes which reveal that the overall

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TABLE 4
Comparison of Intitial Coalescence Rate and Flocculation Rate Constant for Systems A and B

System	Initial slope (s^{-1})	Flocculation rate constant (cm^3/s)
A	3.78×10^{-4}	5.38×10^{-12}
B	2.25×10^{-4}	3.52×10^{-12}

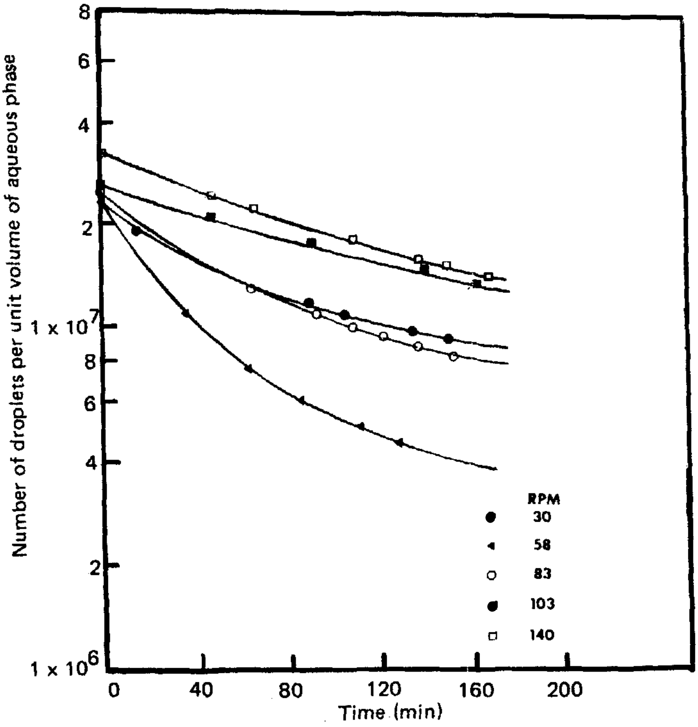

FIG. 10. Coalescence behavior with the speed of agitation as a parameter.

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TABLE 5
Effect of Agitation on Coalescence Rate

Agitation speed (rpm)	Initial slope (coalescence rate constant) (s^{-1})
0	1.19×10^{-4}
30	1.60×10^{-4}
58	3.88×10^{-4}
83	1.91×10^{-4}
103	1.00×10^{-4}
140	0.75×10^{-4}

coalescence rate increases with agitation speed until it attains a maximum value at 58 rpm. As the speed of agitation is increased further, the initial slope decreases continuously. Figure 11 shows the variation of the flocculation rate constant vs the speed of agitation. The flocculation rate constant goes through a pronounced maximum at a critical speed of 58 rpm. The existence of this maximum can be explained by the mechanism of aggregation of the droplets. We propose a mechanism of aggregation–redispersion as shown in Fig. 12. At low speeds of agitation, aggregation is the predominant mechanism, while at high speeds the mechanism of redispersion of the flocculated droplets prevails. Between these two extremes there exists a critical speed for which the flocculation rate constant is maximum. Operation at the optimum speed of agitation gives best overall coalescence rates.

Solids

Different amounts of solid particles (spent shale dust obtained from Exxon R&E Co.) of 4 μm average diameter and 2.610 g/cm^3 density were added to the solids-free shale oil before the emulsions were prepared. The photomicrographic analysis results are shown in Fig. 13. Table 6 lists the initial slopes which depict a decrease in coalescence rate with an increase in solids concentration. The systems we studied were all flocculation rate controlling. There is very little change in coalescence behavior as the solids concentration is increased to 0.1% (w/w). Beyond 0.1% (w/w) solids, the coalescence rate decreases dramatically as can be seen from a plot of the flocculation rate constant with the weight percent of solids (Fig. 14). At low solids

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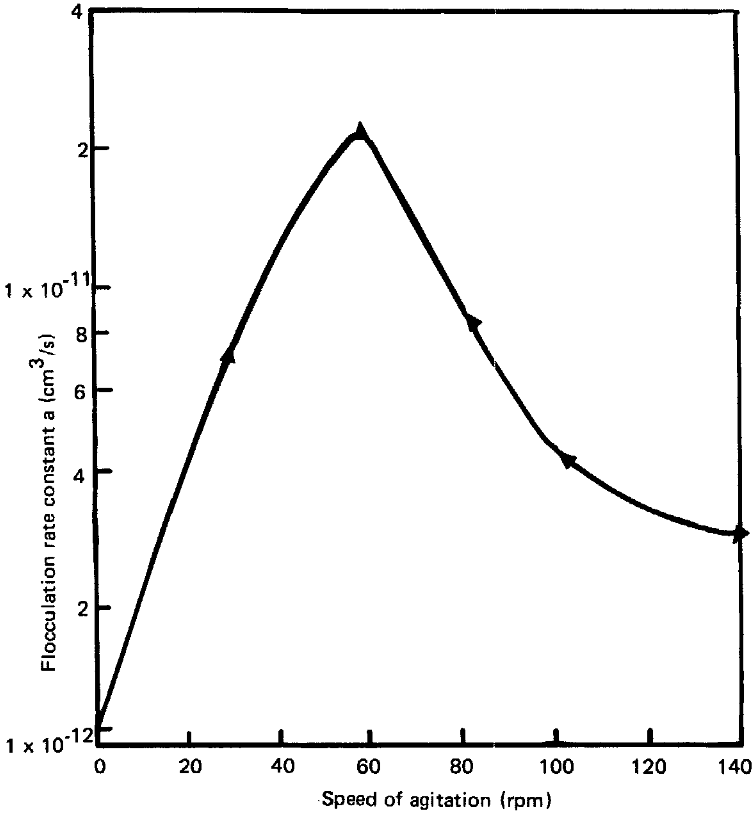

FIG. 11. Variation of the flocculation rate constant with the speed of agitation.

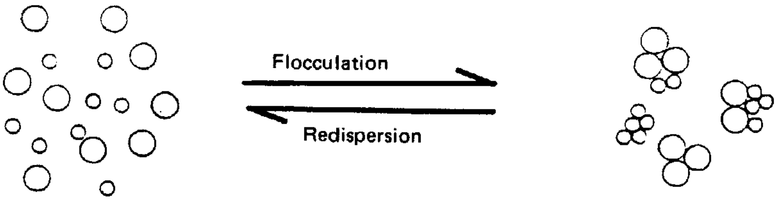

FIG. 12. Flocculation–redispersion mechanism.

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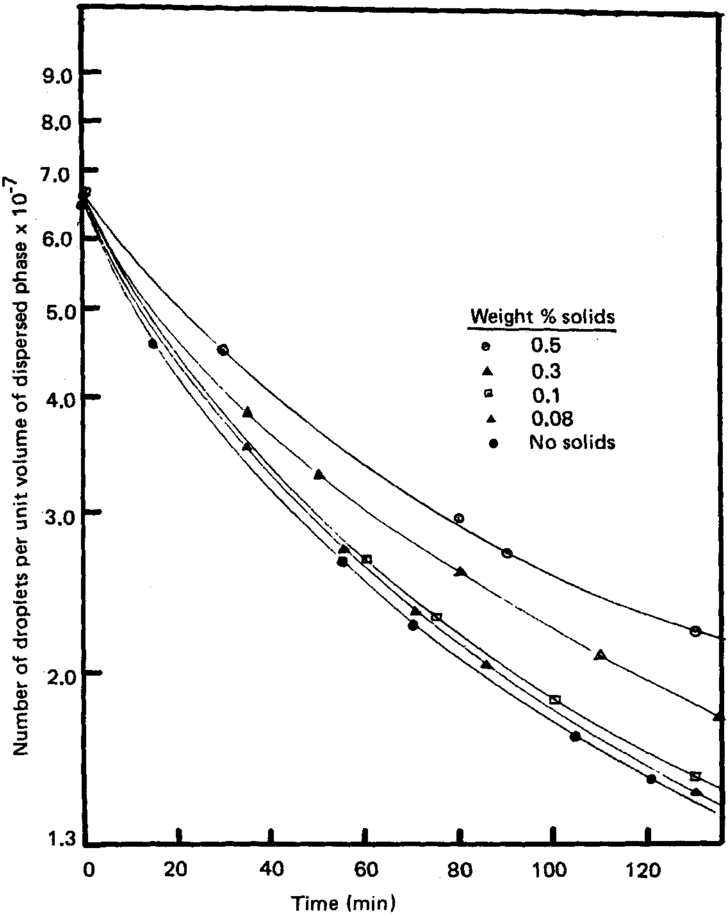

FIG. 13. Coalescence behavior in the presence of solids.

TABLE 6
Variation of the Initial Coalescence Rate Constant with the Weight Percent of Solids

Wt% of solids	Initial coalescence rate constant (s^{-1})
No solids	4.59×10^{-4}
0.08	4.31×10^{-4}
0.1	3.63×10^{-4}
0.3	3.14×10^{-4}
0.5	2.30×10^{-4}

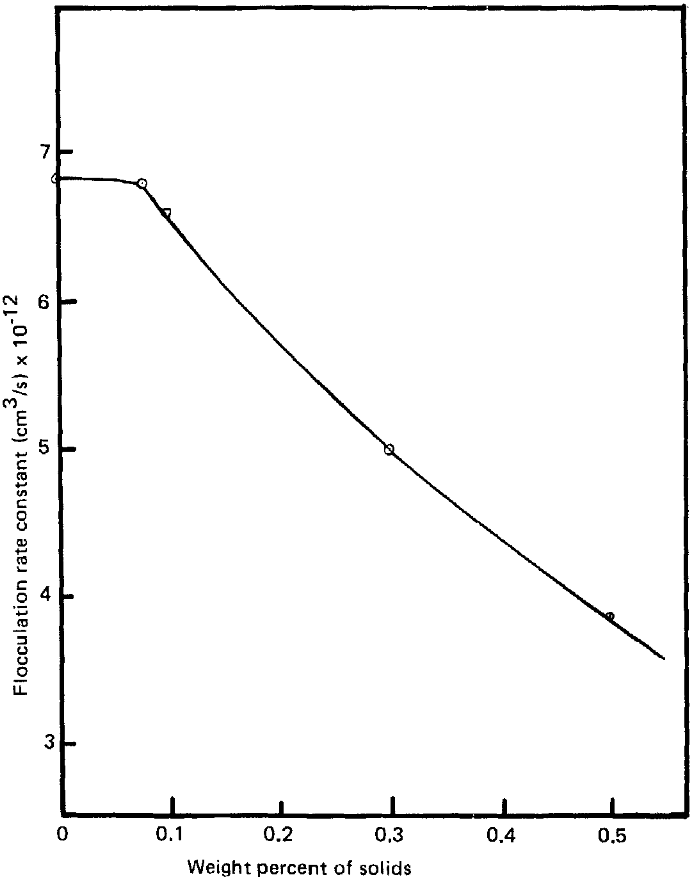

FIG. 14. Variation of the flocculation rate constant with the concentration of solids.

concentration there are not enough particles to cover the droplet surface and hence the coalescence rate does not drop very much, but when the interface is saturated (at concentrations in excess of 0.1%), the resistance to drop–drop coalescence increases sharply due to the rigid nature of the interface. The coalescence rate is dependent upon the competition between demulsifier molecules and solid particles to reach the droplet surface. A detailed study of the nature and behavior of such particles in liquid–liquid systems is underway in our laboratory (*17*).

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CONCLUSIONS

The photomicrographic technique was employed to study the stability of water-in-shale oil emulsions. The coalescence and flocculation rates were determined at different concentrations of demulsifier. From these coalescence measurements we found the optimum concentration of demulsifier for the highest coalescence rate.

The interfacial tension and interfacial viscosity were measured for the shale oil–water interface. A qualitative correlation was found between the interfacial viscosity and the rate of coalescence. The interfacial tension, however, did not correlate. The relation between interfacial viscosity and the rate of coalescence enables us to select and optimize demulsifier systems.

Our study of the coalescence behavior and interfacial viscosity at different temperatures revealed that the rate of coalescence increased and the interfacial viscosity decreased with an increase in temperature.

A comparison of the rates of coalescence of two systems was made: one where the demulsifier was added before homogenization and the other where the demulsifier was added after homogenization. Our experiments revealed that the coalescence rates were enhanced when the demulsifier was added prior to homogenization.

The flocculation rate constant goes through a pronounced maximum with an increase in the speed of agitation of the emulsion. This suggests that there exists an optimum speed of agitation for a given system and that the overall rate of emulsion breakdown is greatest at this speed.

The presence of solid particles at the oil–water interface can dramatically alter the stability of emulsions. In our system we observed that at a solids concentration greater than 0.1%, the coalescence rate dropped significantly.

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