Pipeline Flow of Unstable and Surfactant-Stabilized Emulsions

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The literature available on pipeline flow behavior of emulsions is reviewed critically. New results concerning the laminar and turbulent flow behaviors of unstable (without any added surfactant) and surfactant-stabilized water-in-oil emulsions are presented. The unstable emulsions exhibit drag reduction behavior in turbulent flow; the measured friction factors fall well below the values expected on the basis of the laminar flow properties. Unstable water-in-oil emulsions exhibit much stronger drag reduction activity than the unstable oil-in-water emulsions. The drag reduction activity diminishes (in some cases vanishes completely) upon the addition of a surfactant to the system.

Introduction

There is a substantial amount of literature published on concurrent flow of oil and water in pipelines, but for the most part, it involves separated flow such as annular or stratified flow of oil and water phases (Russell, 1959; Russell and Charles, 1959; Charles et al., 1961; Govier et al., 1961; Charles and Redberger, 1962; Gemmel and Epstein, 1962; Achutaramayya and Sleicher, 1969; Hasson et al., 1970; Soot and Knudsen, 1972; Guzhov et al., 1973; Mukherjee et al., 1981). Only a few articles have been published on pipeline flow of well-dispersed systems such as emulsions (Baron et al., 1953; Cengel et al., 1962; Faruqui and Knudsen, 1962; Ward and Knudsen, 1967; Zakin et al., 1979; Pal, 1987). Even these have been restricted to oil-in-water (O/W) type of emulsions, which consist of oil droplets as the dispersed phase and water as the continuous phase.

To our knowledge, little or no work has been reported on pipeline flow of water-in-oil (W/O) type of emulsions (where water droplets form the dispersed phase and oil forms the continuous phase) although such emulsions are equally important from a practical point of view; for example, most of the world's crude oil is produced in the form of water-in-oil emulsions rather than oil-in-water emulsions (Steinhauff, 1962; Alvarado and Marsden, 1979). Thus, understanding of the flow characteristics of water-in-oil emulsions is important for the design and operation of production gathering facilities and emulsion pipelines.

The main objectives of this work are: to review critically the literature available on pipeline flow of emulsions; to investigate the pipeline flow behavior (laminar and turbulent) of unstable water-in-oil emulsions without any added surfactant; and to

study the influence of surfactant on the pipeline flow behavior of water-in-oil emulsions.

Literature Review

Based on theoretical arguments, Baron et al. (1953) proposed that emulsions can be considered as pseudohomogeneous fluids (one can apply the usual single-phase flow equations using averaged fluid properties) provided that the drag force acting on the droplets is larger than the inertial force. They also carried out an experimental study of turbulent behavior of unstable (without any surfactant) oil-in-water emulsions in a pipeline. The emulsions were prepared from carbon tetrachloride and tap water. The experimental data of pressure loss vs. flow rate were used to calculate the effective viscosities of emulsions from the single-phase friction factor vs. the Reynolds number relationship. The effective viscosities calculated in this manner were found to be close to the values predicted from the empirical viscosity equation proposed by Eilers (1941).

Cengel et al. (1962) studied the laminar and turbulent flow behaviors of unstable oil-in-water emulsions (again without any added surfactant). The oil used was shellsoly, a kerosene-like solvent of viscosity 0.976 mPa·s at 21.67°C. The measured pressure loss data were used to calculate the effective viscosities from the well-known single-phase flow equations (Hagen-Poiseuille equation in laminar flow and Blasius friction factor equation in turbulent flow). The viscosities calculated from vertical turbulent flow data were found to be considerably lower than the corresponding laminar viscosities, and the difference increased with an increase in the dispersed-phase (oil)

concentration. The lower values of viscosities obtained from turbulent data indicate that pressure drop in turbulent flow of emulsions (at a given flow rate) was less than the value expected on the basis of laminar viscosity. In other words, emulsions exhibited drag reduction behavior in turbulent flow. Although the authors offered no explanation for this deviation, it is likely to be due to coalescence and breakup of droplets. The dispersed droplets of the unstable emulsions continually undergo coalescence and breakup processes in a turbulent field. Several articles (Hinze, 1955; Shinnar and Church, 1960; Shinnar, 1961; RajaGopal, 1968; Madden and Damerell, 1962; Howarth, 1964) investigate these processes in turbulent flow of dilute emulsions, although most of them have aimed at prediction of either maximum droplet size or the coalescence frequency of droplets in a turbulent field. In the presence of dynamic coalescence and breakup processes, the turbulence of the carrier fluid (continuous phase) is likely to be modified significantly, resulting in drag reduction behavior. However, the exact mechanism by which the dynamic coalescence and breakup processes interact with the turbulence of the carrier fluid is not clear at the present time.

Faruqui and Knudsen (1962) measured the velocity profiles and pressure losses in vertical turbulent flow of unstable oil-in-water emulsions. The chemical composition of the emulsions was the same as that of Cengel et al. emulsions. The measured velocity profile data (plus pressure-loss data) were used to calculate the effective viscosities of the emulsions from the well-known logarithmic velocity law:

$$u^{+} = 5.75 \log_{10}(y^{+}\eta) + (5.5 - 5.75 \log_{10}\eta)$$
 (1)

where u^+ is dimensionless velocity, y^+ is dimensionless distance, and η is emulsion viscosity. The viscosity of the emulsion was obtained from the intercept of u^+ vs. $y^+\eta$ plot on a semilog scale.

The viscosities calculated from the above equation were found to be independent of the flow rate and were in good agreement with the viscosities obtained by Cengel et al. for the same emulsions (from vertical turbulent flow pressure-loss data). These observations led the authors to the conclusion that their emulsions behaved as truly single-phase fluids. This conclusion, however, is doubtful in light of our earlier discussion that these emulsions exhibited drag reduction behavior in turbulent flow.

Ward and Knudsen (1967) determined the pressure losses, the velocity profiles, and the droplet size distributions in turbulent flow (vertical pipeline) of unstable oil-in-water emulsions. Three different oils were used: shellsolv, light oil, and heavy oil. The viscosities of these oils were 0.95, 13 and 162 mPa·s, respectively, at 23.3°C. The effective viscosities of the emulsions were calculated from turbulent flow data in two different ways: from pressure-loss data using the Blasius friction factor equation and from logarithmic velocity law. For the shellsolv and the light-oil emulsions, the viscosities calculated from the two methods were comparable. The heavy oil emulsions behaved quite differently from the shellsolv and light-oil emulsions. They differed in the following respects: a) the effective viscosity obtained from the Blasius friction factor equation was nearly independent of the oil concentration and even showed a tendency to decrease at high concentrations (the viscosity of other emulsions increased with oil concentration);

b) the viscosities calculated from the logarithmic velocity law were found to vary widely with the flow rate. The droplet size data for the emulsions indicated that the droplet sizes for the heavy-oil emulsions were significantly larger than those of the light-oil and shellsolv emulsions. Therefore, the authors attributed the anomalous behavior of the heavy-oil emulsions to the large droplet size.

However, the anomalous behavior of heavy oil emulsions observed in turbulent flow could be due to modification of the turbulence of the carrier fluid, caused by dynamic coalescence and breakup processes. It should further be noted that the shellsolv (and likely light-oil) emulsions also exhibited anomalous behavior in that the effective viscosities calculated from turbulent data were lower than the corresponding laminar viscosities; only the degree of turbulence modification appeared to differ from that of the heavy-oil emulsions under consideration. This difference is quite natural as the stability characteristics (hence, the nature of coalescence and breakup processes) of emulsions are expected to vary from one oil to another.

Pal (1987) also investigated the laminar and turbulent behaviors of unstable oil-in-water emulsions. Horizontal pipelines with three different internal diameters were used: 8.9 mm, 12.6 mm, and 15.8 mm (the pipes were hydraulically smooth). The emulsions were prepared using tap water and a refined mineral oil (Bayol-35) of viscosity 2.41 mPa·s at 25°C. The dispersed-phase concentration of the oil-in-water emulsions was varied from 0 to 72.31% vol. Fully developed turbulent flow, however, could not be achieved for emulsions with oil concentrations greater than 55.1% vol.; the higher concentration emulsions were too viscous to achieve fully developed turbulent flow. The effective viscosities calculated from the laminar data (using Hagen-Poiseuille law) were clearly much higher than those obtained from the turbulent data (using Blasius friction factor equation), and the difference increased with the increase in the dispersed-phase (oil) concentration much like the emulsions of Knudsen and coworkers discussed earlier.

Figure 1 summarizes the literature results for the unstable oil-in-water emulsions. The relative viscosity is plotted as a function of the dispersed-phase (oil) concentration. The relative viscosities calculated from the laminar data (Hagen-Poiseuille law) and from the turbulent data (Blasius equation) are both included (if available). The following points are to be noted from Figure 1: (a) the relative viscosities obtained from the laminar data of different studies appear to follow the same relative viscosity curve even though different oils were used (as the dispersed phase). This is not surprising as the viscosity of the oil plays only a minor role in determining the viscosity of the oil-in-water emulsions. According to Taylor's equation (1932) for the relative viscosity.

$$\eta_r = 1 + 2.5 \left[\frac{1 + 0.4(\eta_c/\eta_d)}{1 + (\eta_c/\eta_d)} \right] \phi$$
(2)

the factor multiplying ϕ varies only from 2.5 to 1.75 over a wide range of η_c/η_a from 0 to unity (η_c is the continuous-phase viscosity and η_a is the dispersed-phase viscosity); (b) the relative viscosities obtained from the turbulent data of Cengel et al. (1962), Faruqui and Knudsen (1962), Ward and Knudsen (1967) (except heavy-oil emulsions), and Pal (1987) all follow the same

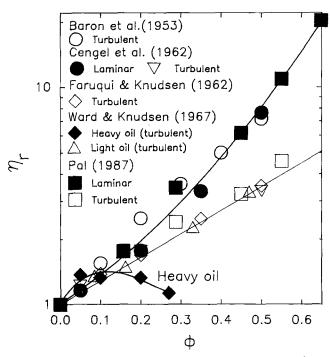


Figure 1. Literature data for the relative viscosity of unstable oil-in-water emulsions.

curve, but the heavy-oil emulsions give much lower viscosities. Also, the relative viscosities of Baron et al. (1953) emulsions (determined from turbulent data) give much higher values; they tend to agree with those obtained from the laminar data of other workers. This indicates that turbulence modulation was negligible in the case of Baron et al. emulsions.

The review of the literature discussed so far has focused only on the unstable (without any added surfactant) oil-inwater emulsions. Recently, several articles have been published on the pipeline flow behavior of surfactant-stabilized oil-inwater emulsions.

Zakin et al. (1979) studied the laminar and turbulent flow behaviors of surfactant-stabilized oil-in-water emulsions. The emulsions were prepared from four different mineral oils varying in viscosity from 1.4 to 113 mPa·s at 25°C. The oil concentration was varied from 50 to 75% wt. The rheological data indicated that the emulsions were quite non-Newtonian. In the laminar region, the data followed the usual relation for non-Newtonian fluids:

$$f = 16/N_{Re,n} \tag{3}$$

where f is the friction factor and $N_{Re,n}$ is a generalized Reynolds number. The turbulent flow data, however, were consistently lower than those predicted from the Dodge-Metzner (D-M) correlation (Dodge and Metzner, 1959) by 8 to 26%.

The drag reduction behavior was thought to be due to viscoelastic effects in emulsions, perhaps because dilute polymer solutions are well known to exhibit drag reduction phenomenon due to viscoelasticity (Metzner and Park, 1964; Seyer and Metzner, 1967, 1969). Viscoelastic effects in emulsions can arise due to elasticity of either individual droplets or a microstructure formed between the droplets. It is doubtful if droplet

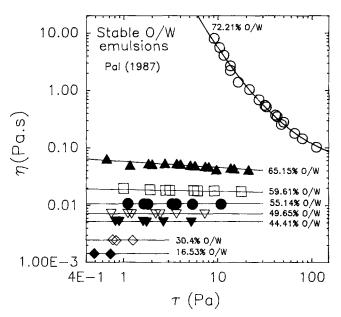


Figure 2. Viscosity as a function of shear stress for stable oil-in-water emulsions (Pal, 1987).

elasticity plays any role in drag reduction, especially in the case of the stable emulsions, which are expected to have much smaller droplets. Furthermore, it is doubtful that droplet-droplet microstructure can exist at high shear rates encountered in turbulent flows. However, an alternative mechanism whereby turbulence in emulsion flow is modified due to dynamic coalescence and breakup processes is quite realistic. This mechanism can explain not only why emulsions do exhibit drag reduction but also why emulsions prepared from different oils exhibit different degrees of drag reduction. On the basis of this mechanism, one would expect a significant decrease in drag reduction upon the addition of a surfactant to the same system, because the surfactant would inhibit dynamic coalescence and breakup processes. It should further be noted that the presence of a surfactant may not completely eliminate coalescence of droplets. The stability of the emulsions (hence coalescence) depends strongly on the nature and concentration of the surfactant and the chemical nature of both dispersed and continuous phases.

Pal (1987) also studied the laminar and turbulent flow behaviors of surfactant-stabilized oil-in-water emulsions. The data were collected from horizontal pipelines with five different IDs (7.15 mm, 8.9 mm, 12.6 mm, 15.8 mm, and 26.54 mm). The emulsions were prepared using tap water and a light mineral oil (same oil as that used in our earlier study on unstable oil-in-water emulsions). The surfactant used was water-soluble Triton X-100 which is nonionic in nature. The concentration of the surfactant in water was kept at 1% wt. The dispersed-phase (oil) concentration was varied from 0 to 72.21% vol. In addition to the pipeline data, the rheological data were measured using a coaxial cylinder viscometer; the information regarding the droplet sizes was obtained by taking photomicrographs which indicated that the droplet size of the emulsions ranged from about 1 to 12 μ m.

The emulsions were Newtonian up to an oil concentration of 55.14% vol.; as shown in Figure 2, the viscosities were

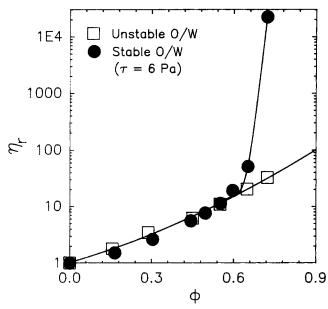


Figure 3. Comparison of relative viscosities for stable and unstable oil-in-water emulsions (Pal, 1987).

Unstable O/W emulsion data from laminar pipeline flow; stable

O/W emulsion data from coaxial cylinder viscometer.

independent of the shear stress (shear rate) for these emulsions. The higher concentration emulsions were non-Newtonian pseudoplastic: that is, the viscosity decreased with an increase in the shear stress. The degree of non-Newtonian character increased with the concentration; the highest concentration (72.21% vol.) emulsion even showed the presence of a yield stress. Figure 3 compares the relative viscosities of stable and unstable oil-in-water emulsions studied by Pal. Interestingly, the unstable and stable emulsions have nearly the same relative viscosities up to an oil concentration of about 60% vol. At higher concentration, however, the relative viscosities of the two systems differ sharply; the relative viscosity of the stable emulsion rises dramatically with the concentration, whereas the rate of increase in the relative viscosity of the unstable emulsions remains nearly the same (as that at low concentrations). This is quite an expected behavior because surfactantstabilized emulsions behave more like suspensions of rigid particles; consequently, particle-particle hydrodynamic interactions (due to crowding/jamming of particles) are dominant at high concentrations, whereas the large droplets of the unstable emulsions deform readily and therefore the emulsion viscosities are low. Note that, in principle, the relative viscosity of the unstable emulsions should be lower than that of the stable emulsions even at low concentrations of dispersed-phase because of the internal circulation effect (internal-circulation is significantly inhibited in surfactant-stabilized emulsions). The probable reason why we do not see any effect of internal circulation is the small value of the viscosity ratio, η_c/η_d ; the larger this ratio, the more significant is the internal circulation effect (in the present case, the viscosity ratio is about 0.38). Another important reason why one may not see any effect of internal circulation is the presence of impurities in the fluids.

The pipeline data for the stable and the unstable oil-in-water emulsions investigated by Pal are compared in Figure 4. The

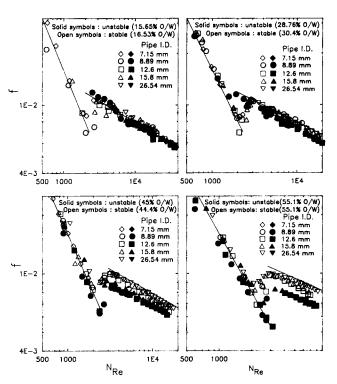


Figure 4. Friction factor vs. Reynolds number for stable and unstable oil-in-water emulsions (Pal, 1987).

data are shown for emulsions with oil concentrations up to about 55% vol. only as fully developed turbulent flow data could not be obtained for emulsions with higher concentrations (also note that these emulsions were Newtonian). For the stable emulsions, the viscosity measured by a coaxial cylinder viscometer was used in the calculation of the Reynolds number. In the case of the unstable emulsions, the viscosity was determined from the pipeline data in the laminar regime using the Hagen-Poiseuille law. The laminar data from different diameter pipelines follow the standard friction factor relation:

$$f = 16/N_{Re} \tag{4}$$

For the stable emulsions, this implies that the rheological measurements from a coaxial cylinder viscometer can adequately predict the laminar flow behavior in pipelines. (It is obvious that the laminar pipeline data for the unstable emulsions would follow the above equation as the very same equation is used to determine the viscosity.) In the turbulent regime, the friction factors for the unstable emulsions fall somewhat below those of the stable emulsions. The difference also increases with the increase in the dispersed-phase concentration. This observation is consistent with the proposed mechanism that the turbulence of the carrier fluid of the emulsions is modified in the presence of dynamic coalescence and breakup processes; with the addition of a surfactant, the stability of the emulsions increases, inhibiting coalescence and breakup of droplets and, therefore, one would expect a decrease in drag reduction. It is interesting to note that with the addition of a surfactant, the emulsions nearly follow the commonly used equation for single-phase Newtonian fluids, that is, Blasius equation.

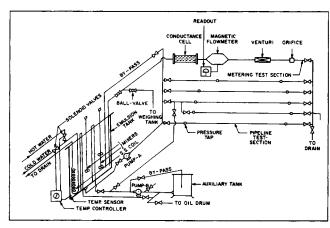


Figure 5. The flow rig.

Experimental Work

Apparatus

Figure 5 shows the flow rig that was designed and developed to allow investigation of the pipeline flow behavior of emulsions. Five different diameter pipeline test sections (stainless steel, seamless) were installed horizontally. The various dimensions of these test sections are summarized in Table 1. The flow rig also consisted of a metering test section where an orificemeter, a venturimeter, a magnetic flowmeter, and an in-line conductance cell were installed.

The emulsions were prepared in a large tank (capacity ≈ 1 m³) equipped with baffles, two high shear mixers, heating/cooling coil, and a temperature controller. The emulsion from the preparation tank was circulated to the pipeline test sections by a centrifugal pump. From the pipeline section, the emulsion was allowed to return to the mixing tank via the metering section where its flow rate was measured (the flowmeters were used only at high flow rates; low flow rates were measured directly by diverting the flow outside the flow loop into a weighing tank). The emulsions were circulated in the flow loop for more than 3 h before collection of any data. The pressure drop across the pipeline test section was measured by variable-reluctance-type pressure transducers. The output signals from the transducers were recorded by a microcomputer data-acquisition system.

Emulsion preparation

Two different sets of emulsions were prepared using tap water and a refined mineral oil (Bayol-35). The oil was supplied

Table 1. Various Dimensions of Pipeflow Test Sections

Pipe No.	ID (mm)	Entrance Length (m)	Actual Length of Test Section (m)	Exit Length (m)
1	8.89	0.89	3.35	0.48
2	7.15	1.07	3.05	0.46
3	12.60	1.19	2.74	0.53
4	15.8	1.65	2.59	0.56
5	25.54	3.05	1.22	0.67

by Esso Petroleum Canada; it had a density of 780 kg/m³ and a viscosity of 2.41 mPa·s at 25°C.

In one set of emulsions, no chemical-emulsifier (surfactant) was added so that the emulsions produced were unstable with respect to coalescence (emulsions readily separated into oil and water phases if left unagitated for sometime). The experiments in this set began with pure oil into which a required amount of water was added to prepare an emulsion. The concentration of water was varied from 0 to 52.1% vol. The emulsions were water-in-oil type until the inversion point (41.7% vol. water) where the water-in-oil emulsion inverted into the oil-in-water emulsion

For the other set of emulsions, a nonionic surfactant, namely SPAN 80 (sorbitan monooleate), was added to the oil. The concentration of the surfactant was kept at 1.5% wt. based on the oil phase. The flow-rig experiments began with a surfactant/oil solution and then a required amount of water was added to obtain a water-in-oil emulsion. The water-in-oil emulsions produced were very stable with regard to coalescence up to a water concentration of 25.85% vol. Upon further addition of water, phase inversion took place at a water concentration of 31.56% vol., resulting in a stable oil-in-water emulsion. The emulsion remained stable oil-in-water type when water concentration was increased further. The inversion of phases in the present set involved an intermediate stage where a multiple emulsion was formed (this emulsion consisted of multiple O/W/O droplets, that is, lots of tiny oil droplets were entrapped within large water droplets, which in turn were suspended in a continuum of oil).

For the stable emulsions, the rheological as well as the droplet size data were measured in addition to the pipeline data. The rheological data were collected in a coaxial cylinder viscometer. The droplet sizes were measured by taking photomicrographs of the emulsion samples (diluted with the same continuous medium) using a Zeiss optical microscope equipped with a camera. For the unstable emulsions, only pipeline data were collected.

The experimental work was conducted at a constant temperature of 25°C (the temperature was maintained constant in the flow loop with the help of a temperature control arrangement installed in the emulsion preparation tank).

Detection of emulsion type

The electrical conductance of emulsions was continuously monitored with an in-line conductance cell. Water-in-oil emulsions had a very low conductance (as nonconductive oil formed the continuous phase), whereas oil-in-water emulsions had a high conductance value. Upon inversion of phases, a sudden change in the conductance occurred.

The magnetic flowmeter also served as an indicator of the emulsion type. This meter functioned only when the emulsions were oil-in-water type.

A phase dilution test (Becher, 1977) was also performed from time to time. This method is based on the fact that an emulsion is readily dilutable by the liquid that constitutes the continuous phase. A small amount of the emulsion was added to two beakers containing pure oil and pure water, respectively. When the emulsion readily dispersed in oil but did not disperse in water, it indicated that the emulsion was water-in-oil type. If the emulsion readily dispersed in water, the emulsion was oil-in-water type.

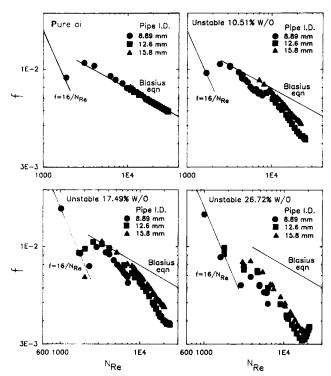


Figure 6. Friction factor vs. Reynolds number for unstable water-in-oil emulsions.

Results and Discussion

Unstable water-in-oil emulsions

The pipeline data for the unstable water-in-oil emulsions (as well as for the unstable oil-in-water emulsions obtained after inversion) are shown in Figures 6 and 7. The data are plotted as friction factor vs. Reynolds number. For the Reynolds number calculation, viscosity is determined from the laminar data by fitting the data with Eq. 4. In the turbulent regime, unstable water-in-oil emulsions exhibit strong drag reduction characteristics. The measured friction factors fall well below the Blasius equation:

$$f = 0.079 N_{Re}^{-0.25} \tag{5}$$

There is clearly some diameter dependence present as well. The smaller-diameter pipe gives larger drag reduction when comparison is made at the same Reynolds number. This agrees with the drag reduction behavior of dilute polymer solutions. Furthermore, the degree of drag reduction increases substantially with the increase in the dispersed-phase (water) concentration. It should also be noted that the transition from laminar to turbulent regime shifts to higher Reynolds numbers (at least for higher water concentration emulsions). The unstable oil-in-water emulsions, obtained after inversion, also exhibit drag reduction (as expected) but to a lesser degree; the flow behavior of these unstable oil-in-water emulsions is similar to what we discussed earlier (Pal, 1987).

Figure 8 shows the plot of viscosity (obtained from laminar data) as a function of water concentration. The viscosity increases initially with an increase in the dispersed-phase concentration, but the rate of increase (of viscosity) is moderate. At a water concentration of 41.7% vol., a sudden increase in

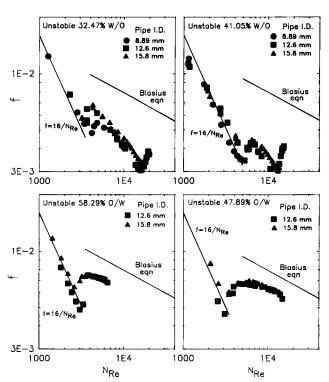


Figure 7. Friction factor vs. Reynolds number for unstable water-in-oil and unstable oil-in-water emulsions.

the viscosity occurs due to inversion of water-in-oil emulsion to oil-in-water emulsion. With further increase in water concentration, the viscosity decreases due to dilution effect.

In Figure 9, we have compared the relative viscosities calculated from laminar data with those obtained from turbulent data (using Blasius equation). The relative viscosity obtained from the turbulent data is not only a decreasing function of

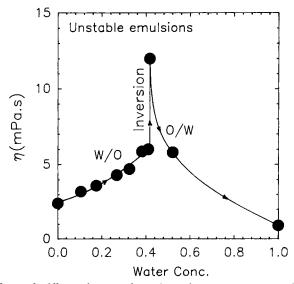


Figure 8. Viscosity as a function of water concentration for unstable emulsions (from laminar pipeline flow).

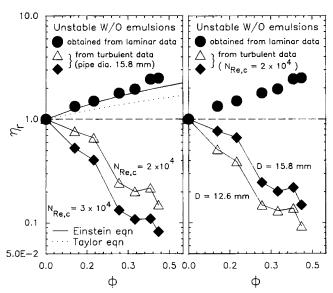


Figure 9. Relative viscosities calculated from laminar and turbulent pipeline data for unstable waterin-oil emulsions.

the dispersed-phase concentration (a behavior similar to unstable heavy oil-in-water emulsions of Ward and Knudsen), but also varies with the flow rate (Reynolds number) and pipe diameter. Also, the difference between the relative viscosities obtained from laminar and turbulent data increases with an increase in the water concentration. Interestingly, the relative viscosities obtained from laminar data tend to agree with the Einstein equation (Einstein, 1956):

$$\eta_r = 1 + 2.5\phi \tag{6}$$

up to a fairly high value of ϕ .

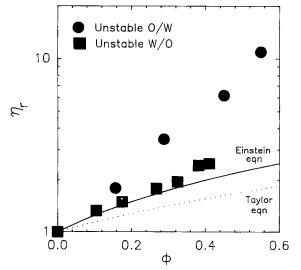


Figure 10. Relative viscosities for unstable water-in-oil and unstable oil-in-water emulsions.

Data from laminar pipeline flow; Taylor equation is plotted for W/O emulsions.

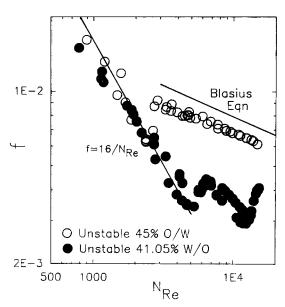


Figure 11. Friction factor vs. Reynolds number for unstable water-in-oil and unstable oil-in-water emulsions.

Figure 10 compares relative viscosities for the unstable water-in-oil emulsions with those for unstable oil-in-water emulsions (Pal, 1987). The relative viscosities for the oil-in-water emulsions fall well above those of the water-in-oil emulsions. The likely cause for this is the internal circulation effect. The viscosity ratio η_c/η_d for the water-in-oil emulsions is much higher (2.67) than that of the oil-in-water emulsions (0.38); the higher this ratio, more significant is the internal circulation effect (see Taylor equation, Eq. 2) and hence lower are the viscosities.

Figure 11 compares the friction factor vs. Reynolds number data for the unstable water-in-oil emulsion and the unstable oil-in-water emulsion at nearly the same dispersed-phase concentration. Clearly, the degree of drag reduction in water-inoil emulsion is much higher. This is probably due to different stability characteristics of water-in-oil and oil-in-water emulsions. In the case of the unstable oil-in-water emulsions, resistance to coalescence can occur due to electrical double-layer effect; the double layer may form due to preferential adsorption of ions from the continuous water phase (Sherman, 1970; Tadros and Vincent, 1983). Collins and Knudsen (1970) also noted that the unstable oil-in-water emulsions prepared from tap water and oil (without any added surfactant) exhibit negligible coalescence under turbulent flow conditions. In the case of unstable water-in-oil emulsions, the continuous phase is nonpolar. When the continuous phase is nonpolar, dispersed droplets tend to flocculate (hence coalesce) rather rapidly due to the very diffuse character of the double layer (if any) and the absence of a significant potential energy barrier (Sherman,

Surfactant-stabilized water-in-oil emulsions

The emulsions with added surfactant were stable water-inoil type for water concentrations less than 25.85% vol. (as discussed earlier). The emulsion at 25.85% vol. water concentration was initially water-in-oil type but later turned into a

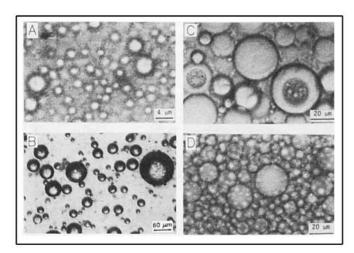


Figure 12a. Typical photomicrographs for surfactantstabilized emulsions.

(A) Stable 25.85% W/O emulsion; (B) multiple emulsions (water concentration is 25.85% vol.); (C) 68.44% O/W emulsion; and (D) 44.9% O/W emulsion.

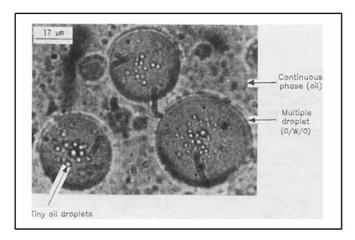


Figure 12b. Multiple emulsion droplets at higher magnification.

multiple emulsion (the data were collected for both stable 25.85% W/O emulsion as well as the multiple emulsion). Complete inversion of phases took place at a slightly higher water concentration (31.56% vol.). Direct microscopic observations indicated that significant changes in droplet sizes occurred near the inversion point. Figure 12a shows the photomicrographs of emulsions before and after inversion. The droplets of stable 25.85% W/O emulsion (photomicrograph A) are quite small (less than about 5 μ m); the multiple emulsion droplets (photomicrograph B) are very large (less than 120 µm); upon inversion to oil-in-water emulsion, the droplet sizes decrease (photomicrograph C, 68.44% O/W) and continue to decrease with further increase in water concentration (photomicrograph D. 44.9% O/W). The photomicrograph of the multiple emulsion at a higher magnification in Figure 12b shows the multiple character of the droplets clearly. The dramatic variations in the droplet sizes with the water concentration are further illustrated in Figures 13 and 14. Note that in Figure 14, the Sauter mean diameter (D_{32}) is plotted.

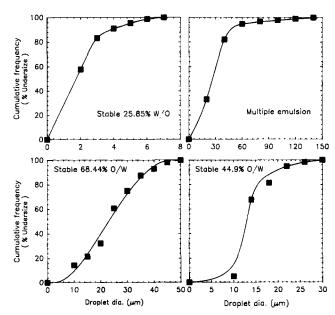


Figure 13. Droplet size distribution for surfactant-stabilized emulsions.

The viscosity for the emulsions as measured by a coaxial cylinder viscometer is shown in Figure 15 as a function of shear rate $(\dot{\gamma})$. The stable water-in-oil emulsions are Newtonian; viscosity is constant independent of the shear rate. The stable oil-in-water emulsion obtained after inversion was shear-thinning type initially at a dispersed-phase (oil) concentration of 68.44% vol. With further addition of water, the emulsion turned Newtonian at an oil concentration of 44.9% vol. The 68.44% O/W emulsion followed the power-law behavior:

$$\tau = K\dot{\gamma}^n \tag{7}$$

or

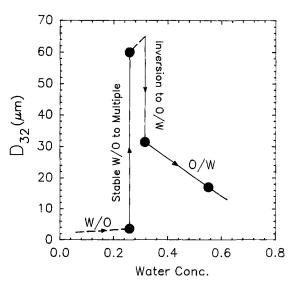


Figure 14. Sauter mean diameter (D_{32}) as a function of water concentration.

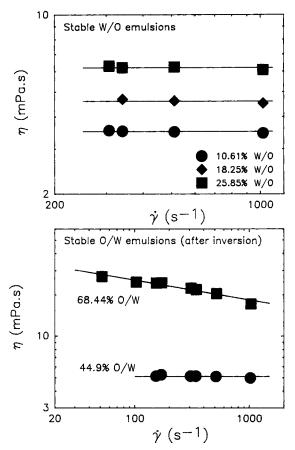


Figure 15. Viscosity as a function of shear rate for surfactant-stabilized emulsions.

$$\eta = K\dot{\gamma}^{n-1} \tag{8}$$

The power-law index (n) was 0.856. Figure 16 shows the viscosity as a function of water concentration. The viscosity of the water-in-oil emulsions increases with the water concentration at a moderate rate, but upon inversion to the oil-in-water emulsion there occurs a sudden increase in the viscosity; this is obviously due to a sharp increase in the dispersed-phase concentration of the emulsion. The viscosity then decreases with further increase in the water concentration due to dilution of the emulsion. A similar behavior was observed earlier in the case of unstable emulsions.

The friction factor vs. Reynolds number data for the surfactant-stabilized water-in-oil emulsions and for the stable oil-in-water emulsions (obtained after inversion) are shown in Figures 17 and 18. For most of the emulsions (except the multiple one), viscosity used in the calculation of the Reynolds number was obtained through the coaxial cylinder viscometer. In the case of the multiple emulsion, the effective viscosity was determined by fitting the laminar pipeline data with Eq. 4. For the non-Newtonian (power-law type) 68.44% O/W emulsion, the generalized Reynolds number was used.

It is obvious from the friction factor vs. Reynolds number plots that the surfactant-stabilized water-in-oil emulsions (as well as the stable oil-in-water emulsions obtained after inversion) exhibit little or no drag reduction. In the laminar regime, the friction factor data from various different diameter pipes

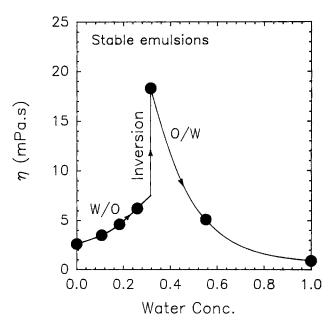


Figure 16. Viscosity as a function of water concentration for stable emulsions (from coaxial cylinder viscometer).

follow the commonly used equation for single-phase flows (Eq. 4). For the non-Newtonian emulsion, the data fall slightly above Eq. 3, but the deviation is only marginal. In the turbulent regime, the friction factor data from different diameter pipes follow the Blasius equation reasonably well. Note that even in

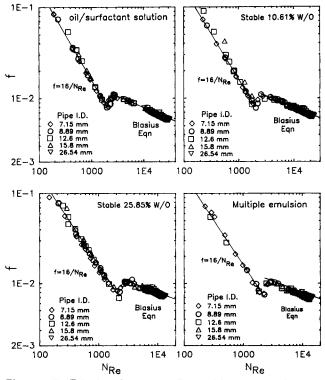


Figure 17. Friction factor vs. Reynolds number for surfactant-stabilized emulsions.

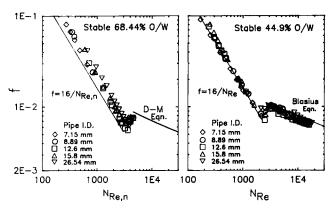


Figure 18. Friction factor vs. Reynolds number for surfactant-stabilized emulsions.

the case of the multiple emulsion, the drag reduction effect is negligible.

Conclusions

Based on the critical review of the literature and new experimental work, the following conclusions can be made regarding the pipeline flow behavior of liquid/liquid emulsions:

- The unstable oil-in-water emulsions (without any added surfactant) exhibit drag reduction behavior in the turbulent regime. The degree to which drag reduction occurs depends on the nature of the oil and the dispersed-phase concentration; the drag reduction activity becomes stronger with the increase in the dispersed-phase concentration.
- The unstable water-in-oil emulsions (without any added surfactant) also exhibit drag reduction phenomenon. Again, the degree of drag reduction increases with an increase in the dispersed-phase concentration. Also, the transition from laminar to turbulent regime is delayed. Upon comparing the unstable water-in-oil emulsions with the unstable oil-in-water emulsions (prepared from the same oil and water) at the same dispersed-phase concentration, the drag reduction activity in water-in-oil emulsions is much more severe.
- The surfactant-stabilized emulsions exhibit relatively little drag reduction. In some cases, the drag reduction activity vanishes completely (for example, the stable water-in-oil emulsions of this work show no drag reduction behavior). Therefore, the pipeline flow behavior of the surfactant-stabilized emulsions could be predicted reasonably well using the usual equations of single-phase flow.
- The drag reduction behavior observed in the emulsions is believed to be due to the turbulence modification of the carrier fluid (continuous phase) in the presence of dynamic coalescence/breakup processes. According to this mechanism, the drag reduction activity is expected to diminish upon the addition of a surfactant (as surfactant stabilizes the emulsion droplets against coalescence and hence inhibits coalescence/breakup processes). This is confirmed by the experimental results.

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Notation

D = pipe diameter

f = friction factor

K =consistency index in power law, Eq. 7

n = power law exponent, Eq. 7

 N_{Re} = Reynolds number $(\rho D\overline{V}/\eta)$ $N_{Re.c}$ = Reynolds number based on continuous phase viscosity $(\rho D\overline{V})^2$

 η_c

 $N_{Re,n}$ = generalized Reynolds number for power law fluids,

 $8\rho D^n \overline{V}^{2-n} n^n / K(6n+2)^n$

O/W = oil-in-water

 u^+ = dimensionless velocity, Eq. 1

 \overline{V} = average velocity

W/O = water-in-oil

 y^+ = dimensionless distance, Eq. 1

Greek letters

 $\dot{\gamma}$ = shear rate

 $\eta = viscosity$

 η_c = continuous-phase viscosity

 η_d = dispersed-phase viscosity

 η_r = relative viscosity

 $\rho = density$

 τ = shear stress

 ϕ = dispersed-phase concentration

Literature Cited

Achutaramayya, G., and C. A. Sleicher, "Analysis of Stratified Laminar Flow of Immiscible Liquids in Circular and Non-circular Pipes," Can. J. Chem. Eng., 47, 347 (1969).

Alvarado, D. A., and S. S. Marsden, "Flow of Oil-in-Water Emulsions through Tubes and Porous Media," SPE J., 369 (Dec., 1979).

Baron, T., C. S. Sterling, and A. P. Schueler, "Viscosity of Suspen-

Baron, T., C. S. Sterling, and A. P. Schueler, "Viscosity of Suspensions—Review and Application to Two-Phase Flow," *Proc. Midwestern Conf. on Fluid Mechanics*, p. 103, Univ. of Minnesota Institute of Technology, Minneapolis (1953).

Becher, P., Emulsions: Theory and Practice, Robert E. Krieger Publishing (1977).

Cengel, J. A., A. A. Faruqui, J. W. Finnigan, C. H. Wright, and J. G. Knudsen, "Laminar and Turbulent Flow of Unstable Liquid-Liquid Emulsions," AIChE J., 8(3), 335 (1962).

Charles, M. E., G. W. Govier, and G. W. Hodgson, "Complexities Inherent in the Study of Two-Phase Flow," Can. J. Chem. Eng., 39, 67 (1961).

Charles, M. E., and J. Redberger, "Reduction of Pressure Gradients in Oil Pipelines of Stratified Flow," Can. J. Chem. Eng., 40, 70 (1962).

Collins, S. B., and J. G. Knudsen, "Drop-Size Distributions Produced by Turbulent Pipe Flow of Immiscible Liquids," AIChE J., 16(6), 1072 (1970).

Dodge, D. W., and A. B. Metzner, "Turbulent Flow of Non-Newtonian Systems," AIChE J., 5(2), 189 (1959).

Eilers, von H., "Die Viskositat von Emulsionen Hochviscoser stoffe als Funktion der Konzentration," Kolloid-Z, 97, 271 (1941).

Einstein, A., Investigations on the Theory of Brownian Movement, Dover, New York (1956).

Faruqui, A. A., and J. G. Knudsen, "Velocity and Temperature Profiles of Unstable Liquid-Liquid Dispersions in Vertical Turbulent Flow," Chem. Eng. Sci., 17, 897 (1962).

Gemmel, A. R., and N. Epstein, "Numerical Analysis of Stratified Laminar Flow of Two Immiscible Newtonian Liquids in a Circular Pipe," Can. J. Chem. Eng., 40, 215 (1962).

Govier, G. W., G. A. Sullivan, and R. K. Wood, "The Upward Vertical Flow of Oil-Water Mixtures," Can. J. Chem. Eng., 39, 67 (1961).

Guzhov, A. I., A. P. Grishin, V. F. Medvedev, and L. P. Medvedeva, "Formation of Emulsions during Flow of Two Liquids in a Pipeline," Neftkhoz, 8, 58 (1973).

Hasson, D., U. Mann, and A. Nir, "Annular Flow of Two Immiscible Liquids," Can. J. Chem. Eng., 48, 514 (1970).

Hinze, J. O., "Fundamentals of the Hydrodynamic Mechanism of Splitting in Dispersion Processes," AIChE J., 1(3), 289 (1955).

- Howarth, W. J., "Coalescence of Drops in a Turbulent Flow Field," Chem. Eng. Sci., 19, 33 (1964).
- Madden, A. J., and G. L. Damerell, "Coalescence Frequencies in Agitated Liquid-Liquid Systems," AIChE J., 8(2), 233 (1962).
- Metzner, A. B., and M. G. Park, "Turbulent Flow Characteristics of Viscoelastic Fluids," J. Fluid Mech., 20(2), 291 (1964).
- Mukherjee, H., J. P. Brill, and H. D. Beggs, "Experimental Study of Oil-Water Flow in Inclined Pipes," J. Energy Res. Tech. (Trans. ASME), 103, 56 (1981).
- Pal, R., "Emulsions: Pipeline Flow Behaviour, Viscosity Equations and Flow Measurement," PhD Thesis, Univ. of Waterloo, Ontario (1987).
- RajaGopal, E. S. R., "Principles of Emulsion Formation," *Emulsion Sci.*, P. Sherman, ed., Academic Press, London (1968).
- Russell, T. W. F., and M. E. Charles, "The Effect of the Less Viscous Liquid in the Laminar Flow of Two Immiscible Liquids," Can. J. Chem. Eng., 37, 18 (1959).
- Russell, T. W. F., G. W. Hodgson, and G. W. Govier, "Horizontal Pipeline Flow of Mixtures of Oil and Water," Can. J. Chem. Eng., 37, 9 (1959).
- Seyer, F. A., and A. B. Metzner, "Turbulent Flow Properties of Viscoelastic Fluids," Can. J. Chem. Eng., 45, 121 (1967).

- Seyer, F. A., and A. B. Metzner, "Turbulent Phenomena in Drag Reducing Systems," AIChE J., 15(3), 426 (1969).
- Sherman, P., Industrial Rheology, Academic Press, London (1968). Shinnar, R., "On the Behaviour of Liquid Dispersions in Mixing Vessels," J. Fluid Mech., 10(2), 259 (1961).
- Shinnar, R., and J. M. Church, "Predicting Particle Size in Agitated Dispersions," *Ind. & Eng. Chem.*, 52(3), 253 (1960).
- Soot, P. M., and J. G. Knudsen, "Two Phase Liquid-Liquid Flow in Pipes," AIChE Symp. Ser., 68(118), 38 (1972).
- Steinhauff, E., "Modern Oil Field Demulsification: I," Petrol., 25, 294 (1962).
- Tadros, T. F., and B. Vincent, "Emulsion Stability," Encyclopedia of Emulsion Technology, Vol. 1, Marcel Dekker, New York (1983).
 Taylor, G. I., Proc. Roy. Soc. London, A138, 41 (1932).
- Ward, J. P., and J. G. Knudsen, "Turbulent Flow of Unstable Liquid-Liquid Dispersions: Drop Sizes and Velocity Distributions," AIChE J., 13(2), 356 (1967).
- Zakin, J. L., R. Pinaire, and M.E. Borgmeyer, "Transportation of Oils as Oil-in-Water Emulsions," J. Fluids Eng., 101, 100 (1979).

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