Flow of High Internal Phase Ratio Emulsions through Pipes

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Abstract. The flow behavior of W/O type of HIPRE stabilized by hydrogen bonds with a sugar (sorbitol) in the aqueous phase, was studied. Two groups of experiments were done in this work: The effect of wall shear stresses were investigated in flow through pipes of different diameters. For this end, HIPREs prestirred at constant rate for the same duration were used to obtain similar drop size distributions. Existence and extent of elongational viscosity were used as a probe to elucidate the effect of drop size distribution on the flow behavior: HIPREs prestirred for the same duration at different rates were subjected to flow through converging pipes. The experimental flow curves for flow through small cylindrical pipes indicated four different stages: 1) initial increase in the flow rate at low pressure difference, 2) subsequent decrease in the flow rate due to capillary flow, 3) pressure increase after reaching the minimum flow rate and 4) slip flow after a critical pressure difference. HIPREs with sufficient external liquid phase in the plateau borders can elongate during passage through converging pipes. In the absence of liquid stored in the plateau borders, the drops rupture during extension and slip flow takes place without elongation.

1. Introduction
High internal phase ratio emulsions (HIPRE) have a structured microstructure that is employed in a wide spectrum of applications. The volumetric concentration of the internal phase can be increased to values greater than 74% with the use of appropriate surfactant-solvent systems. The external phase and the surfactants are then present as a thin film surrounding the polyhedral internal phase and in the Plateau borders at the corners. Thus many polyhedral cells of micrometric dimensions are formed separated by thin films of solution making up the continuous phase. HIPRE’s were originally designed for the synthesis of polymeric solid foams of high porosity and low density, that were later used as supports for catalytic reactions[1], in the synthesis of porous inorganic metal oxides[2], and enzymatic biotransformations [3,4]. Resistance to diffusion caused by these thin films [5] make these emulsions promising in controlled release applications in drug delivery [6]. The large surface area of the polyhedral cells increases the rate and yield of interfacial reactions between organic and aqueous phases. The compartmentalized volumes of controllable dimensions of the dispersed phase make these emulsions a suitable medium in the synthesis of organic chemicals [4,7].

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Rheology and flow properties of these emulsions bear significance in these applications. Rheological properties of HIPRE depend on the interfacial properties such as interfacial tension and contact angle[8]; molecular structure of the surfactants used and the microstructure of the emulsion; physical properties such as density and viscosity of the dispersed and continuous phases. Flow behavior of HIPRE through pipes depends in turn, on the rheological properties. This complex interrelationship between physical properties of the aqueous and oil phases used in the composition of the emulsion and the shear history dependence of the rheological properties of these emulsions have precluded a generalized treatment of the flow properties of these emulsions. Consequently theoretical analyses of the rheology of these systems are few [8-11] and the experimental reports on the rheology and flow behavior pertain to the special cases under consideration: Capdevilla et al.[12] report that the shear stress applied in the preparation of the emulsion is responsible for the formation of small drops in the emulsion through shear rate. In cases where the emulsions are formed in a mixer, the angular velocity of the impeller is used as the scale-up criterion [13-16]. Shear and elongational stresses in flow through pipes and converging-diverging nozzles also affect the drop size distribution [17]. Princen [8] predicted an increase in the yield stress that is inversely proportional with the average drop diameter of the emulsion that is also confirmed by Pal [18].

The reports on the flow of HIPRE in pipes are also limited to a few cases. Becu et al. [19] have observed that HIPRE are in a jammed state at wall stresses below the yield stress, slipping undeformed over a lubricating layer of continuous phase along the walls. Above the yield stress, the emulsion flows homogeneously and exhibits slip flow. Masalova, et al. [20] working with W/O emulsions with 94% (v) dispersed phase of liquid explosives of high electrolyte concentration have reported a power-law model of the rheology that later converts into a Herschel-Bulkley model. In a later work Herschel Bulkley model was found to be satisfactory in explaining the pipe-flow behavior [21]. Slip flow was neglected in flow through pipes of 64 and 89 mm internal diameter, but proposed to be significant in flow through small diameter pipes.

The aim of this research was to investigate the flow behavior of W/O type of HIPRE stabilized by hydrogen bonds with a sugar (sorbitol) in the aqueous phase, instead of electrostatic forces with the addition of electrolytes of high ionic strength, as generally used in the stabilization of HIPRE in the literature. Two groups of experiments were done in this work: The effect of wall shear stresses were investigated in flow through pipes of different diameters. For this end, HIPREs prestirred at constant rate and for the same duration were used to obtain similar drop size distributions. In the second group of experiments, existence and extent of elongational viscosity were used as a probe to elucidate the effect of drop size distribution on the flow behavior: HIPREs with different drop size distributions, obtained by prestirring for the same duration at different rates, were subjected to flow through converging pipes.

2. Experimental

2.1 Preparation of emulsions:
High internal phase ratio emulsions with 94% volumetric concentration of internal phase were prepared as a function of prestirring rate. The internal phase consisted of 1% (w) sorbitol solution, and the external phase, a mixture of mineral oil (Paraffin oil of average hydrocarbon chain length = 15C) and polyoxyethylene (2) oleyl ether (Brij 92) at a 1/1 volumetric ratio. The emulsions were formed at 60 °C with stirring at a rate of 400 rpm, the minimum rate for the formation of stable HIPRE.

2.2 Measurement of emulsion viscosities:
The emulsions were stirred at the rates of 400, 600, 800 or 1000 rpm for 20 minutes before the viscosity measurements. The viscosities of the emulsions were measured with Haake Mars rheometer (Thermo Electron Co.), using the vane rotors.
2.3 Flow Experiments: The flow set-up consisted of a storage tank held under nitrogen atmosphere, with horizontal pipe attachment and pressure gages that could be replaced by a converging pipe. The flow rate was adjusted with the pressure of the nitrogen gas in the storage tank. The glass pipes with a length of 1.5 m in 3.5, 5.6 and 14.7 mm inner diameters were used in the horizontal pipe flow experiments. Two different converging pipes were used for elongational flow of HIPRE. The outlet to inlet diameter ratio of the stainless steel converging pipes was, $D_o/D_i = 9/21$, in both cases. Other dimensions of the nozzles are summarized in table 1. The emulsions were prestrirred at 400 rpm for 20 minutes before flow through the horizontal cylindrical pipes and at 400, 600, 800 or 1000 rpm rates for flow through converging pipes.

2.4 Determination of drop diameters: 1 mL HIPRE samples were diluted with oil-surfactant solution of the same composition as the external continuous phase and optical observations were carried out using an Olympus BX 50 polarizing microscope by spreading the solutions as a thin film on glass slides. Structure evolution was observed under cross-polarized light and was recorded by photography. The drops became spherical when suspended in sufficient amount of the external phase. The drops are polyhedral in shape, separated by films of continuous phase.

Table 1. Dimensions of converging pipes used in the experiments.

| Dimension              | Short (20 mm) | Long(30 mm) |
|------------------------|---------------|-------------|
| Pipe length, mm        | 18.4          | 28.6        |
| Wall length, mm        | 20.0          | 30.0        |
| Angle of convergence   | 23.2°         | 18.4°       |

3. Results and Discussions

3.1 Microstructure of HIPRE

High internal phase ratio emulsions (HIPRE) have microstructures that cause these emulsions to exhibit different rheological behavior under different flow conditions. The continuous phase is usually a polymer or a surfactant in solution. The drops are spherical when the volumetric concentration of dispersed phase in the emulsion is less than 74%, as given in figure 1(a). The internal phase concentration of an emulsion can be increased above 74% when appropriate surfactant-solvent systems are used at a high ratio of surfactant/solvent. The external phase and the surfactants are then present as a thin film surrounding the polyhedral internal phase and in the Plateau borders at the corners. At dispersed phase volumetric concentrations greater than 74%, drops can no longer remain spherical and are flattened at contact points with plateau borders at the junction of three drops in 2-D, as shown by the dashed-lined circle in figure 1(b). Hexagonal drops in figure 1 (b) and (c) are in the form of polyhedra in the case of actual 94% internal phase emulsions in 3-D, with the appearance of miniaturized foams.

Surfactants with a linear hydrophobic chain and a small hydrophilic group with approximately the same cross sectional area as the hydrocarbon chain form lyotropic liquid crystals. Molecular structure of polyoxyethylene (2) oleyl ether (Brij 92) has these properties, suitable for the formation of liquid crystals. The compact orientation of the surfactant molecules at the interface are further stabilized by forming hydrogen bonds with sorbitol in the subphase.
3.2 Rheological behavior of HIPRE

When the volume of the continuous phase around the drops is sufficient for free motion of the drops, as given in figure 1(a), the drops line up under the action of shear and the emulsion behaves as a power law fluid:

$$\tau = K\dot{\gamma}^n$$  \hspace{1cm} (1)

The close-packed polyhedral structures, as given in figure 1(b) and (c), develop a yield stress as any force applied to the structure is transferred throughout the network of bilayers forming the walls of the drops. The emulsion then conforms to Herschel-Bulkley model.

$$\tau = \tau_0 + K\dot{\gamma}^n$$  \hspace{1cm} (2)

The yield stress is proportional to the compactness of the network evidenced by the yield stress increase with a decrease in drop size [8, 18]. Mechanical energy input, as in the case of stirring of the emulsion is converted into surface energy, reducing the size of the drops, increasing the interfacial area and reducing the amount of bulk liquid in the Plateau borders. On further concentration, the continuous phase film around the drops is reduced to a bilayer. The yield stress of the emulsion increases with the extent of the interfacial contact area among the drops. The rheological constants of the 94% emulsions used in this work are given in table 2 as a function of the prestirring rate.

Due to errors inevitably introduced in handling, the trends rather than absolute values of the rheological constants in table 2 are significant in work dealing with shear history fluids such as high internal phase ratio emulsions: Initially undeformable gel behavior was observed in emulsions prestirred at 1000 and 800 rpm. Aging is very rapid in this case, due to decreased drop diameter with increased total interfacial area among the drops. Aging can be interpreted in terms of the microstructure of the emulsions as follows: As the total amount of the surfactant is constant independent of the prestirring rate, interfacial concentration of the surfactant stabilizing the interfacial film is decreased, facilitating the coalescence of small drops with time. The yield stress decreases when the compactness of the network structure decreases due to coalescence of drops. The enlargement of the drop sizes causes liquid to accumulate in the plateau borders. This causes the rheological response of the emulsion toward shear stress to change, with a reduction in the yield stress and consistency. The low values of yield stress in spite of the high prestirring rates reflect the rapid aging behavior in the time span between the preparation of the emulsion and the initiation of the viscosity measurement. Emulsions prestirred at 400 and 600 rpm conform to the Herschel-Bulkley model throughout the aging period. In general, due to the network structure of HIPRE, the effect of yield stress is observed to be predominant in the rheological behavior, as indicated by the relative values of the yield stress, $\tau_0$, and the consistency index, K. Viscosity index, $n$, in power law terms
reflect the deformability of the emulsions; all emulsions approach Newtonian behavior (n→1) with aging.

Table 2. A summary of aging behavior of HIPRE used in this work.

| N (rpm) | t(h) | \( \tau_o (Pa) \) | K(Pa s\(^n\)) | n (-) |
|--------|------|----------------|----------------|-------|
| 400    | initial | 107 | 1.4 | 0.77 |
|        | 24    | 40  | 1.0 | 0.97 |
| 600    | initial | 101 | 1.1 | 0.41 |
|        | 24    | 43  | 0.9 | 0.58 |
| 800    | initial | 97  | -  | -   |
|        | 24    | 41  | 1.4 | 0.37 |
| 1000   | initial | 87  | -  | -   |
|        | 24    | 12  | 1.1 | 0.69 |

3.3 Flow of HIPRE through pipes
At the start of the experiments, the paraboloid shape of the moving front of the emulsion could be observed visually in 3.5 and 5.6 mm pipes. This shape could reflect the velocity profile within the pipe; it could also be due to the convex shaped meniscus of the W/O HIPRE that does not wet the glass walls of the pipe. After an entrance length that depended on the flow rate (applied pressure) the walls were smeared by the emulsion. Velocities were determined from the mass flow rates. The experimental flow curves for flow through 3.5 and 5.6 mm pipes indicated four different stages: 1) initial increase in the flow rate at low pressure difference, \( \Delta P \), 2) subsequent decrease in the flow rate, 3) pressure increase after the minimum flow rate and 4) slip flow after a critical pressure difference (\( \Delta P > \Delta P_{cr} \)) as given in figure 2(a) and (b): The flow rate initially increased with increasing pressure difference, then decreased within a small pressure differential range. After the minimum flow rate was reached, the pressure difference increased within a very small range of flow rates. Finally flow rate increased considerably with the applied pressure after a critical pressure difference, wall shear stress as a function of pipe diameter. The first three stages were not observed in flow through 14.7 mm pipe as illustrated in figure 2(c).

In the first step of the experimental curve, the flow may be due to capillary forces only as the wall shear is much less than the yield stress (\( \tau_w \ll \tau_o \)) and the emulsion moves as a block. Capillary motion is enhanced by the non-wetting hydrophobic oil flowing within the hydrophilic glass capillary [22]. Evidence of slip due to non-wetting is the convex (paraboloid) meniscus of the moving front of the emulsion at the start. Hydrostatic pressure of the emulsion in the storage tank also contributes to the bulk flow of the sliding emulsion. The pressure difference is the sum of capillary and viscous pressure drops under the hydrostatic head in the storage tank [23],

\[
\Delta P = -4 \frac{\gamma \cos \theta}{D} + 3 \frac{2VL\mu}{D^3} \tag{3}
\]

where, \( \gamma \) is the interfacial tension, \( \theta \) the contact angle, \( \mu \) viscosity of the emulsion, \( V \) the velocity of the emulsion, \( L \) the length and \( D \) the diameter of the pipe. Although capillary forces are dominant in the first stage of the flow, viscous forces additionally start to be effective in the second stage, with subsequent decrease in the flow rate. Wall shear stresses cause deformation and subsequent division of the drops to smaller sizes resulting in an increase in yield stress. Hence the flow rate decreases due to the shift of drop size distribution to smaller sizes. Pressure increases after the minimum flow rate is reached in the experiments because the high-yield-stress fluid cannot deform in spite of the high wall shear stresses along the pipe. Increasing the pressure cannot bring about further increase in the flow rate. When the pressure reaches to a critical pressure difference, \( \Delta P_{cr} \) corresponding to the prevalent yield stress with respect to aging time and shear-history of the flowing emulsion, deformation (flow)
begins. $\Delta P_{cr}$ values for flow in each pipe were calculated using the yield stress value ($\tau_o = 64 \text{ Pa}$) found by interpolation of the aging trend of the emulsion in the Hershel-Bulkley constitutive equation

$$\tau = 64 + 1.03\dot{\gamma}^{0.85}$$

and equating $\tau$ to the wall shear stress $\tau_w$,

$$\tau_w = \frac{\Delta P_{cr} D}{4L}$$

$\Delta P_{cr}$ value in flow through 3.5mm pipe was found to be 109 714 Pa; 68 571 Pa and 27 430 Pa for the flows through 5.6 mm and 14.7 mm, respectively. These confirm $\Delta P_{cr}$ values observed in the experimental data plotted in figure 2(a) and (b). At greater pressure differences, increase in the number and decrease in the size of the drops produced within a thin film along the wall causes a decrease in the surfactant concentration in the bilayers forming the drop boundaries in this region. Irregularity of the drop shapes resist alignment in the direction of the shear stress, and the drops rupture. As a consequence slip flow takes place at pressure differences higher than $\Delta P_{cr}$. Apparent viscosity was calculated to verify the existence of the slip flow: It was found to be 18. 3 cP for flow through 3.5 mm pipe; 1.1 cP, for 5.6 mm pipe and 1.9 cP, for 14.7 mm pipe that are in the order of magnitude of water-oil mixture. The emulsion viscosity was calculated as 6 Pas from rheological data at 1 s$^{-1}$ shear rate, for comparison, indicating the existence of a high shear film along the walls, conforming observations made in the literature [17, 19].

The experimental flow curves can be interpreted in terms of the microstructure of the emulsions as: In the absence of stored liquid in the corners, stretching of the walls increases the distance between the liquid crystal surfactant molecules. The van der Waals forces among the hydrocarbon chains and the hydrogen bonds among the hydrophilic groups of the closed packed surfactant molecules at the interface resist stretching under the action of shear stresses. When the shear stresses exceed a critical value greater than the attractive forces between the liquid crystal surfactant molecules, the drops rupture. The aqueous phase entrained within the drops forms a film along the hydrophilic pipe walls. The emulsion then slides over the aqueous film without deformation or a change in the microstructure (drop size).

Using the yield stress given in equation (4), a pressure difference $\Delta P$ was assumed, then shear stress at the pipe wall $\tau_w$, theoretical, $Q_{theo}$ and slip, $Q_{slip}$, flow rates were calculated using equations (6), (7) and (8) for all ranges of the experimental pressure differences to compare the experimental flow curves with the theoretical.

$$\tau_w = \frac{\Delta P D}{4L}$$

(6)

$$Q_{theo} = \frac{\pi D^3}{8\tau_w^3} \left( \frac{1}{K} \right)^n \left\{ \frac{n(\tau_w - \tau_o)^{(1+3n)/n}}{1+3n} + \frac{2n\tau_o(\tau_w - \tau_o)^{(1+2n)/n}}{1+2n} + \frac{n\tau_o^2(\tau_w - \tau_o)^{(1+n)/n}}{1+n} \right\}$$

(7)

$$Q_{exp} = Q_{theo} + Q_{slip}$$

(8)

Calculation results together with the experimental flow curves are given in figure 3. The theoretical flow rates calculated from equation (7) is found to be extremely small with respect to the experimental values, and the slip flow rates, to be in the same order of magnitude with the experimental flow rates in all pipes. All stages existing in the experimental flow curves in 3.5 and 5.6 mm pipes (figure 3(a) and (b)) and the slip flow from the beginning to the end of flow through 14.7 mm pipe (figure 3(c)) were verified by the calculation results. The study also indicated that only slip flow exists in flows through pipes with an inner diameter greater than 5.6 mm. The initial stages before the onset of slip flow are observed only in small pipes; therefore, the transformation to slip flow is not evident in literature based on observations in larger diameter pipes [21, 22, 24].
Shear stresses exist along the walls of converging pipes. In addition normal stresses exist due to extensional (elongational) flow. Extensional flow is mainly responsible for drop deformation and consequent break-up [17]. As a result, variation in the drop size is expected, provided there is no slip.
at the walls. For this end, HIPREs at different prestirring rates were prepared and their initial drop size distributions are given in figure 4(a). Emulsions tend to be monodisperse at lower rates of prestirring, but the predominant (mode) drop diameters are larger.

The variations in the drop size distributions after passage through short (20 mm) and long (30 mm) converging pipes are plotted in figure 4(b) and (c) for emulsions prepared at 600 and 800 rpm prestirring rates: Drop sizes are reduced on initial application of shear: The sizes at 800 rpm prestirring rate are less than those at 600 rpm. If the number of drops is not large and thick liquid films with plateau borders exist, the drops are stretched and reformed as larger drops as observed at 600 rpm prestirring rate after flow through converging pipes. Formation of large drops increases with increasing length of the converging pipe. For small sizes of drops and thin films, stretching ruptures the drops leading to slip flow. Emulsions prestirred at 800 rpm ruptures under the effect of wall shear stress with resultant slip flow. Therefore, the variation in the drop size distribution is negligible.

![Figure 4](image.png)

**Figure 4** Variations in drop size distribution before and after the flow through converging pipes as a function of prestirring rate: a) before the flow, b) emulsions prestirred at 600 rpm after the flow, c) emulsions prestirred at 800 rpm after the flow

### 4. Conclusion

In conclusion, the stability of drops in a thin film along the walls determines the onset of slip flow in pipes. Only HIPREs with sufficient external liquid phase in the plateau borders can elongate during passage through converging pipes. Greater size of drops is pre-requisite: In the absence of liquid stored in the plateau borders, the drops rupture along the high-shear pipe walls and slip flow takes place without elongation during passage through the converging pipe.

### References

[1] Cameron N R and Sherington D C. 1996 *Adv Polym Sci* 126 163
[2] Maekawa H, Esquena J, Bishop S, Solans C and Chmelka BF 2003 *Adv Mater* 15 591
[3] Espelt L, Clape’s P, Esquena J, Manich A and Solans C 2003 *Langmuir* 19 1337
[4] Solans C, Esquena J and Azemar N 2003 *Current Opinion in Colloid and Interface Science* 8 156
[5] Calderó G, Patti A, Llinàs M and García-Celma M J 2012 *Current Opinion in Colloid and Interface Science* 17 255
[6] Llinàs M, Calderó G, García-Celma M J, Patti A and Solans C 2013 *Journal of Colloid and Interface Science* 394 337
[7] Solans C, Pinazo A, Calderô’ G and Infante M R 2001 *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 176 101
[8] Princen H M 1983 *Journal of Colloid and Interface Science* 91 160
[9] Princen H M, Aronson M P and Moser J C 1980 *Journal of Colloid and Interface Science* 75 246
[10] Princen H M 1985 *Journal of Colloid and Interface Science* **105** 150
[11] Princen H M and Kiss A D 1989 *Journal of Colloid and Interface Science* **128** 176
[12] Capdevila M, Maestro A, Porras M and Gutiérrez J M 2010 *Journal of Colloid and Interface Science* **345** 27
[13] Metzner A B and Otto R E 1957 *AIChE J* **3** 3
[14] Bakker A and Gates L E 1995 *Chem. Eng. Prog.* **25**
[15] Okufi S, Pérez de Ortiz E S and Sawistowski H 1990 *Can. J. Chem. Eng.* **68** 400
[16] Galindo S A, Puel F, Briançon S, Allémann E, Doelker and Fessi H 2005 *Eur. J. Pharm. Sci.* **25** 357
[17] Akay G 1998 *Chemical Engineering Science* **53** 203
[18] Pal R 2006 *Food Hydrocolloids* **20** 997
[19] Becu L, Grondin P, Colin A and Manneville S 2004 *Colloids and Surfaces A: Physicochem. Eng. Aspects* **263** 146
[20] Masalova I, Malkin A Y, Slatter P, Wilson K 2003 *J. Non-Newtonian Fluid Mech.* **112** 101
[21] Masalova I and Malkin A.Y 2013 *Chemical Engineering Research and Design* **91** 204
[22] Lee H-B, Yeo I W, Lee K-K 2013 *Advances in Water Resources* **53** 242
[23] Du L, Bodiguel H, Cottin C and Colin A 2013 *Chemical Engineering and Processing* **68** 3
[24] Al-Yaari M., Al-Sarkhi A., Hussein I A, Chang F and Abbad M 2013 *Chemical Engineering Research and Design* (http://dx.doi.org/10.1016/j.cherd.2013.09.001) in press