Available online at www.sciencedirect.com

ScienceDirect

Journal of Colloid and Interface Science 304 (2006) 562–565

Journal of
Colloid and
Interface Science

www.elsevier.com/locate/jcis

Note

Filtration of deformable emulsion droplets

T.F. Headen [a], S.M. Clarke [a,*], A. Perdigon [a], G.H. Meeten [b], J.D. Sherwood [b], M. Aston [c]

[a] *BP Institute and the Department of Chemistry, University of Cambridge, Madingley Road, Cambridge, UK*
[b] *Schlumberger Cambridge Research, High Cross, Madingley Road, Cambridge, CB3 0EL, UK*
[c] *BP Exploration, Sunbury on Thames, London, UK*

Received 11 April 2006; accepted 9 September 2006

Abstract

Oil-in-water (o/w) emulsions of different droplet size were filtered on membranes of various pore sizes to investigate the growth and behaviour of o/w filter cakes. The cake desorptivity S and the filter membrane resistance R were measured at various filtration pressures P. The variation of S with P shows that filter cake oil droplets of radius a are effectively rigid for $P \ll \gamma/a$ and fully deformable for $P \gg \gamma/a$, where γ is the oil–water interfacial tension. For the largest P, when S became P-independent, the filter cake remained water-permeable as expected from theory.

Keywords: Emulsion; Emulsion fractionation; Soft solids; Monodisperse; Ion-track etched membranes; Filtration; Desorptivity; Permeability; Deformation; Push through

1. Introduction

The deformation of liquid droplets in emulsions is important in a variety of consumer and industrial products; e.g., oil-based drilling fluids which are water-in-oil emulsions containing oleophilic colloidal clay particles [1]. When drilling a well bore through permeable rock formations, the fluid pressure usually exceeds that of connate fluid in the formation, and the resulting flow of oil into the rock leaves a filter cake of drilling fluid particles at the fluid/rock interface [2,3]. The filter cake (essentially concentrated drilling fluid) has a low permeability and so controls loss of oil filtrate into the rock while drilling, but should allow hydrocarbons to flow back during production [1–3]. Hence control of the filtercake growth and properties is important.

The permeability of a filter cake of deformable droplets is expected to decrease with increasing filtration pressure, but droplets deformed too much may be pushed through pores in the filter. Thus there may be some optimal deformability relative to the applied pressure and the filter pore size.

Spherical droplets have the minimum surface area for a given volume. Deforming the droplet therefore increases the total surface area (at constant volume) and the interfacial tension at the oil–water interface provides an elastic restoring force related to the droplet radius, as discussed below.

2. Experimental

We used the well-characterised emulsion system developed by Bibette and co-workers [4]. Silicone oil droplets were dispersed in water using the surfactant sodium dodecyl sulfate (SDS). The measured interfacial tension was $\gamma \approx 8.9\ \mathrm{mN\,m^{-1}}$. The initially polydisperse emulsions were size-fractionated by controlling the SDS concentration [4]. In outline, the depletion potential arising from increasing concentrations of surfactant micelles was used to cream selectively the larger emulsion droplets. A single initial emulsion gave about 7 fractions, some being large enough to allow further fractionation. From optical microscopy, a typical sample's polydispersity was 30%, although some samples had regions of close-packing, suggesting 5–10%.

The oil volume fraction of each emulsion was estimated by repeated centrifugation and material balance calculations.

---

[*] Corresponding author.
E-mail address: stuart@bpi.cam.ac.uk (S.M. Clarke).

0021-9797/\$ – see front matter
doi:10.1016/j.jcis.2006.09.014

The droplet size distribution was measured using dynamic light scattering (Malvern Zeta Sizer).

Filtration measurements at room temperature were made on two emulsion fractions; 1.1.1 ($a = 3$ μm from microscopy), and 2.1.1.1 ($a = 2$ μm from Zeta-sizing), with a filtration pressure P either from compressed air or the emulsion's hydrostatic head. Millipore and Whatman track-etched filter membranes were used with well-defined monodisperse pore sizes. The hydraulic resistance R of these membranes was measured using water, and also in the presence of the filtercake using the approach of Meeten [5].

3. Results and analysis

Theoretical models of constant-pressure filtration [5–7] give the filtrate volume V to vary with time t as $V = ASt^{1/2}$, where A is the area of the filter and S is the desorptivity. In a recent filtration model of emulsions [7] the filtercake emulsion droplets of radius a form a cubic array without coalescence and deform under the filtration pressure. The model predicts that S asymptotes when the non-dimensional pressure Pa/γ is sufficiently large, and that it scales as $(\gamma a/\eta)^{1/2}$ where η is the filtrate viscosity. The model [7] was valid only for emulsions with initial volume fraction greater than approximately 0.5, but it can be shown that a similar pressure dependence of filtration is to be expected when the emulsion to be filtered is dilute. At low pressures we expect incompressible behaviour [5], for which $S \propto P^{1/2}$. At higher pressures of order γ/a the emulsion droplets become deformable and S is predicted to vary more weakly than $P^{1/2}$. At pressures $P \gg \gamma/a$ the droplets are completely deformable and S becomes independent of P.

Fig. 1 shows an example of the data analysis. Fig. 1a plots V versus $t^{1/2}$ at $P = 1228$ and 6110 Pa. The evident non-linearity was attributed mainly to a non-negligible resistance R of the filter. When the method of Meeten [5] can be used, as shown in Fig. 1b, both low and high-pressure data gave linear plots with good regression coefficients. The gradient and the intercept gave S and R, respectively. The resistance R compared well with that measured using water without the filter cake.

Fig. 1c gives a representative example of $S(P)$, showing that S increased with increasing pressure at small P but that it asymptoted to a limiting value at large P. This behaviour was similar for different membranes, and for a given emulsion changing the membrane did not change S or the pressure P_c at which S reached its limiting value, showing that the behaviour is a property of the emulsion rather than of the membrane. A key experimental finding of our work is the similarity of the pressure dependence of S to that predicted by Sherwood [7].

There are a number of approaches to compare experiment and theory. The model [7] predicts that P_c varies as γ/a so that if P_c is obtained from experiment we might determine the effective radius γ/P_c and compare it with a measured directly. However, there is uncertainty in estimating P_c from the experimental data. Hence we compared the measured S with that predicted by the model over the whole accessible pressure range using only two parameters; a droplet radius a (which gives the pressure scale γ/a) and a simple multiplicative scale factor A for S constrained to be identical for different fractions of the same emulsion. The qualitative behaviour of the data and model agree very well (Fig. 2) showing that the model captures many of the key aspects of the emulsion behaviour. The values of a used were: fraction 1.1.1, $a = 1.7$ μm (cf. 3 μm from microscopy); fraction 2.1.1.1, $a = 1$ μm (cf. 2 μm from Zeta-sizing). The quantitative agreement is only fair between the effective droplet size determined from the fits and from Zeta-sizing. This could arise from deficiencies in the model or from several features of the experimental emulsions, particularly polydispersity.

4. Summary and conclusions

The filtration properties were investigated of model oil in water emulsions with a range of different droplet sizes. Fractionation of emulsions by the depletion approach provided fairly monodispersed samples of sufficient quantity. The experimental data treatment of Meeten [5] gave the desorptivity S and the membrane resistance R.

The dependence of S on filtration pressure P followed a characteristic trend; S increased at low pressures (although more weakly than $P^{1/2}$ for rigid particles) before becoming P-independent. The variation in desorptivity clearly indicates that the droplets controlling the permeability are increasingly deformed with increasing filtration pressure, but that they do not deform to close all the pores in the filter cake, even at high P, when the filter cake remains permeable. The independence of S on filtration pressure P results from the local curvature of the deformed droplets which varies as $1/P$.

The pressure at which S becomes independent of P is found to depend upon the size of the droplets, in good agreement with the predictions of the model [7]. This indicates that smaller emulsion droplets are more rigid and less deformed than larger droplets. However because there is no well-defined point where desorptivity reaches its limiting value, the correlation between P_c and γ/a is difficult to assess. More complete modelling of the whole pressure dependence of the desorptivity indicates that the data follows the model reasonably well over a wide range of pressures.

Our approach to study model fractionated emulsions on well-characterised membranes can be used to probe the influence of a variety of physical parameters on the system behaviour. Subtle variations in interfacial tension and the effects on the limiting values for desorptivity are of great interest.

It was found that small droplets could be pushed through the filter at sufficiently large filtration pressure, and also an unexpected dependence was found of S on the dispersed phase viscosity η. These aspects will be studied further.

Acknowledgments

We thank Schlumberger Cambridge Research for the loan of filtration equipment, the Nanoscience Centre at Cambridge University for our droplet sizing measurements, the Cavendish Laboratories, Cambridge University for use of a Zeiss optical microscope with digital camera, and BP Ltd. for financial support for this work.