CHAPTER 6

SURFACTANT STABILISATION

1. INTRODUCTION

The requirements to ensure stability against settling were discussed in Chapter 2. Amongst others, a repulsive force is required to overcome the London-type Van der Waals attractive forces. The mechanism of steric repulsion is introduced by coating the particles with long chain molecules which act as elastic bumpers. Adjacent particles may compress the adsorbed layer surrounding each particle. [7]

Mackor obtained an expression for the repulsive energy for flat surfaces onto which a molecule is adsorbed. The molecule is said to consist of a polar head and a tail. The number of molecules adsorbed onto the surface is such that under the influence of thermal motions, the tail rod can take up any hemispherical orientation. The expression for this energy is given by eq. (6.1) with the graphical illustration of the scenario given in Figure 6.1. [7]

$$\frac{E_f}{kT} = \begin{cases} \xi(1-\frac{s}{2\delta}), & \frac{s}{2\delta} \leq 1 \\ 0 & \frac{s}{2\delta} > 1 \end{cases} \qquad (6.1)$$

where ξ is the surface concentration of the absorbed molecules, s is the surface to surface separation, k is the Boltzmann constant, E_f is the repulsion energy per unit area of the flat surface and δ is the length of the absorbed molecule.

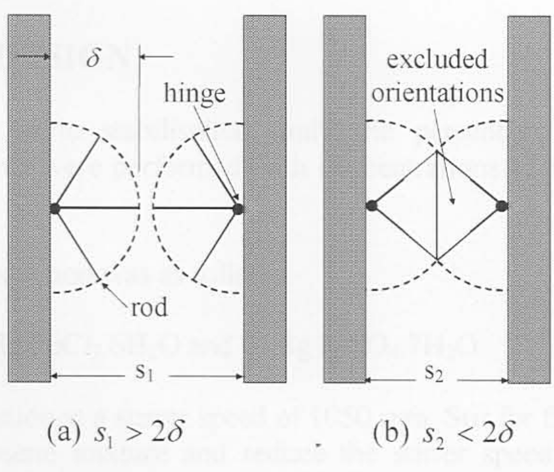

Figure 6.1 Illustration of steric repulsion

In Figure 6.1 (a), where the separation between surfaces is greater than twice the length of the tails, there will be no repulsion. In Figure 6.1 (b) the volume available to the tails is reduced and a gaslike repulsion pressure is produced. [7]

Oleic acid is a common dispersing agent in the manufacture of ferrofluids. The oleic acid has a double bond at the ninth carbon position. The double bond is rigid and allows no free rotation to occur. Consequently, the likelihood of neighbouring molecules nesting together and crystallising is greatly reduced. [7]

Reimers and Khalafalla [36] performed investigations into the relationship between the quantity of magnetic material dispersed and the saturation magnetisation. Their results indicated that there is an optimum point where magnetic fluids have the highest magnetisation dependent on the quantity of dispersing agent. For oleic acid, they found this volume percent to be in the region of 8.5 to 10%. In their investigations, the magnetisation seemed to drop off after a certain percentage of dispersing agent had been added (this was for different dispersing and carrier agents). In later work Reimers and Khalafalla (in the production of relatively dilute fluids of 0.045 volumetric packing fraction) found that when manufacturing an aqueous magnetic liquid there was no loss in magnetisation with increase in dispersing agent. However, a scum-like substance appeared on the surface of the liquid when additional dispersing agent was used. [37] In other words, it appeared that a maximum was reached where additional surfactant proved to be detrimental to the fluid manufacture.

From experimental investigations in the laboratory in the past, higher percentages of oleic acid seemed to result in fluids of higher magnetisation with 12% being a common percentage that has been used. This, however, has not been quantified. It was decided to perform an investigation into the effect of the volume of the dispersing agent on the saturation magnetisation of the fluid. In this experimental work, much greater volumes of magnetite were required to be suspended: it was attempted to obtain a volumetric packing fraction of 0.1 as opposed to 0.045 as obtained by Khalafalla and Reimers.

2. EXPERIMENTAL DESIGN

For the investigation into steric stabilisation, only the percentage surfactant added was investigated. Four experiments were performed with concentrations of 8, 10, 12 and 14% oleic acid.

The method of ferrofluid production was as follows:

1. Add 400 ml water to 31.8g $FeCl_3.6H_2O$ and 21.8g $FeSO_4.7H_2O$.
2. Stir for 3 minutes.
3. Rapidly add NH_4OH solution at a stirrer speed of 1050 rpm. Stir for five minutes.
4. Add the oleic acid-kerosene mixture and reduce the stirrer speed to 650 rpm. The four different combinations were as follows:

- 2.2 and 27 ml (run 1),
- 3 and 26 ml (run 2),
- 3.5 and 26 ml (run 3) and
- 4 and 25 ml (run 4) respectively.

5. The mixture is heated to 68°C over approximately 10 minutes but not maintained at this temperature for any length of time.
6. Remove from stirrer and allow the mixture to settle and cool on a barium ferrite magnet. The aqueous and organic layers can then be separated.
7. Centrifuge for 30 minutes.
8. Dilute to 0.98 g/cm^3.
9. Measure the saturation magnetisation.

3. RESULTS

As the percentage oleic acid increased, the volume of magnetite remaining suspended above the ferrofluid appeared to decrease. At 14%, however, suspended magnetite was still visible. Table 6.1 gives the results for the experimental runs.

Table 6.1 Results for experimental runs

Run number	Percentage oleic acid (%)	Density (g/cm^3)	Saturation magnetisation (Gauss)
1	8	0.9762	149.3
2	10	0.9716	158.7
3	12	0.9750	161.5
4	14	0.9718	203.8

A plot of the saturation magnetisation versus the percentage oleic acid is given in Figure 6.2. A straight line has been fitted to these points.

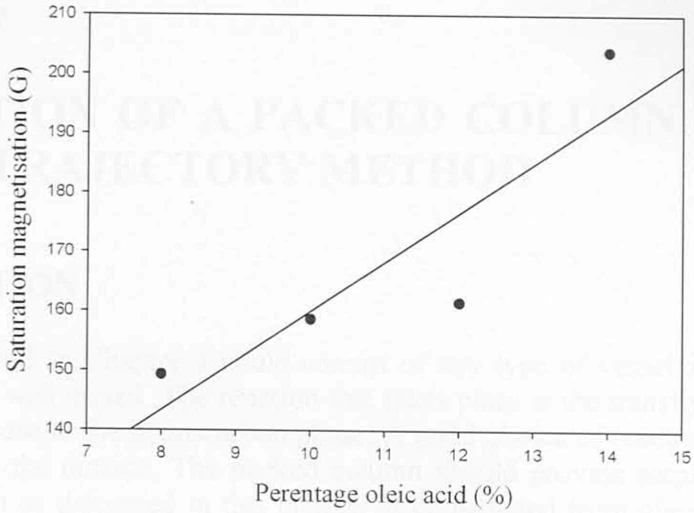

Figure 6.2 Plot of saturation magnetisation versus percentage oleic acid

4. DISCUSSION

As shown in Figure 6.2, as the percentage oleic acid increases, the trend is that saturation magnetisation increases. It is likely that the additional surfactant allows more magnetite particles to be coated. The uncoated magnetite particles remain in the aqueous phase and these particles are lost when the aqueous-hydrocarbon phases are separated. It does not appear that a maximum saturation magnetisation has been reached. Additional oleic acid should be added to see if a maximum can be reached.

5. CONCLUSIONS AND RECOMMENDATIONS

For this brief investigation into steric stabilisation, as the percentage oleic acid increased, the volume of magnetite remaining suspended above the ferrofluid appeared to decrease. It would have been interesting to measure the viscosity of the fluids after each run. It is possible that too high a percentage of oleic acid would result in a fluid of unacceptably high viscosity. It appears that different saturation magnetisations are also obtained using different peptizing times. [36] The fluid should therefore possibly have been maintained at a certain temperature for a certain period of time instead of simply reaching the desired temperature and removing it from the heat source. In addition, it is recommended that an estimate be made of the volume of oleic acid molecules required to coat a magnetite particle of a certain diameter. An initial estimate of the maximum percentage surfactant required could then be established.