

# A Study of the Formation of Water-in-Oil Emulsions

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## Introduction

The formation of stable water-in-oil emulsions (mousse) has long been a source of problems for the oil industry. In the oil field, emulsions cause difficulties in production, storage and transportation. When oil is spilled in the marine environment, its emulsification behaviour will play a crucial role in determining the ultimate fate of the oil, and the effectiveness of countermeasure techniques.

Canevari (1982) pointed out that there are two possible mechanisms that are responsible for the formation of stable water-in-oil emulsions. The first mechanism is due to the action of naturally occurring surface active agents (surfactants) in petroleum and the second is due to the presence of solid particles. The mechanism by which surfactants stabilize emulsions is fairly well understood. Briefly, surfactants are amphiphathic molecules which means that one section of the molecule is soluble in oil (lipophilic) and the other section is soluble in water (hydrophilic). Because of this molecular structure, surfactants tend to concentrate at the oil-water interface where they form interfacial films. This film reduces the interfacial tension between oil and water, thereby decreasing the amount of work required to introduce one phase into the other; and this film forms a barrier around droplets thus inhibiting coalescence. A general rule of thumb in surfactant chemistry is that surfactants with mainly lipophilic character (that is, predominantly oil soluble) form water-in-oil emulsions. Whereas, surfactants with mainly hydrophilic character (predominantly water soluble) produce oil-in-water emulsions. Examples of the latter are oil spill dispersants. (Rosen 1978, Becher 1983)

In the second mechanism of emulsion stabilization, the emulsifying agents are solid particles which in only a specialized sense can be considered to be surface active (Becher 1977). For solids to act as emulsifying agents, the particles must possess certain properties. The particles must be very small relative to the droplet size. The particles must collect at the interface and they must be 'wetted' by both the oil and water phases. Figure 1 shows three ways that particles may distribute themselves between an oil-water interface. If the particle is preferentially wetted by the oil, the contact angle between the oil-water-solid boundary,  $\theta$  is greater than  $90^\circ$  and a water-in-oil emulsion will form. If the particle is preferentially wetted by water,  $\theta$  is less than  $90^\circ$  and an oil-in-water emulsion will form. If the contact angle is much greater or lesser than  $90^\circ$ , the emulsion will be unstable. Stable emulsions form when the contact angle is near  $90^\circ$ .

It has long been recognized that indigenous petroleum emulsifying agents are concentrated in the higher boiling fractions (boiling point  $> 370^\circ\text{C}$ ) and particularly in the residuum (Lawrence and Killner 1948). Likewise, it is generally accepted that asphaltenes and waxes play key roles in the emulsion process (Birdie et al. 1980; Mackay 1987). These compounds are believed to be the main constituents of interfacial films which encapsulate water droplets within mousse. These films have been shown to have high mechanical strength and thus act as physical barriers which prevent droplet coalescence (Blair 1960, Hasiba and Jessen 1967). This in turn gives rise to the extreme stability of mousse. The phenomena of

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film formation has yet to be fully understood.

Although the role of solid particles in petroleum emulsification has been recognized for some time (van der Waarden 1958), the importance of this mechanism to mousse formation has not been completely appreciated. Eley et al. (1976) examined the interfacial surfaces of water-in-oil emulsions using an electron microscope. Their micrographs clearly showed particulate formations on the oil side of the interface. They isolated structures which they concluded to be asphaltene granules (dimensions: 10-30 nm) and plates of wax (<100nm). Thompson et al. (1984) showed that wax particles and associated solids exert considerable influence upon the emulsion stability of a waxy North Sea crude. They found that removal of particles reduced emulsion stability. They also showed that the emulsion behaviour of an oil can be changed dramatically by altering the size of the wax particles. The importance of this finding is that whether or not the oil formed a stable emulsion was dependent upon the physical form of the emulsifying agent (small versus large wax crystals) and not upon any changes in the oil's chemical composition or bulk properties. Similarly, Eley et al. (1988) demonstrated that by varying the aromatic/aliphatic ratio of a synthetic oil they could control the precipitation of asphaltenes and in turn, the extent of emulsification.

The aim of the work described in this paper was to elucidate the role that physiochemical factors play in determining an oil's susceptibility to emulsify. This was done by using model oils of known composition to examine the importance of oil chemistry in the emulsification process.

### **Oil Chemistry**

The main constituents of any oil can be grouped into four broad classes of chemicals. These being: Alkanes (also sometimes called saturates or aliphatics); Aromatics; Resins; and Asphaltenes. Previous studies have identified that asphaltenes, resins and waxes (which are part of the alkane group) play a role in emulsification. It is important to realize how these components are defined and to have an understanding of their basic chemistry. Different methods of separating these fractions from oil are likely to produce different materials.

### Waxes

Simple definitions of petroleum wax are: the material in an asphaltene/resin-free oil which are insoluble in the solvent methyl ethyl ketone or insoluble in dichloromethane at 32°C. Another definition for petroleum wax is the high molecular weight paraffinic substances which crystallize out from an oil when cooled below the pour point. Petroleum wax is normally divided into two sub-categories: paraffin wax and microcrystalline wax. Paraffin waxes are normal alkanes with 20 to 40 carbon atoms and melting points from 32 to 71°C. Microcrystalline wax mainly consists of iso-alkanes with 35 to 75 carbon atoms and has a melting point from 54 to 93°C (Clark 1988).

### Resins

Resins are complex high molecular weight compounds containing oxygen, nitrogen and sulphur atoms. They are polar and have strong adsorption tendencies. The term "resins" has been defined in various ways but it is generally considered to be the material that remains in solution after the asphaltenes have been removed by precipitation and which will adsorb onto surface-active material (such as Fuller's earth).

Petroleum resins are often considered to be low molecular weight asphaltenes but usually contain a higher percentage of saturated aliphatic and naphthenic structures in their molecules. Molecular weights of resins are assumed to range from about 800 to 1500.

### Asphaltenes

Asphaltenes are defined by their solubility behaviour; asphaltenes are soluble in aromatic solvents and insoluble in alkane solvents. Asphaltenes are generally considered to consist of condensed aromatic nuclei which carry alkyl and alicyclic systems with heteroatoms (nitrogen, oxygen, sulphur, metals, salts) scattered throughout in various locations. Asphaltene molecules can have carbon numbers from 30 to over 40, and molecular weights from 500 to 10,000 have been cited in the literature. Asphaltenes are characterized by a C-H ratio of close to one and a specific gravity near one. Relatively little is known about asphaltene structures and much of the data is inferred. Figure 2 shows a hypothetical structure of an asphaltene (Speight 1981).

The physical nature of asphaltenes as they exist in petroleum is still speculative. But it is now generally accepted that petroleum should be viewed as a colloidal system. Asphaltene molecules agglomerate to form clusters similar to micelles. These asphaltene micelles interact with the resins which in turn peptize the asphaltenes and enables a stable colloidal dispersion to exist. Since these colloids contain most of the polar material found in the oil, they essentially determine the interfacial properties (Clark 1988; Long 1979; Speight 1981; Neumann et al. 1981).

### Solubility Theory

Griffith and Siegmund (1985) used the concept of solubility to describe the precipitation behaviour of asphaltenes from fuel oils. In this context, oil is viewed as being comprised of a solute and a solvent; the solute being the asphaltenes and the solvent being the rest of the oil. The Hildebrand-Scatchard equation (Barton 1983) is the basic equation that can be used to describe the solubility behaviour of asphaltenes in petroleum.

$$RT \ln (A_a/X_a) = \frac{M_a \phi_s^2 (\sigma_a - \sigma_s)^2}{\rho_a}$$

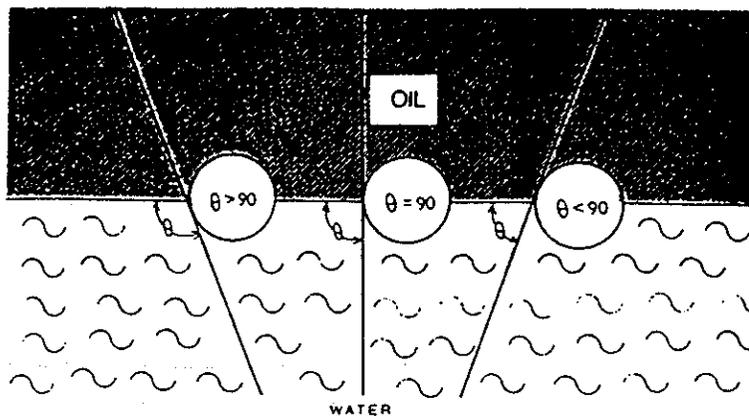
where:

- $A_a$  = activity coefficient of asphaltenes
- $X_a$  = mole fraction of asphaltenes
- $M_a$  = molecular weight of asphaltenes
- $\phi_s$  = volume fraction of solvent
- $\sigma_a$  = Hildebrand solubility parameter of the asphaltenes
- $\sigma_s$  = Hildebrand solubility parameter of the solvent
- $\rho_a$  = density of asphaltenes
- $R$  = gas constant
- $T$  = temperature

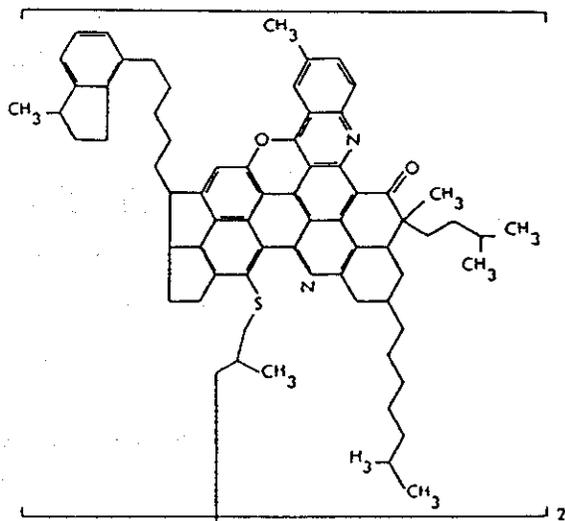
It is assumed that asphaltenes can be treated as homogeneous material and that  $A_a = 1$ . The equation can be written in terms of the maximum amount of asphaltenes soluble in oil,  $X_a$ . If the amount of asphaltenes present in the oil exceeds  $X_a$ , the excess asphaltenes will precipitate.

$$\ln X_a = \frac{-M_a \phi_s^2 (\sigma_a - \sigma_s)^2}{\rho_a RT}$$

**Figure 1** Three ways solid particles may be distributed in an oil/water interface. The particle on the left is more wetted by the water than the oil thus being situated primarily in the aqueous phase, whereas the particle to the right exists primarily in the oil phase. The center situation illustrates a solid particle equally wetted by both the oil and water phase.



**Figure 2** Hypothetical structure of a California crude oil asphaltene.



## Experimental

The model oils used in these experiments consisted of three main components: 1. an alkane component; 2. an aromatic component; and 3. the potential emulsifying agent(s). The alkanes tested were n-octane, n-tetradecane, a light paraffin oil, and a heavy paraffin oil. The aromatics used were p-xylene, phenyl octane, dimethyl naphthalene, and diphenyl methane. Asphaltenes were precipitated from a California crude oil (API gravity: 11) using n-pentane at a pentane to oil ratio of 40:1 (Speight 1981). Asphaltenes and resins were precipitated together from the California crude using ethyl acetate (Neumann et al. 1981). Resins were precipitated from de-asphaltized oil using ethyl acetate. Precipitated materials were collected on a 0.45 micron filter, dried by a nitrogen purge, and stored in the dark under a nitrogen headspace. Other materials used were paraffin wax (Aldrich Chemical Company, melting point: 56-61°C) and graphite powder (Aldrich Chemical Company).

Model oils were prepared by adding the emulsifying agent to the aromatic component. The mixture was vigorously shaken for one hour on a shaker table. The alkane component was then added and the mixture was again shaken for one hour. 30 mL of the oil was poured into a 500 mL Fleaker containing 300 mL of artificial seawater. The Fleaker was sealed and allowed to stand for approximately 20 hours before undergoing the emulsion formation and stability test described by Bobra (1989). Briefly, the test involves rotating the Fleaker at 65 rpm for one hour and then allowing the mixture to rest for one-half hour before measuring the size of the emulsion and the fraction of oil that emulsifies,  $F$ . The rotation/rest cycle is repeated three more times. An indication of an oil's tendency to emulsify is given by  $F_0$ , the fraction of oil that emulsifies when  $F$  is extrapolated to time zero. The stability of the emulsion is obtained by allowing the emulsion to rest for 24 hours and then measuring the fraction of oil that remains in the emulsion,  $F_f$ . The water content of stable emulsions were also measured. The following criteria set by Mackay et al. (1982) classify emulsion behaviour.

$F_0$	Emulsion formation tendency
0 to 0.25	not likely
0.25 to 0.75	fairly likely
0.75 to 1	very likely
$F_f$	Emulsion stability
0 to 0.25	unstable
0.25 to 0.75	fairly stable
0.75 to 1	very stable

The rheological properties of stable emulsions were measured using a Haake RV20 Rotoviscometer equipped with a M5/SV1 sensor. The programmed shear rate was 0 to 100 ( $s^{-1}$ ) in 10 minutes and 100 to 0 ( $s^{-1}$ ) in 10 minutes. The yield point values were determined from the increasing shear rate curves. The yield point can be considered to be an indication of the "solid" character of the emulsion. It is the force required to change the emulsion from a "solid" to a flowing liquid. For the sake of comparison, under these same shear conditions mayonnaisse has a yield point of 114 Pa and two samples of 18 day-old mousse from the Valdez spill had values of 17 and 121 Pa.

The size distribution of water droplets were determined using a Lab-Tec 1000 particle size analyser and a Zeiss Axioskop light/fluorescence microscope.

All experiments were conducted at 15°C.

## Results and Discussion

### Effect of Asphaltenes

Figures 3 to 6 show the influence of the alkane/aromatic ratio and the influence of increasing asphaltene content upon  $F_o$ ,  $F_f$ , water content and yield point. The alkane component is heavy paraffin oil and the aromatic component is xylene. At an asphaltene concentration of 0.01 g/mL (1%), no stable emulsions are formed. At an asphaltene concentration of 0.025 g/mL (2.5%), the model oil has a tendency to emulsify ( $F_o = 1$ ) when the oil is 50% alkane and 50% aromatic, and this emulsion is only marginally stable ( $F_f = 0.5$ ). When the asphaltene content is increased to 0.05 g/mL (5%), stable emulsions are readily produced for oils containing 50 to 95% alkane component. Likewise, at an asphaltene concentration of 0.1 g/mL, stable emulsions form for oils containing 35 to 80% alkane. Figure 5 shows that the water content of stable emulsions are between 80 to 90%. The change in yield point as a function of alkane composition, Figure 6, clearly shows that there is a maximum value for each concentration of asphaltenes. For oils containing 5% asphaltenes this maxima occurs at 80% alkane, and for oils containing 10% asphaltenes this occurs at 70%.

The results illustrate several important points concerning the influence of the alkane/aromatic ratio upon an oil's emulsification behaviour. The amount of asphaltenes precipitated out of solution is determined by the alkane concentration. Figure 7 shows the percent of asphaltenes precipitated as a function of alkane concentration for an oil containing 5% asphaltenes. Clearly, the amount precipitated is important in determining the emulsification of the oil. But it would also appear that the alkane/aromatic ratio controls other factors which are involved in emulsification. The size of the asphaltene particles are determined by the alkane/aromatic ratio and this is particularly true given the method by which these model oils were prepared. Asphaltenes were first dissolved in the appropriate quantity of xylene and then the paraffin oil was added which causes the asphaltenes to precipitate out of solution. When the model oil is predominantly composed of paraffin oil, this precipitation mechanism does not occur and the asphaltene particles maintain their original dimensions ( $> 1$  microns). These particles are too large to effectively stabilize water droplets. This was confirmed by microscopic examination of the oils. When model oils which were prone to emulsification were examined under the microscope, individual particle sizes could not be accurately determined because the particles were at the limit of resolution ( $< 0.5$  microns). But it could be seen that collectively the particles formed a continuous layer of finely dispersed particulates which are closely packed together. As the alkane content of the oil increased, the particles became more tightly packed and increased in size. An interesting phenomenon was observed when model oils with high aromatic content were viewed under the microscope. The actual precipitation of asphaltenes could be observed as the oil evaporated. Particles would precipitate out in a uniform distribution covering the slide with a film of sub-micron particles.

Figure 8 shows the interfacial tension, as measured by the duNuoy ring method, decreases as the aromatic content of the oil increases. It would appear that changes in interfacial tension have little to do with the emulsification behaviour of the model oils.

It would be expected that the alkane/aromatic ratio will have some effect on the contact angle between the particles and the interface, since oil composition will influence the wettability of particles. A simple experiment was performed which demonstrated the importance of the alkane/aromatic ratio on the contact angle. A series of oils of the same alkane/aromatic composition as previously tested were prepared and subjected to the emulsification test but instead of asphaltenes, graphite powder (0.05 g/mL) was used as the emulsifying agent. Graphite is insoluble in both xylene and paraffin oil. Therefore, there will

be no changes in its physical form. The results from this experiment showed that stable emulsions only formed at an alkane/aromatic ratio of 1:1. Unfortunately, facilities to measure contact angle were not available and therefore, this effect of alkane/aromatic ratio upon contact angle, and in turn upon emulsification, could not be substantiated. The results from this experiment indicate that this influence upon contact angle is an extremely important determinant for emulsification by solid particles.

Figure 3:  $F_0$  versus % alkane at different asphaltene concentrations

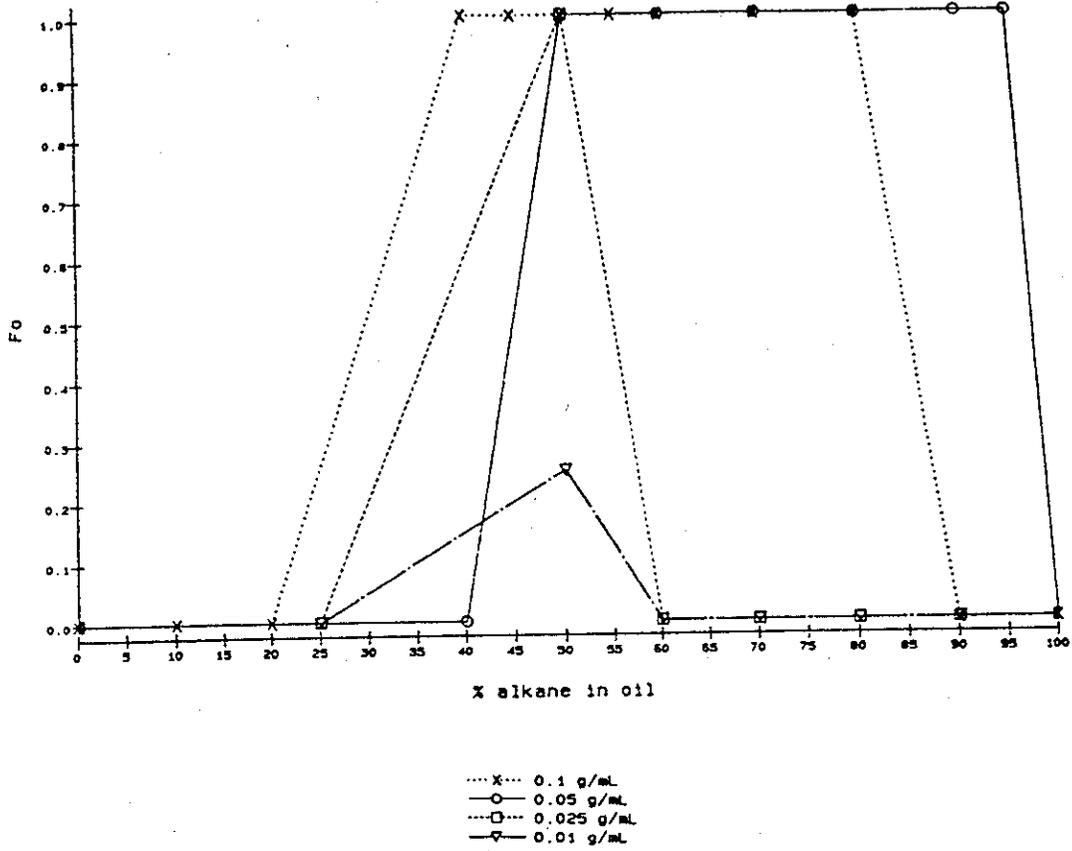


Figure 4:  $F_{final}$  versus % alkane

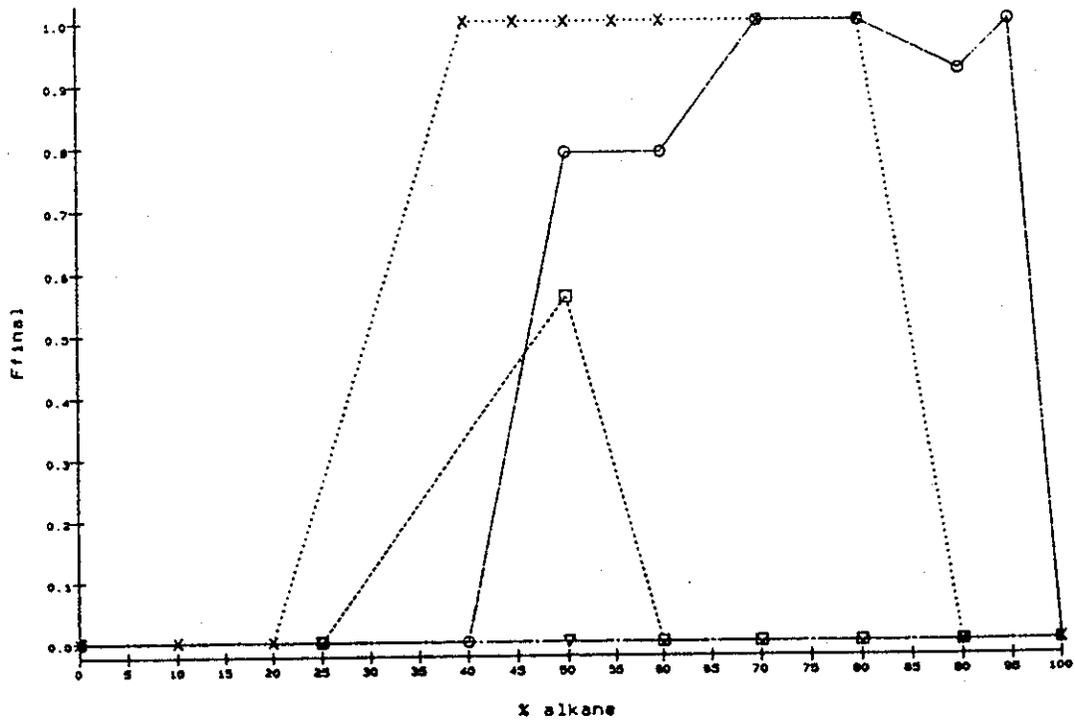


Figure 5: Water content vs % alkane

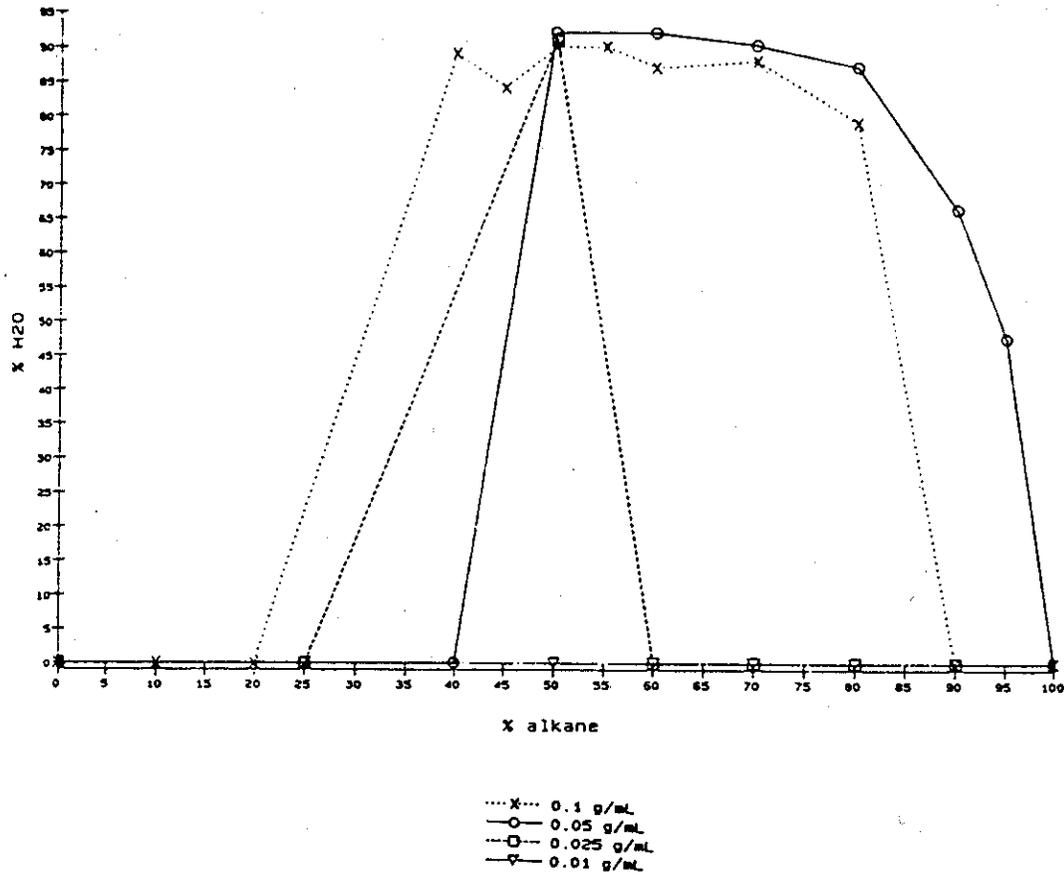


Figure 6: Yield point vs % alkane

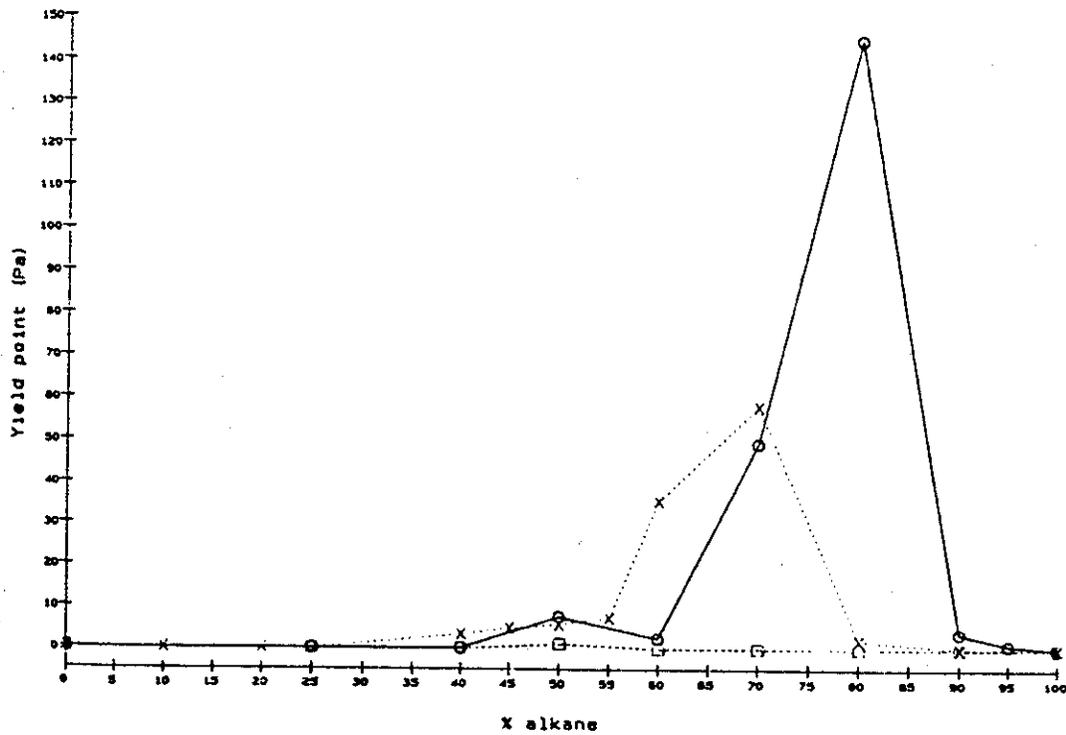


Figure 7: % asphaltenes precipitated versus % alkane in oil.  
model oil: heavy paraffin oil/xylene containing 0.05 g/mL asphaltenes

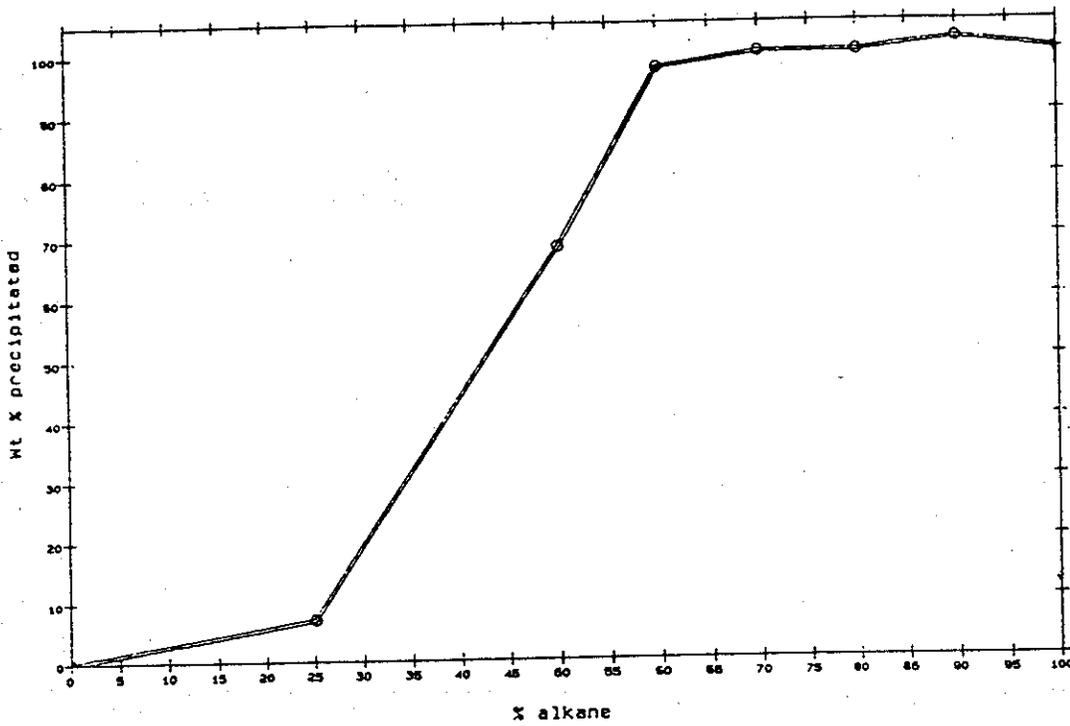
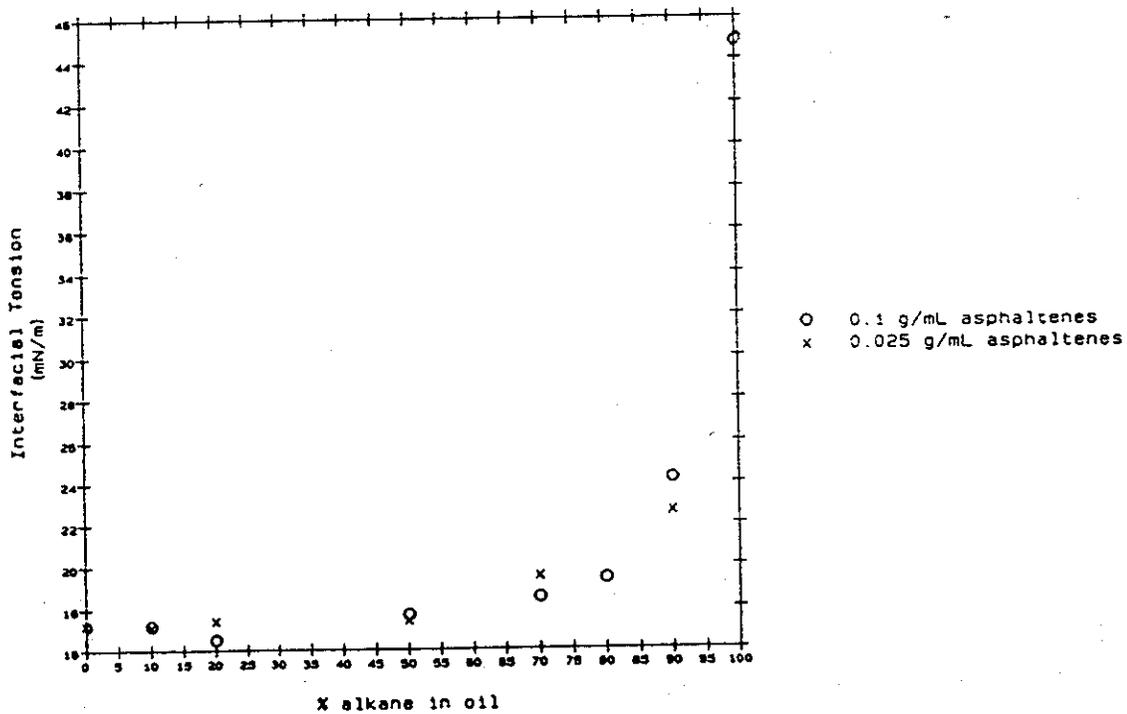


Figure 8: Interfacial Tension vs % alkane  
for heavy paraffin oil/xylene model oil



### Effect of Aromatic Component

Figures 9 to 12 show  $F_o$ ,  $F_f$ , water content, and yield point versus percent alkane for five different model oils consisting of heavy paraffin oil (HPO), 5% asphaltenes, and five different aromatic solvents. These being xylene; phenyl octane (PO); dimethyl naphthalene (DMN); diphenyl methane (DPM); and an equal volume mixture of the four solvents (MIX). As the results illustrate the aromatic component has a profound effect upon the emulsification behaviour of the oil. This can be best explained in terms of the Hildebrand solubility parameter,  $\sigma$  (units:  $\text{MPa}^{1/2}$ ). These parameters can be either determined experimentally, calculated, or found in reference text (Barton 1983). The values for these parameters are 24.7 for the asphaltenes; 15.0 for heavy paraffin oil; 18.0 for xylene; 17.5 for phenyl octane; 21.0 for dimethyl naphthalene; 19.5 for diphenylmethane; and 19.0 for the mixture. From the Hildebrand-Scatchard equation, it can be seen that the amount of asphaltenes soluble in oil,  $X_a$ , is controlled by the term  $(\sigma_a - \sigma_s)^2$ . As  $(\sigma_a - \sigma_s)^2$  increases, the amount of asphaltenes soluble in oil decreases, and any excess asphaltenes will precipitate. Therefore, the likelihood of producing a stable emulsion increases.

Figures 13 to 16 show  $F_o$ ,  $F_f$ , water content, and yield point as a function of  $(\sigma_a - \sigma_s)^2$  for the five model oils. It can be seen that most stable emulsions are formed when  $(\sigma_a - \sigma_s)^2$  has a value between 60 and 90. Stable emulsions are not formed above a  $(\sigma_a - \sigma_s)^2$  value of 90 in these experiments because, as previously mentioned, the asphaltene particles are too large to stabilize the water droplets. This is an artifact of the experimental design. It is expected that stable emulsions would form above this value if the chosen alkane/aromatic pairs allowed for the precipitation of asphaltenes to occur within the oil, thus providing particles which are an effective size.

The solvency power of the model oil,  $\sigma_s$ , controls the amount of asphaltenes that precipitate. If the solvency strength of the aromatic component is decreased, asphaltenes will be less soluble in the oil. This is shown in Figures 9 and 10, the oil containing phenyl octane (the lowest  $\sigma$  value of the aromatics tested) has the largest range over which stable emulsions are formed.

Figure 9: Fo vs % alkane  
different aromatic components

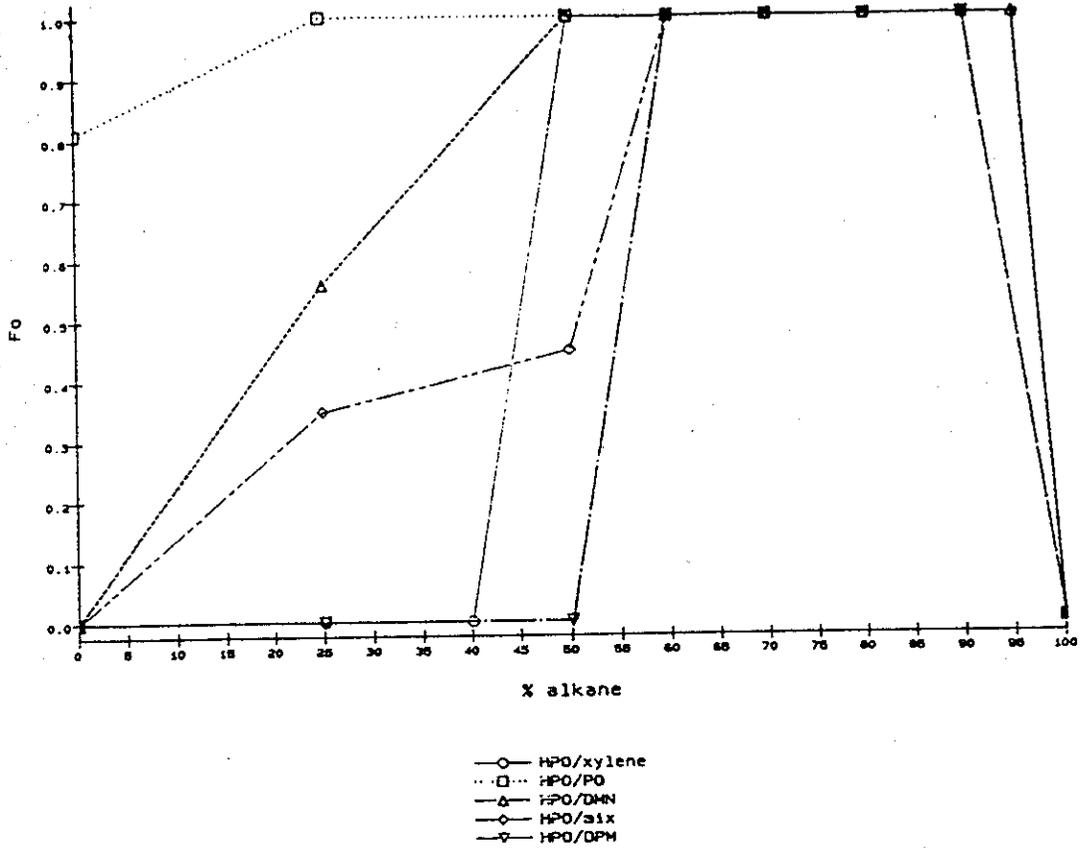


Figure 10: F final vs % alkane

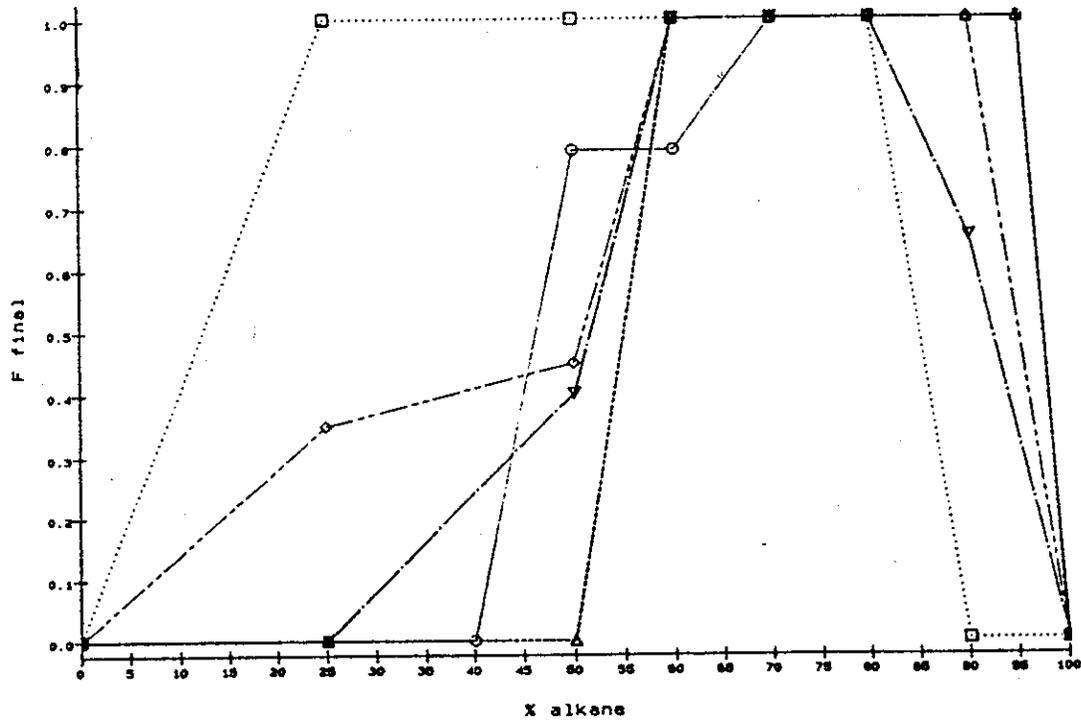


Figure 11: Water content vs % alkane

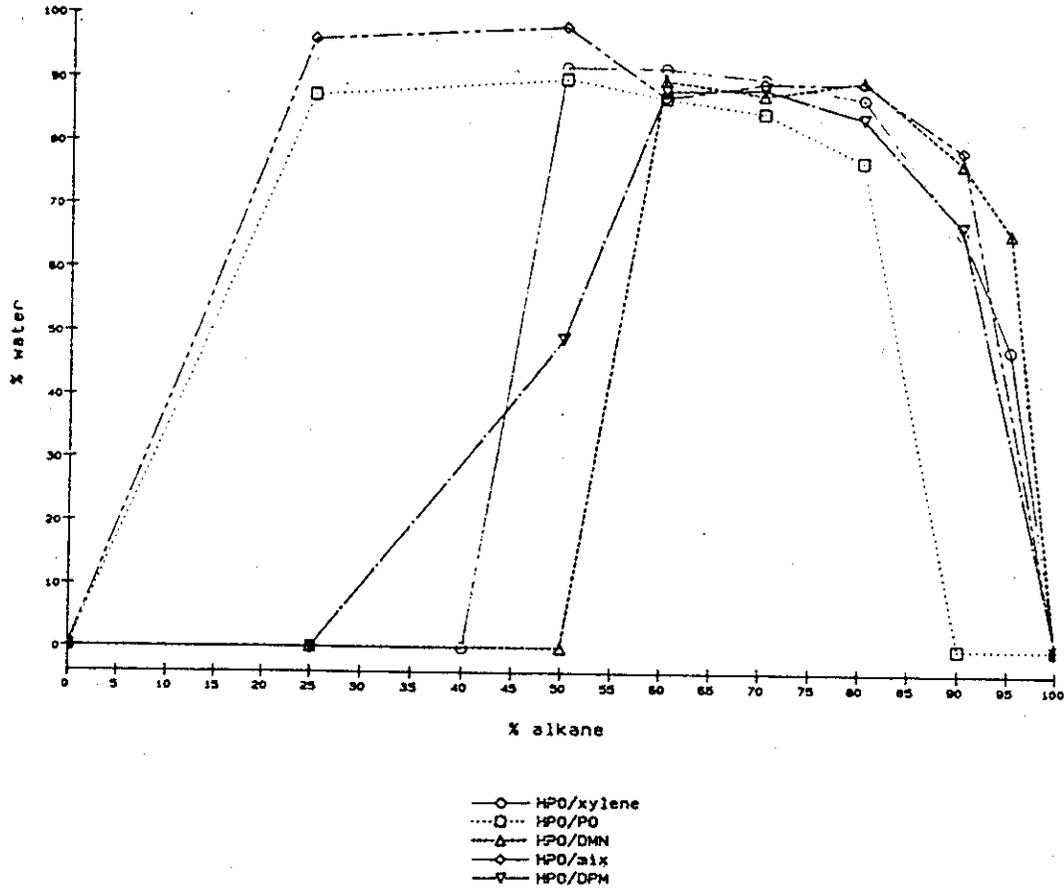


Figure 12: Yield point vs % alkane

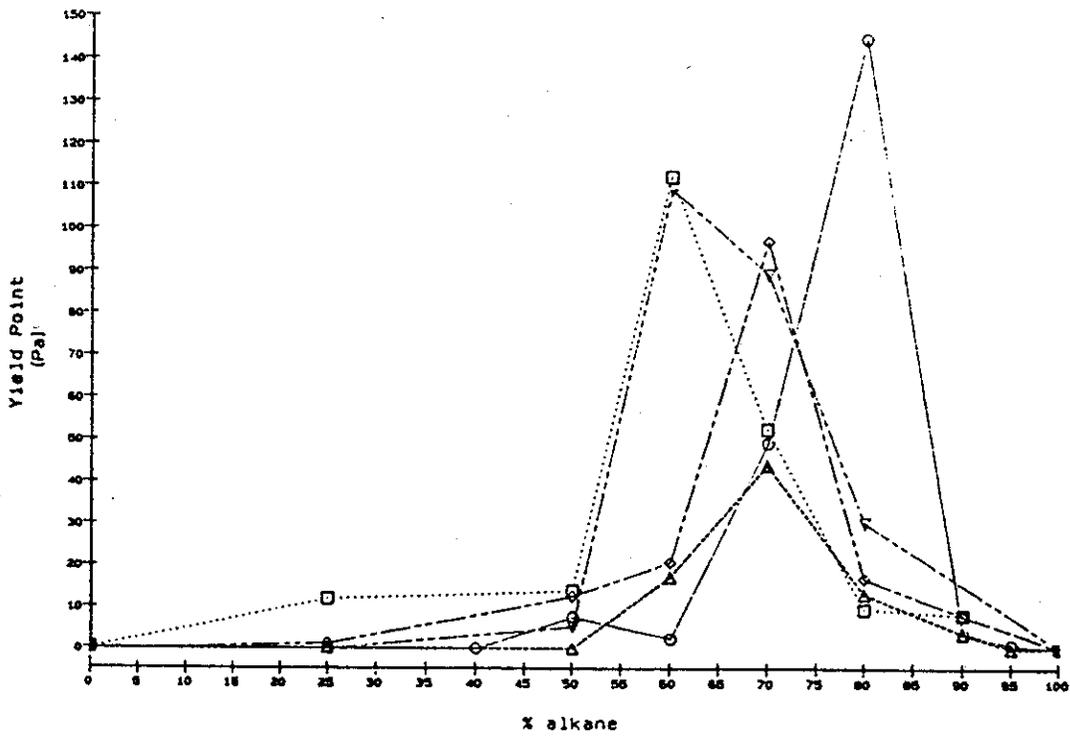


Figure 13:  $F_0$  vs  $(0a-0s)^{-2}$   
for different aromatic components

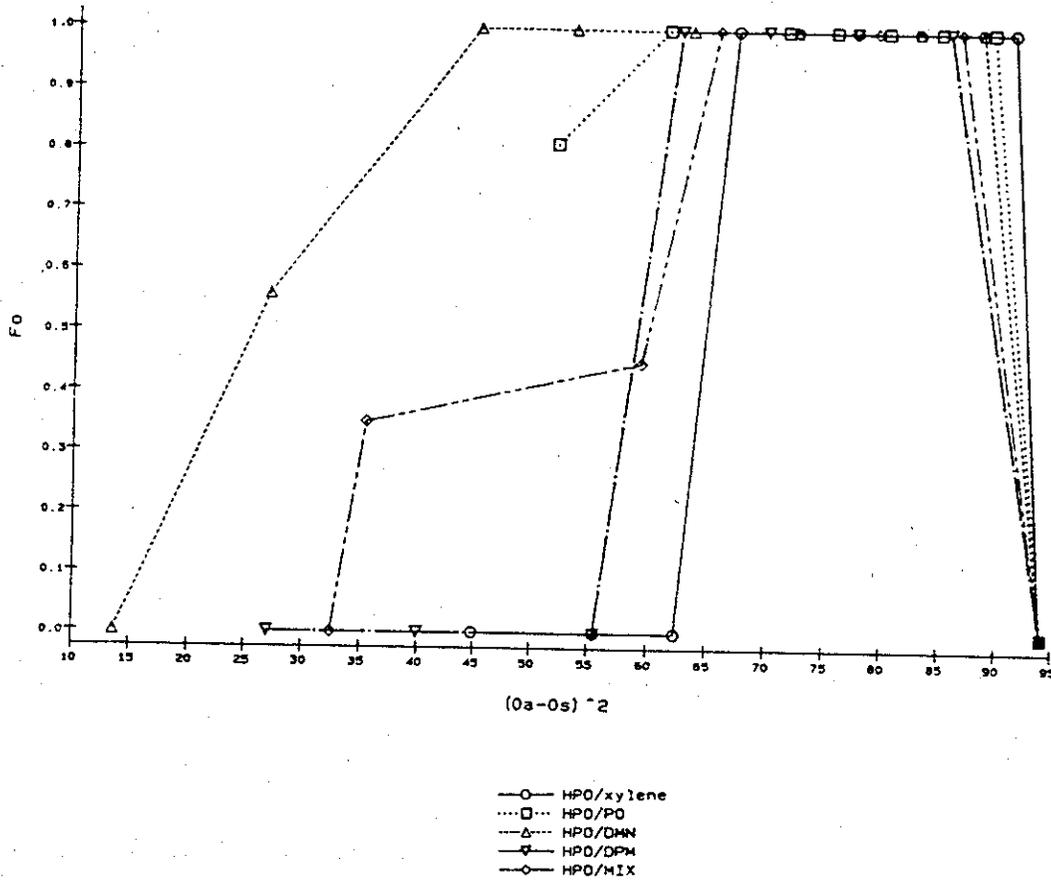


Figure 14:  $F_{final}$  vs  $(0a-0s)^{-2}$

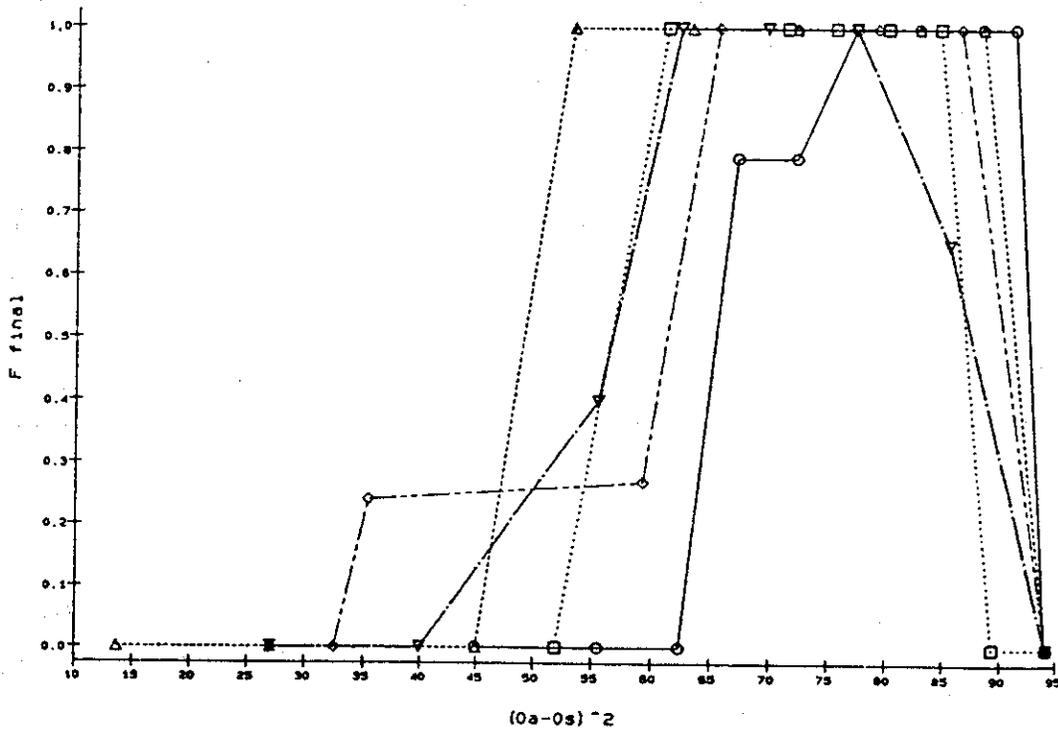


Figure 15: Water content vs  $(0a-0s)^{-2}$

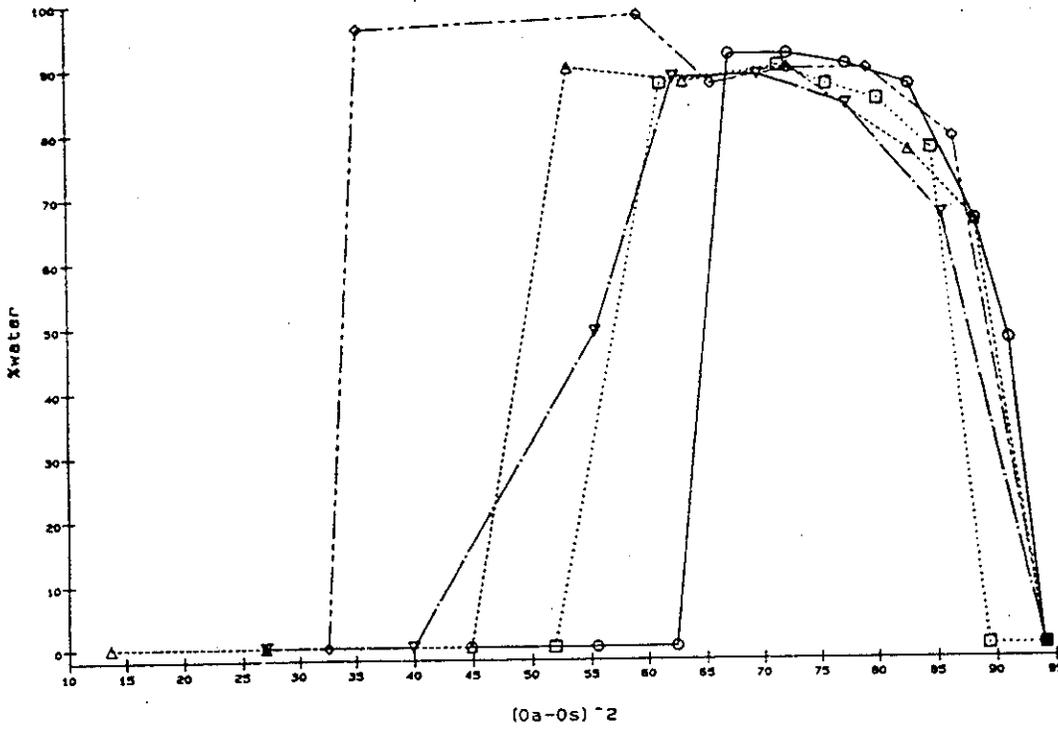
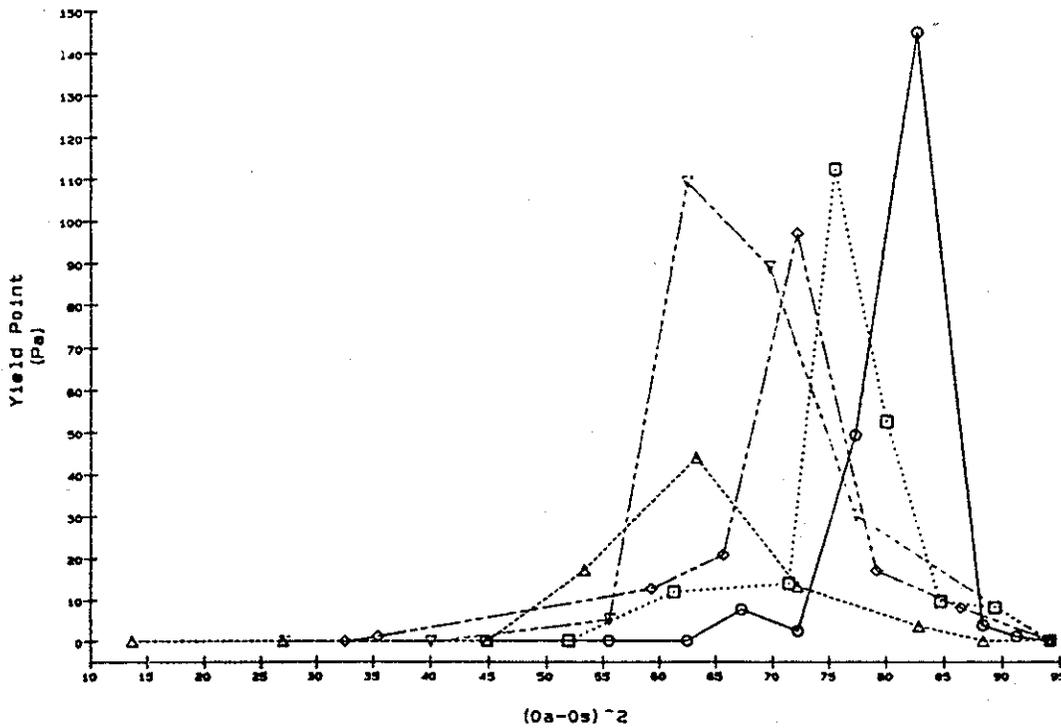


Figure 16: Yield point vs  $(0a-0s)^{-2}$



### Effect of Alkane Component

The effect of using different alkane solvents as the precipitation medium for asphaltenes has been studied by Long (1979), Speight and Moschopedis (1979). Their findings indicate that as the carbon number of the alkane solvent increases, the amount of asphaltenes which precipitate decreases, and that the composition of the precipitated material also changes. Higher alkane solvents were shown to yield asphaltenes which have a higher degree of aromaticity, a higher proportion of heteroatoms, a higher degree of polarity, and higher molecular weights.

Figures 17 to 20 show  $F_o$ ,  $F_f$ , water content, and yield point versus percent alkane for four different model oils consisting of xylene (XYL), 5% asphaltenes, and four different alkane components: n-octane (OCT)( $\sigma=15.4$ ), n-tetradecane (C14)( $\sigma=16.3$ ), light paraffin oil (LPO)( $\sigma=14.7$ ), and heavy paraffin oil (HPO)( $\sigma=15.0$ ). The results show that the model oils containing the paraffin oils (a complex mixture of alkanes) have a stronger tendency to form stable emulsions than do the oils made with the n-alkane solvents. The emulsions formed by oil containing the heavy paraffin oil are structurally stronger (higher yield points) than those formed by the light paraffin oil. When the emulsification behaviour of the model oils containing octane and tetradecane are compared, the tetradecane/xylene oil has a stronger tendency to form stable emulsions (higher  $F_f$  values), but these emulsions have less structural strength (lower yield point).

### Comparison of Asphaltenes from Different Crudes

Asphaltenes from different oils will differ in elemental composition, structure and molecular weight. Therefore, the solubility/precipitation behaviour of asphaltenes from different sources could potentially differ. The experiments using the heavy paraffin oil/xylene oil containing 5% asphaltenes were repeated for asphaltenes extracted from Prudhoe Bay crude oil. Overall the emulsification behaviour was very similar to the California crude asphaltenes. The asphaltenes from the California crude were slightly more effective emulsifiers.

Figure 17:  $F_0$  versus % alkane for different alkane components

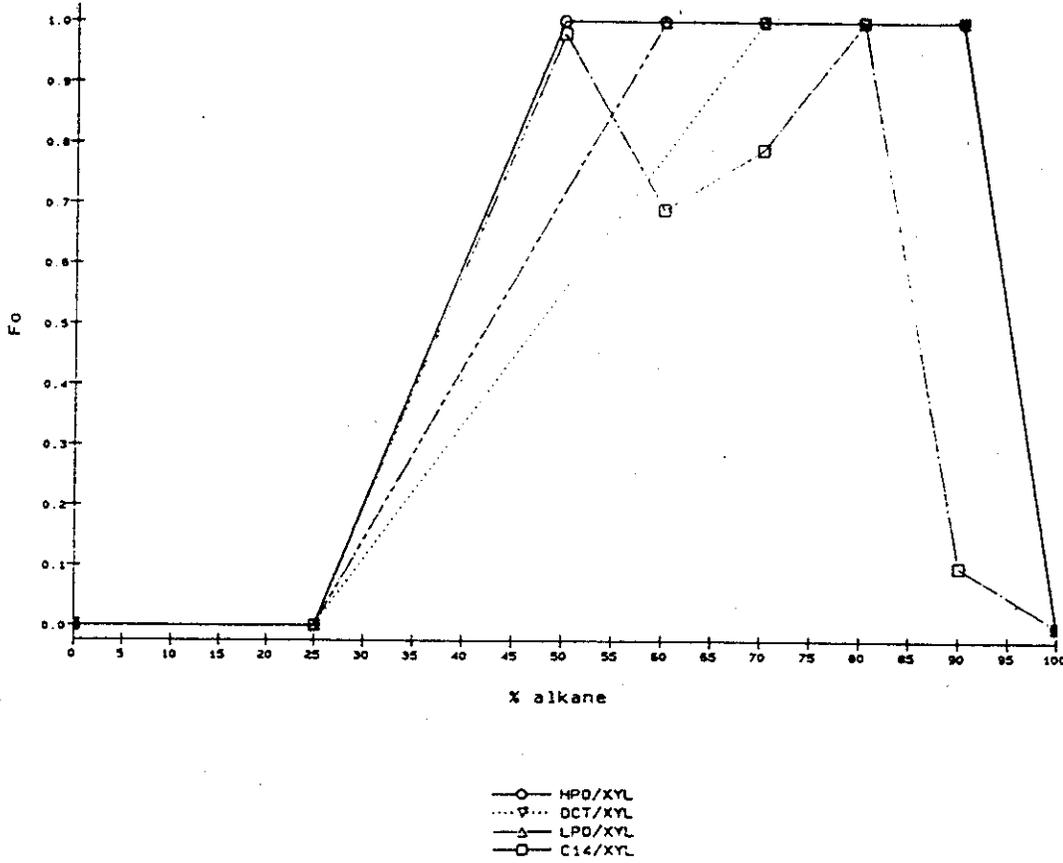


Figure 18:  $F_{final}$  vs % alkane

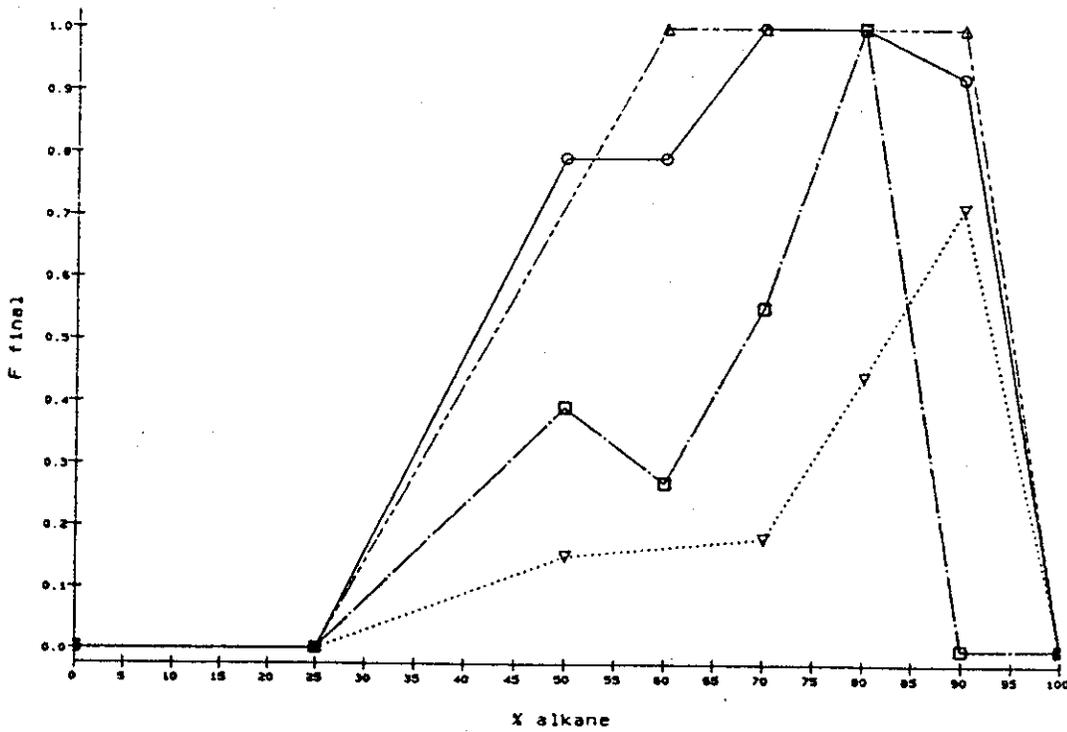


Figure 19: Water content vs X alkane

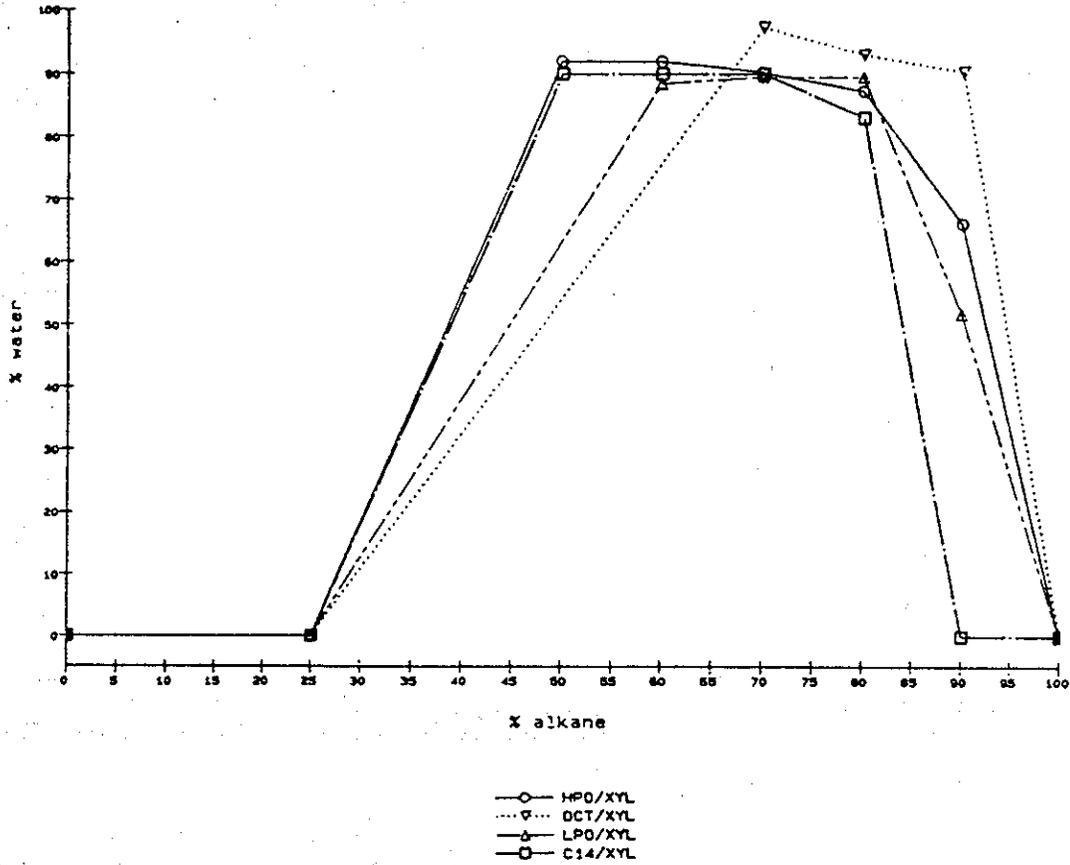
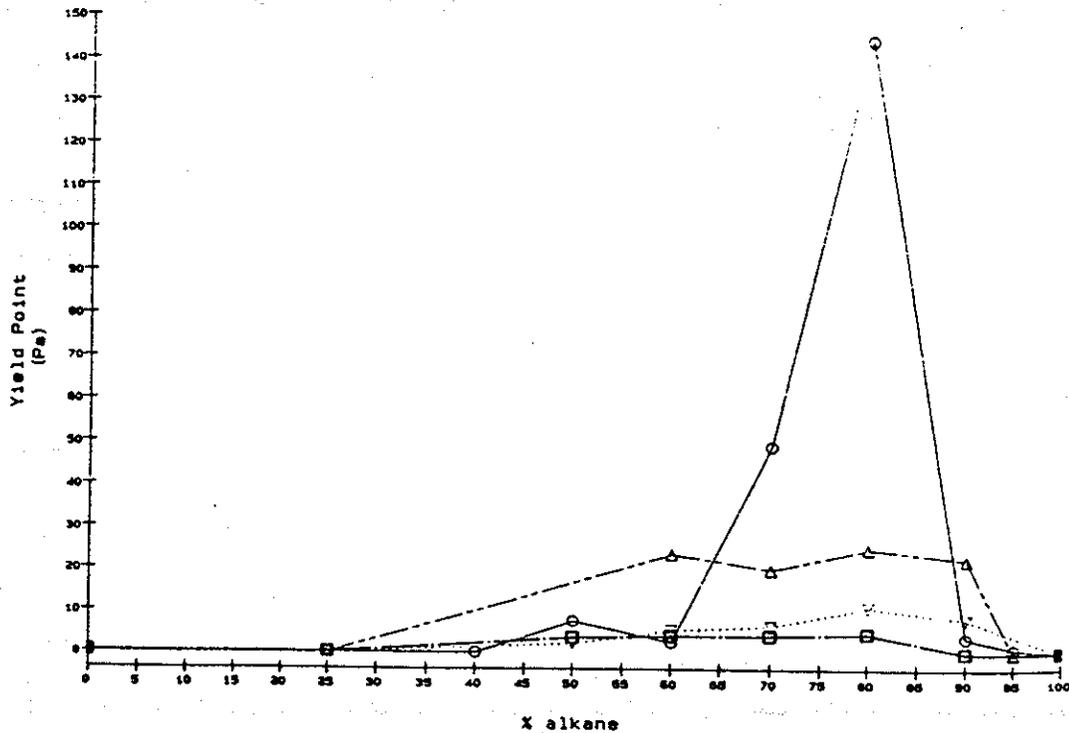


Figure 20: Yield Point vs X alkane



### Effect of Resins

Figures 21 to 24 present the emulsification behaviour for model oils where the emulsifying agents are: 1. asphaltenes; 2. resins; and 3. asphaltenes and resins together. The results show that stable emulsions can be produced by resins alone. Although the range of alkane/aromatic ratios over which stable emulsions are produced is small, these emulsions have greater structural strength than emulsions stabilized by asphaltenes. When asphaltenes and resins are both present, the range over which stable emulsions are formed is larger than either resins or asphaltenes alone. But emulsions stabilized by the asphaltene/resin combination lack the maxima peak in yield point.

### Effect of Wax

Figures 25 to 28 show the effect of adding 0.05 and 0.1 g/mL of wax to a model oil containing 1% asphaltenes. The model oil containing 1% asphaltenes has no tendency to form stable emulsions, but the addition of wax increases the emulsification tendency at all alkane/aromatic ratios. The range of alkane/aromatic ratios over which stable emulsions are produced increases as wax content increases. Increasing the wax content also increased the mechanical strength of the emulsions. Similar results were obtained when wax was added to the oil containing 2.5% asphaltenes.

The effect of adding 0.1 g/mL of wax to the model oil containing 5% asphaltenes is shown in Figures 29 to 32. The addition of wax has little effect upon  $F_o$ ,  $F_i$  and water content but decreases the maxima yield point of the emulsions formed.

Figures 33 to 36 show the effect of increasing asphaltene content upon an oil containing 0.05 g/mL grams of wax. Model oils containing only wax as the emulsifying agent had no tendency to emulsify. As the Figures illustrate, the addition of asphaltenes results in the formation of stable emulsions. As the concentration of asphaltenes is increased, the oils have a greater tendency to produce stable emulsions.

Figure 21:  $F_0$  versus % alkane  
effect of resins

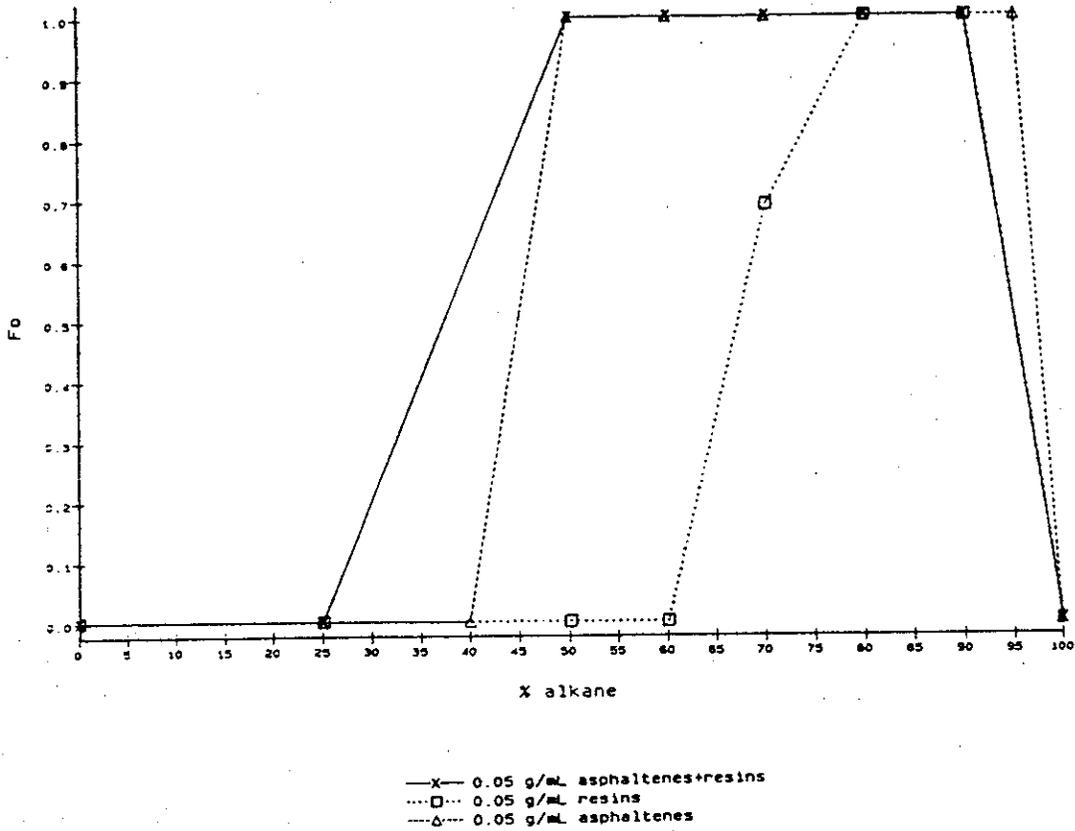


Figure 22:  $F_{\text{final}}$  vs % alkane

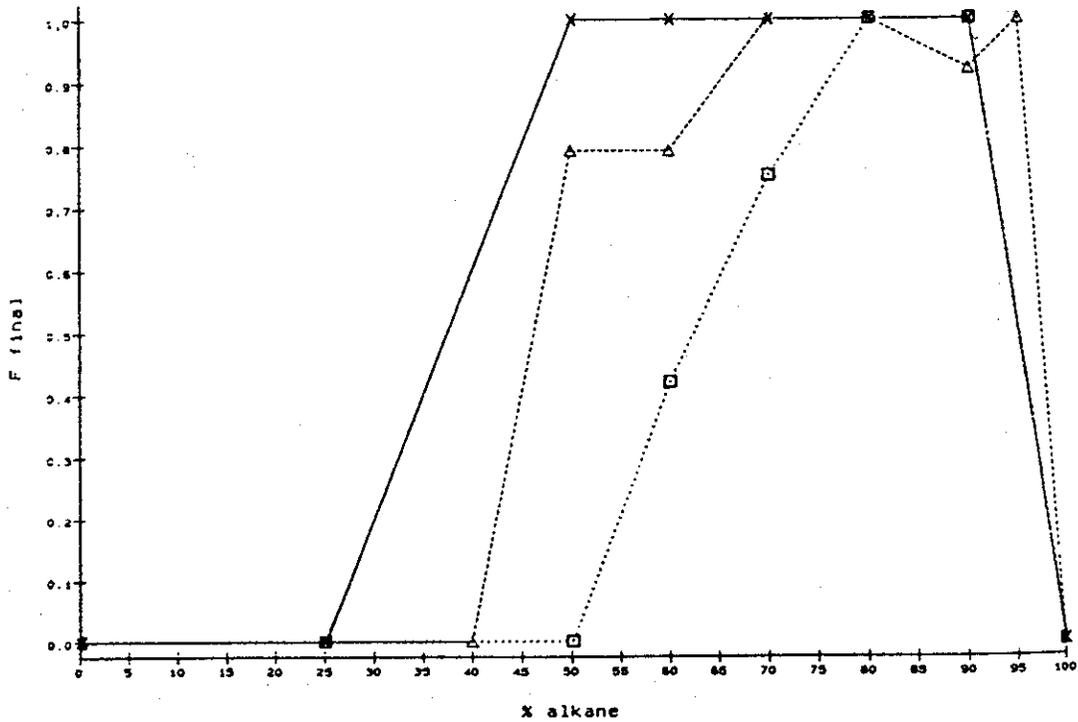


Figure 23: Water content vs % alkane

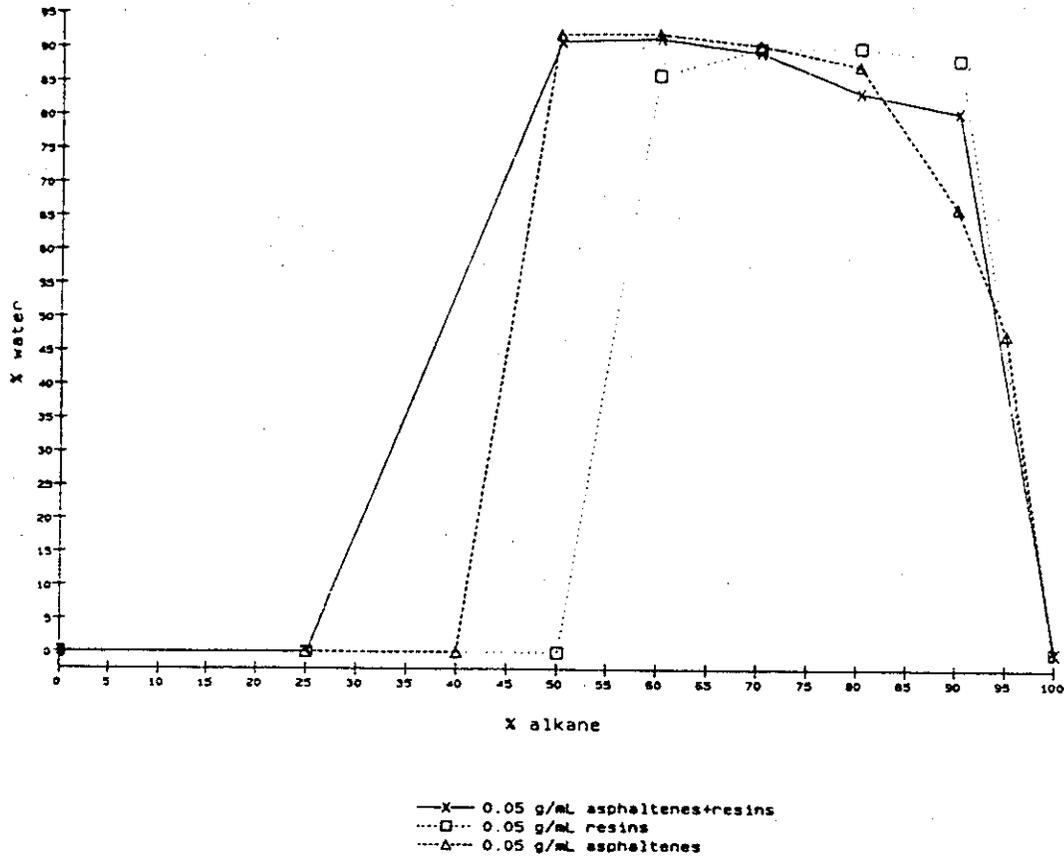


Figure 24: Yield Point vs % alkane

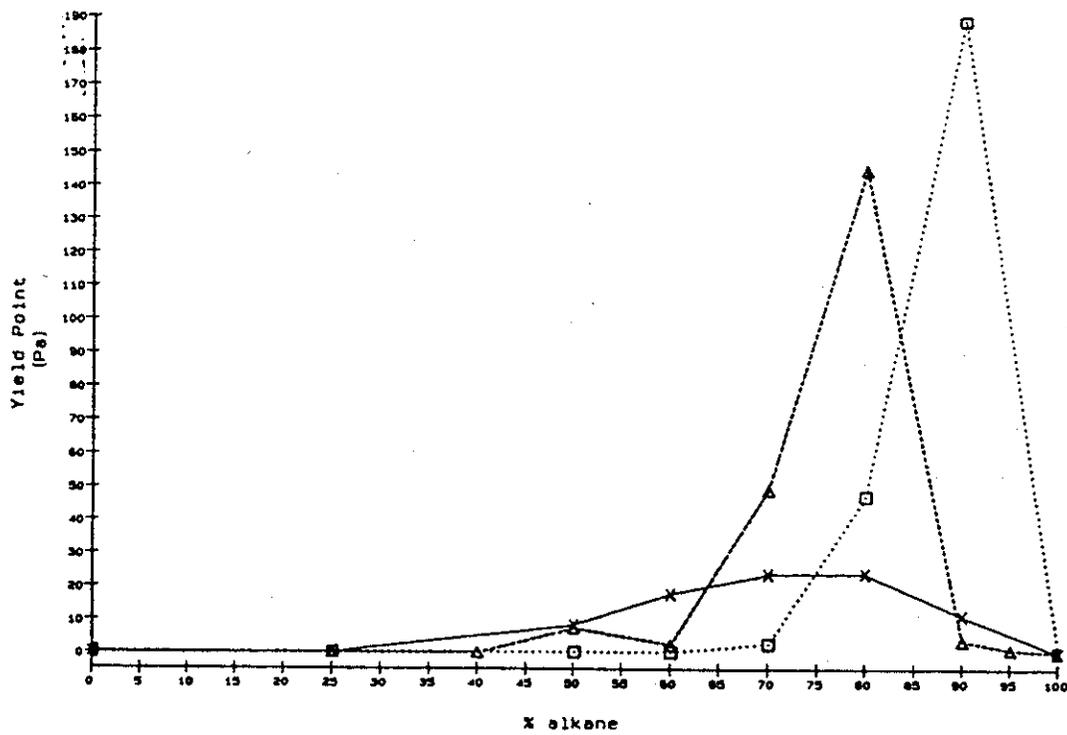
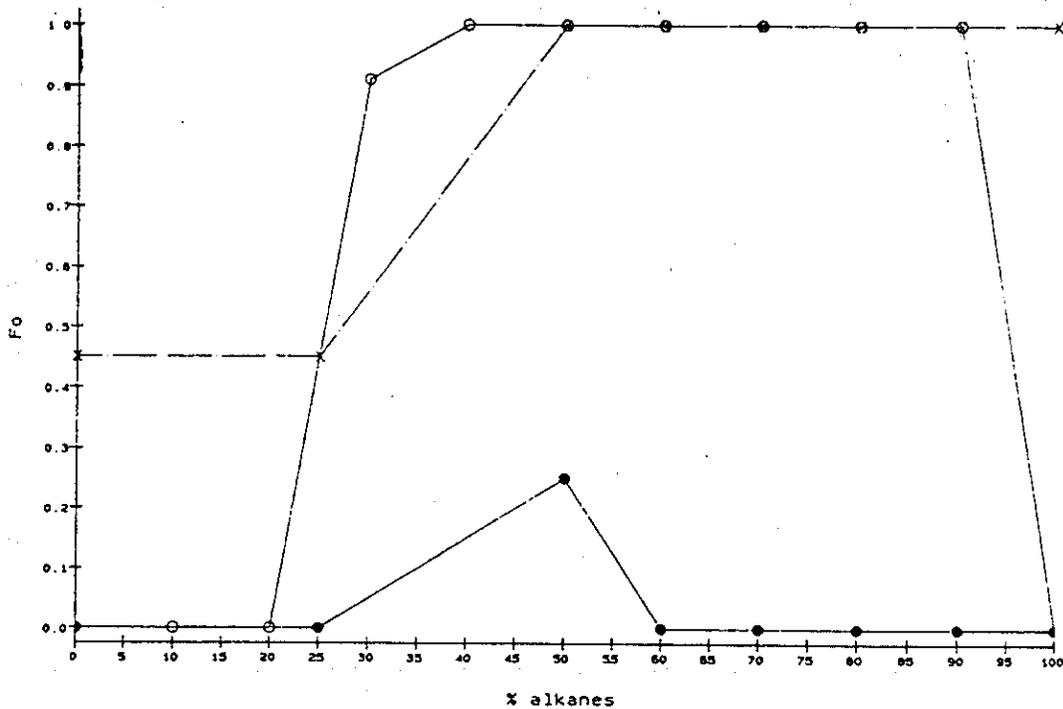


Figure 25:  $F_o$  vs % alkane  
effect of increasing wax content



● 0.01 g/mL asphaltenes/ 0 wax  
 ○ 0.01 g/mL asphaltenes/ 0.05 g/mL wax  
 x 0.01 g/mL asphaltenes/ 0.1 g/mL wax

Figure 26:  $F_{final}$  vs % alkane

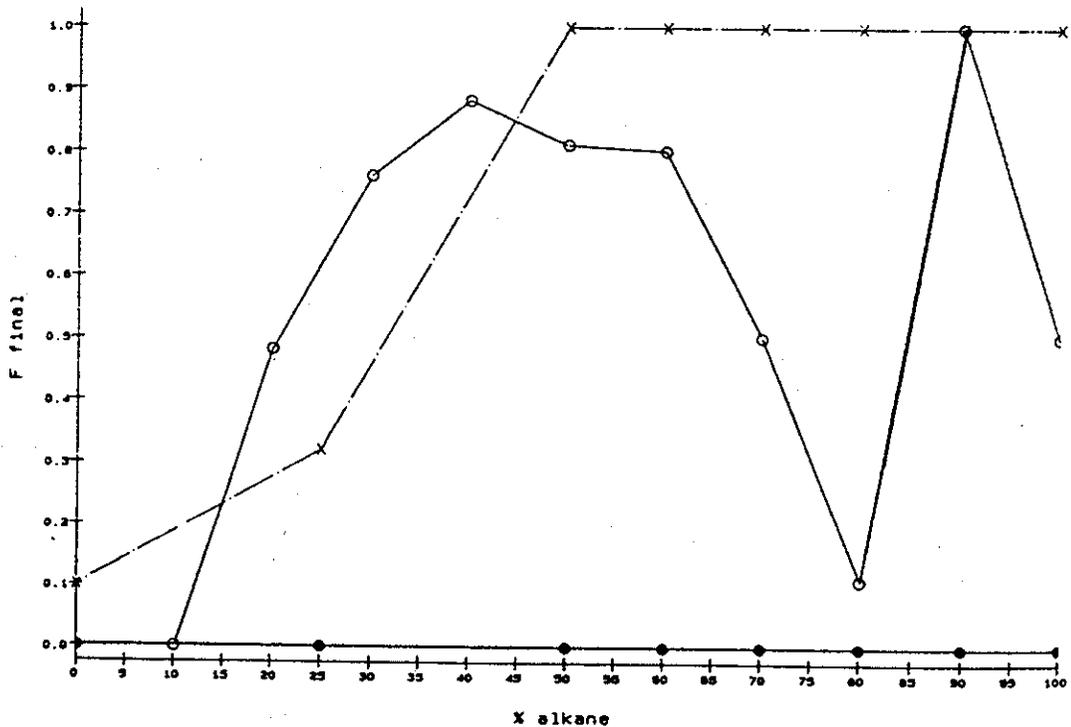


Figure 27: Water content vs % alkane

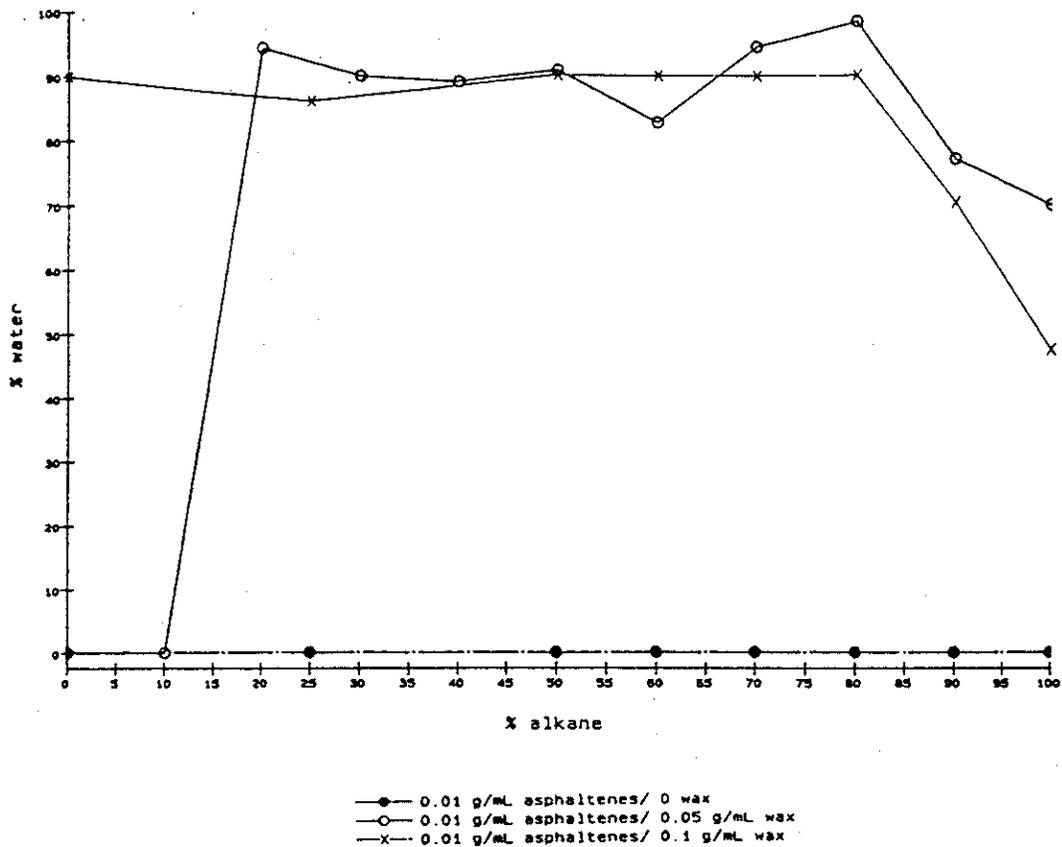


Figure 28: Yield Point vs % alkane

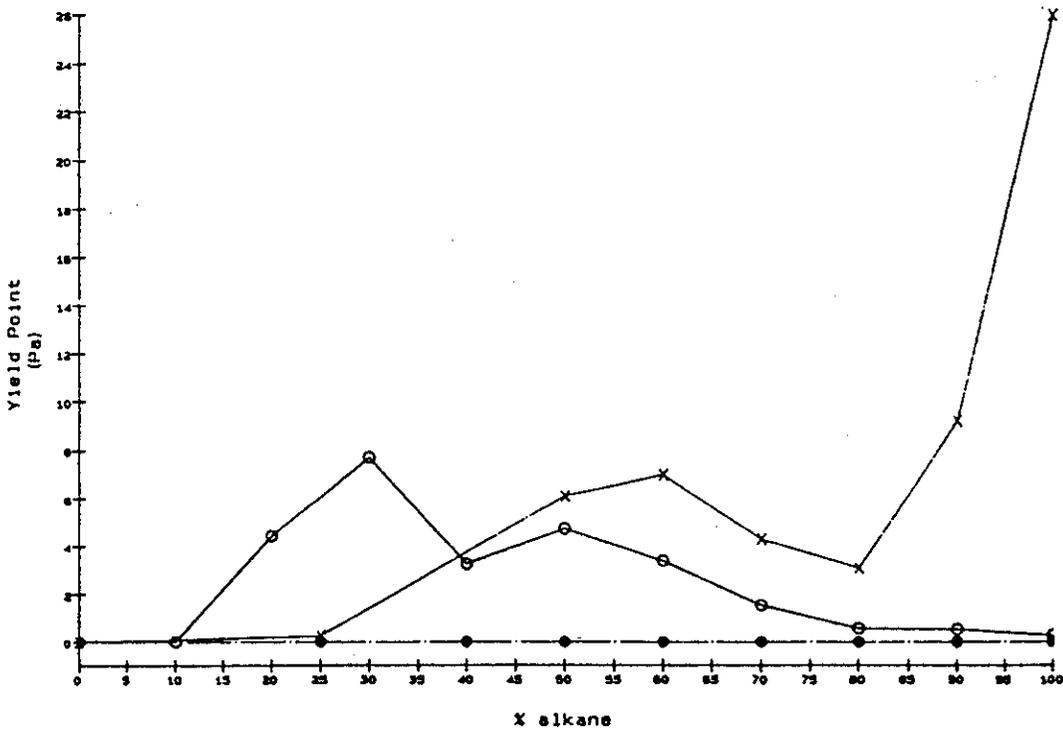
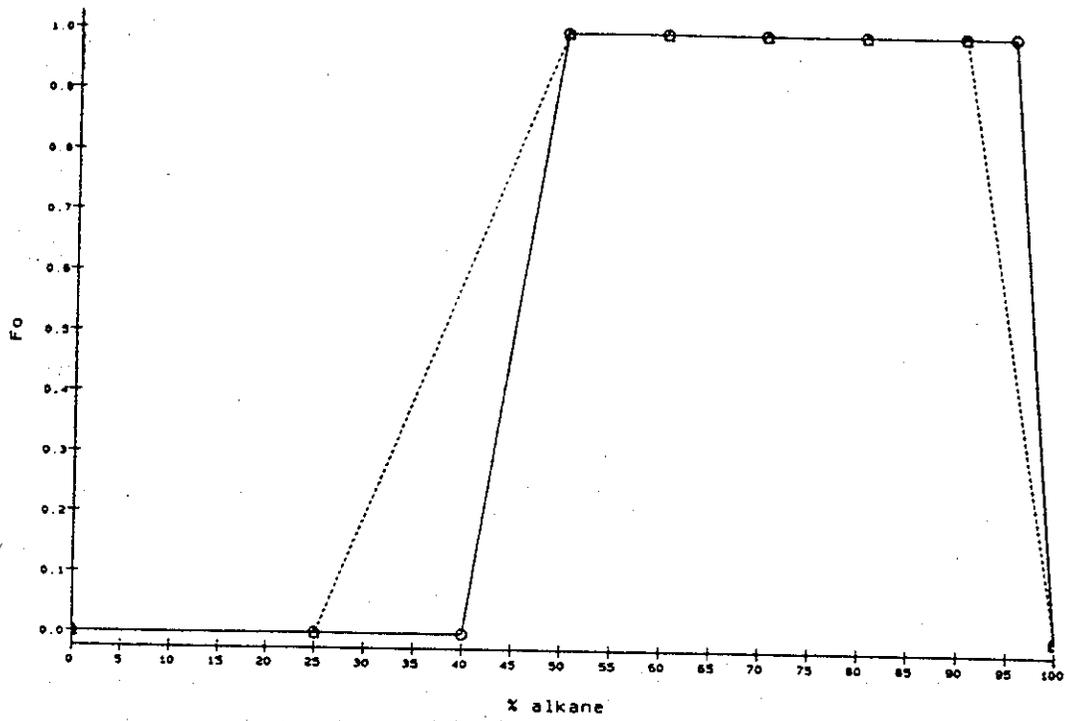


Figure 29:  $F_0$  versus % alkane  
effect of adding wax



—○— 0.05 g/mL asphaltene / 0 wax  
- - -△- - - 0.05 g/mL asphaltene / 0.1 g/mL wax

Figure 30:  $F_{final}$  vs % alkane

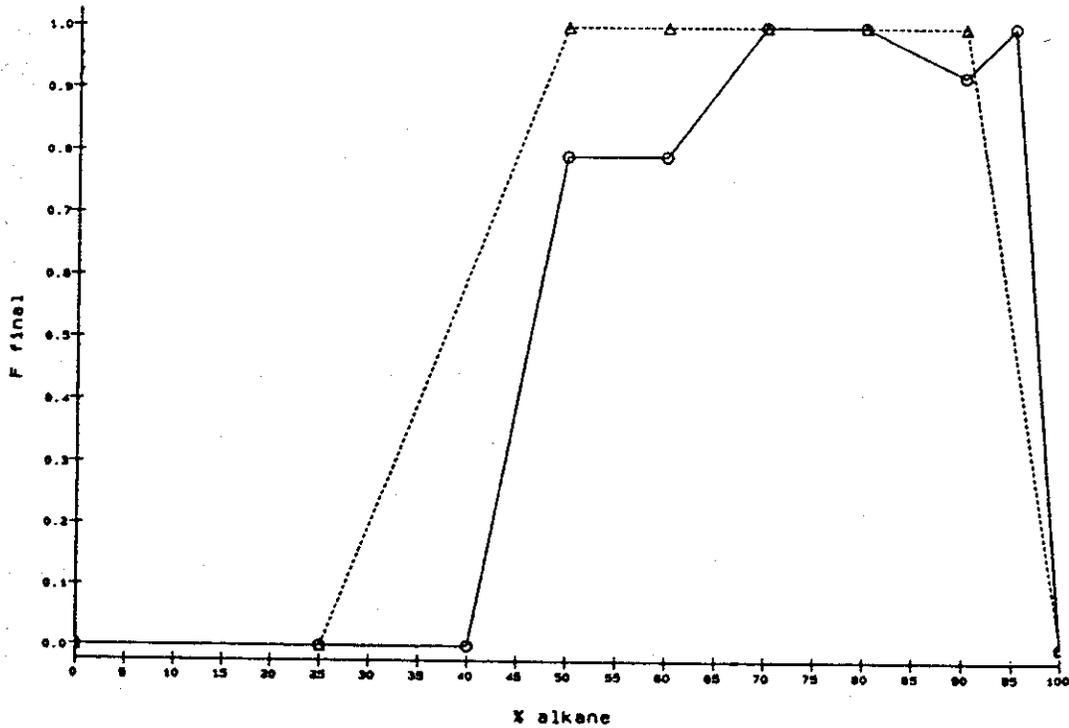


Figure 31: water content vs % alkane

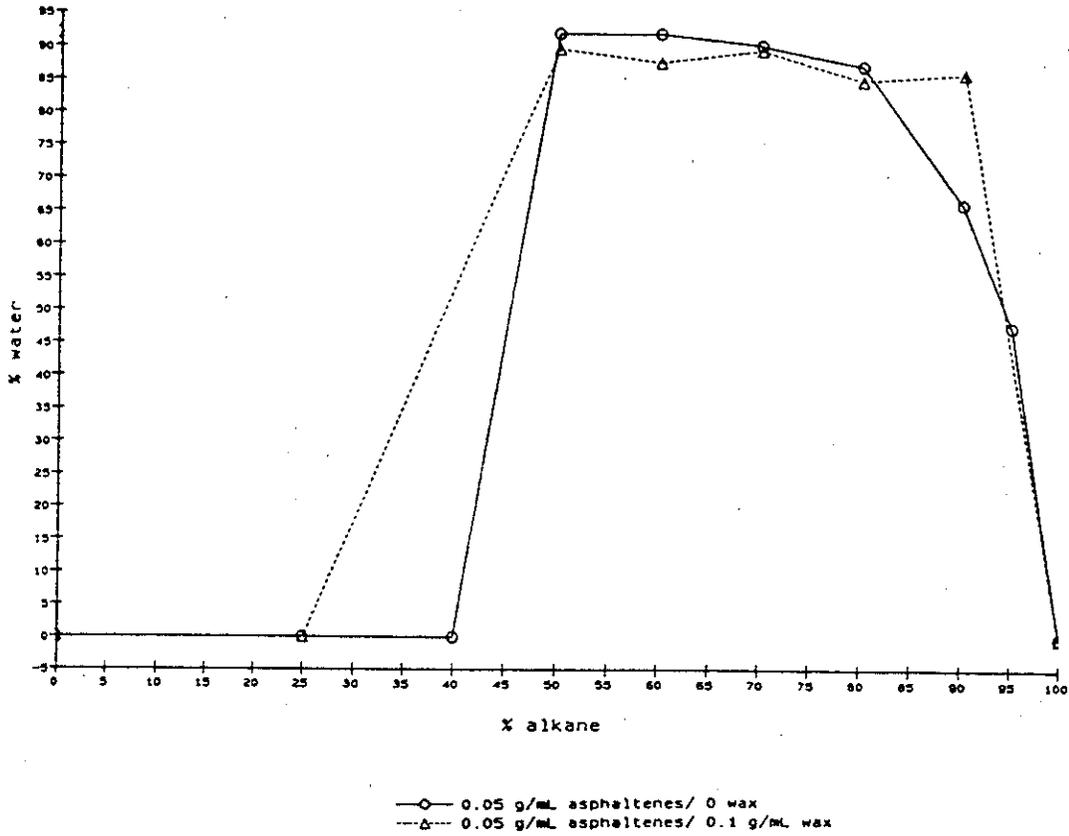


Figure 32: Yield point vs % alkane

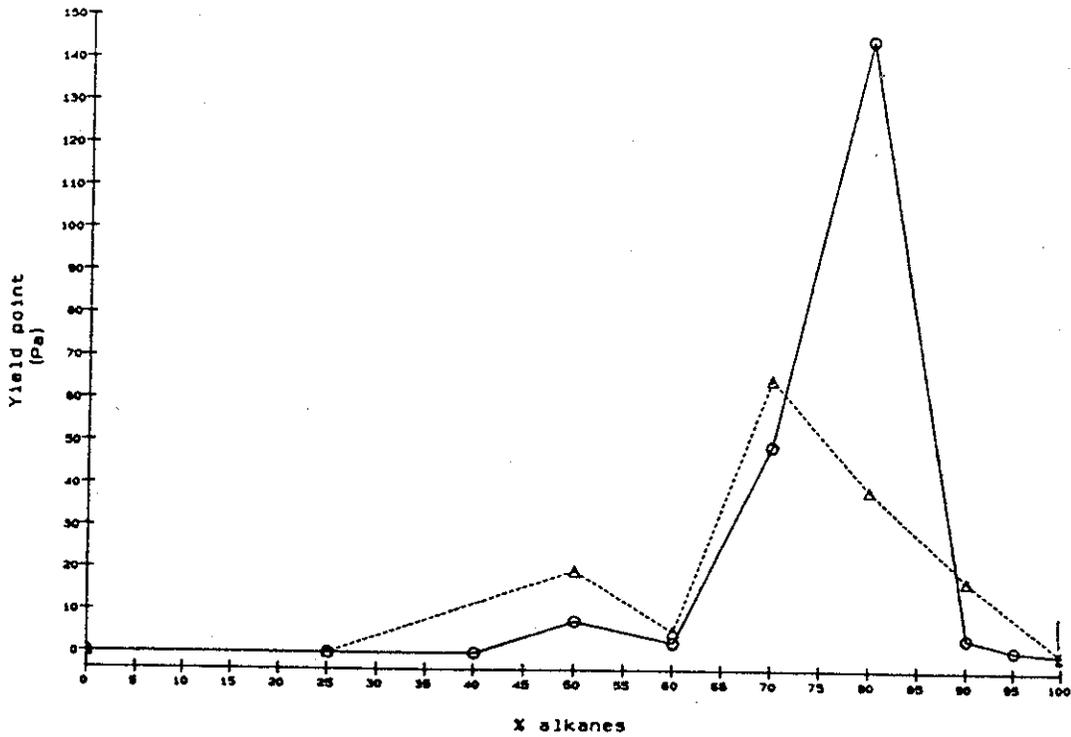


Figure 33:  $F_0$  versus  $X$  alkane  
 effect of increasing asphaltene concentration  
 in an oil having a wax concentration of 0.05 g/mL

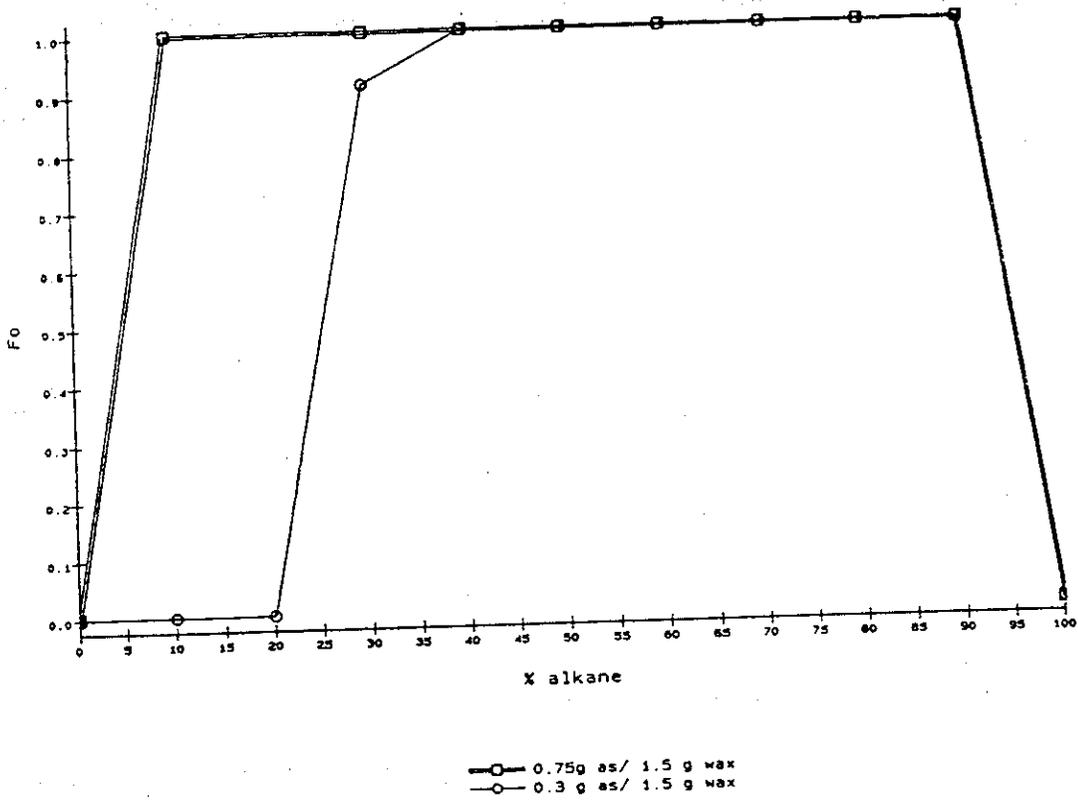


Figure 34:  $F$  final vs  $X$  alkane

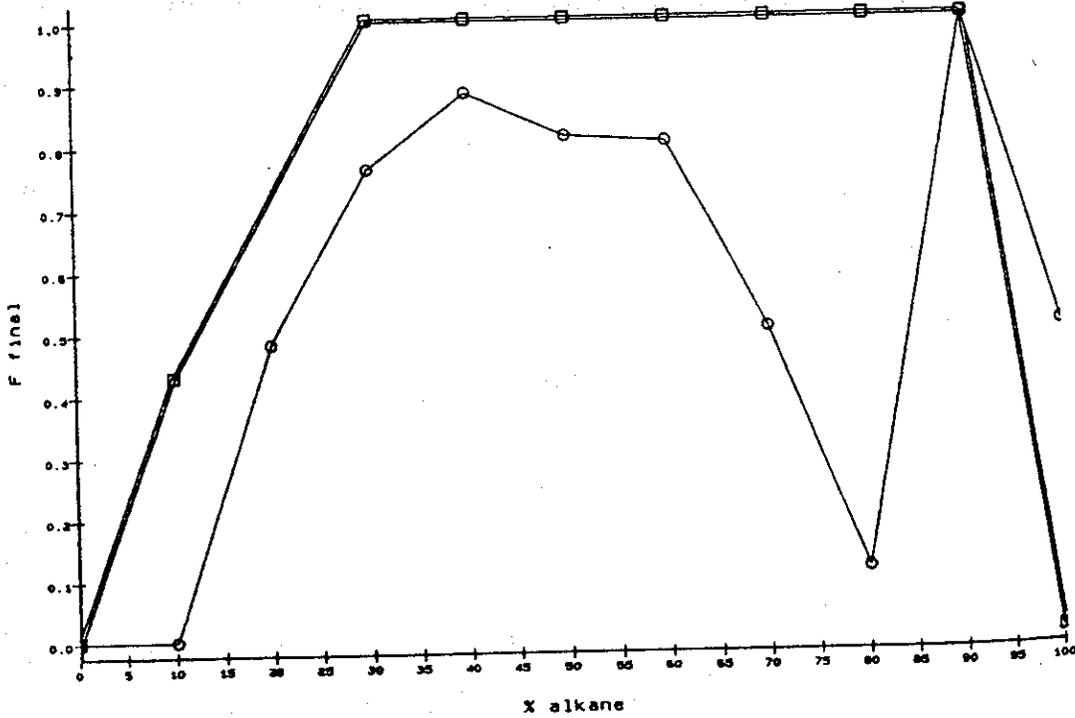


Figure 35: Water content vs % alkane

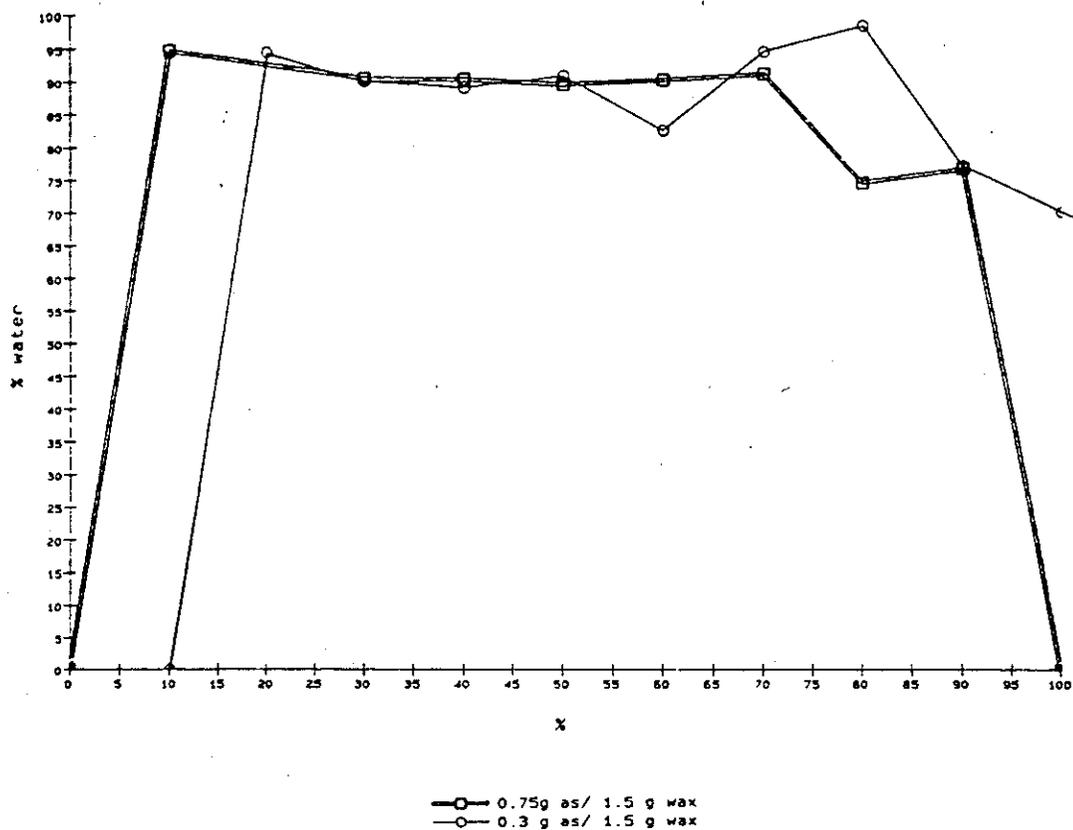
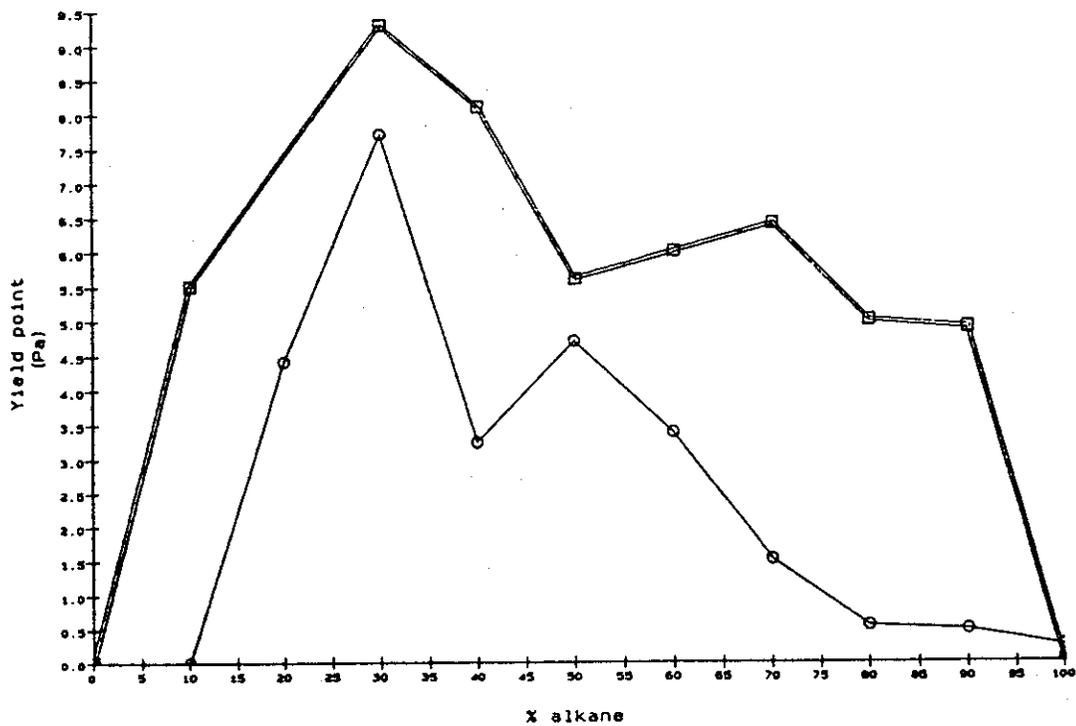


Figure 36: Yield point vs % alkane



### Rheological Properties

All the stable emulsions formed during this study exhibited non-Newtonian flow behaviour. Flow curves for mousse (Figure 37) indicate that they behave as pseudoplastic liquids which have a definite yield point and a thixotropic flow behaviour. This complex flow behaviour means that viscosity is extremely dependent upon shear conditions (shear rate and length of time shear is applied). Therefore, a single viscosity number can not properly characterize the fluidity of mousse. Figure 38 demonstrates this effect of shear rate on apparent viscosity.

### Droplet Size Distribution

Figure 39 shows the droplet size distribution for a typical mousse formed by the model oils. The droplet diameters are very heterogeneous and appear to have at least a bi-modal distribution. This multi-modal size distribution means that the water content of emulsions can exceed the water content of uni-modal distributions which theoretically has a maximum value of 74%. In effect, this allows droplets of a smaller size to occupy the gaps between larger droplets, thus creating an extremely dense packing of droplets. The yield point of emulsions increases as the droplet size distribution shifts to smaller values.

Figure 37: Flow curve for mousse  
Shear stress versus shear rate

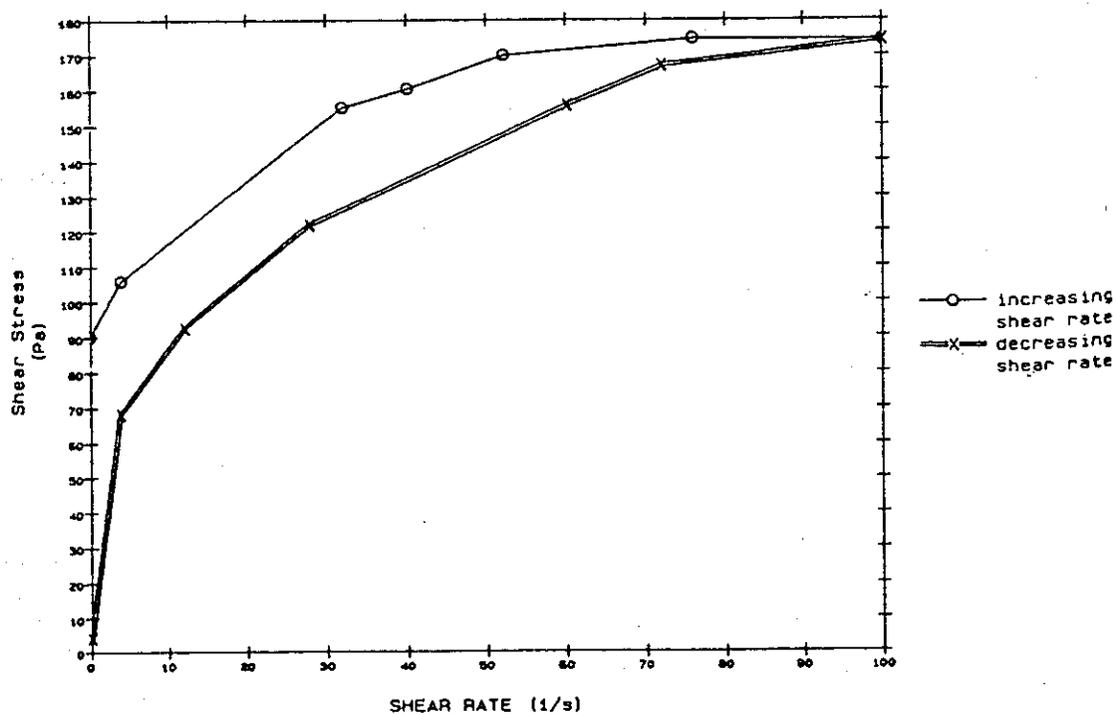


Figure 38: Effect of shear rate on apparent viscosity of mousse

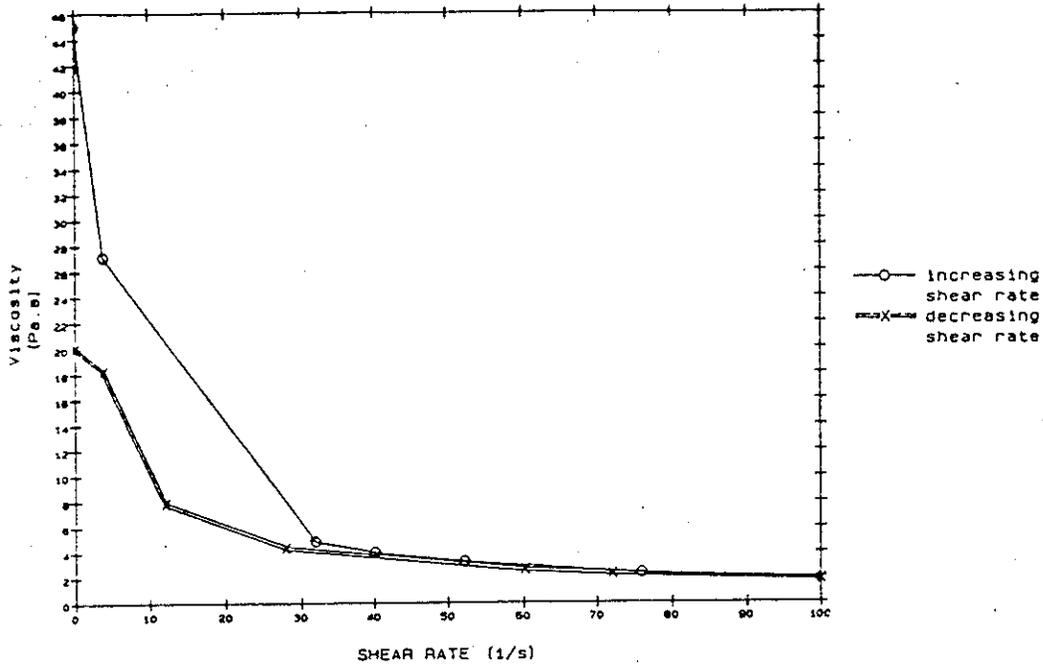
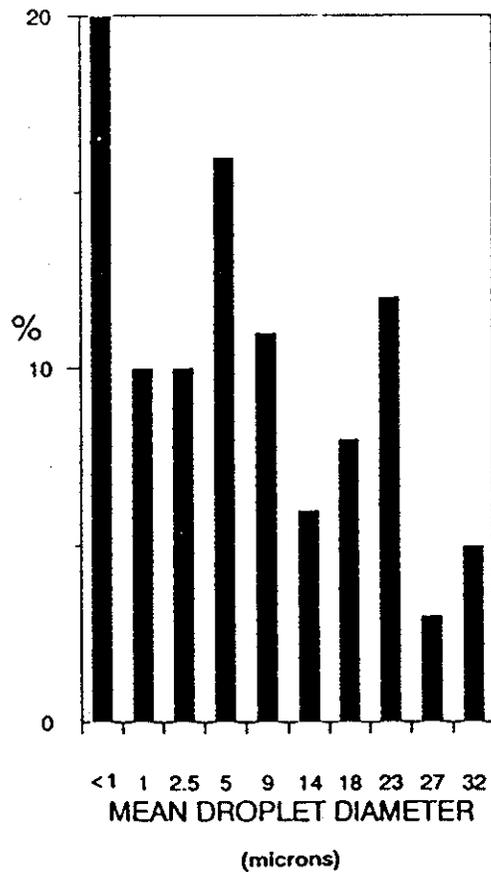


Figure 39: Droplet size distribution



### Conclusions

The results from this study demonstrate the importance that the physical state of an emulsifying agent has upon its ability to stabilize emulsions. It was found that to be effective emulsifiers, asphaltenes, resins and waxes must be in the form of finely divided particles. The chemical composition of the oil determines not only the amount and size of these particles but also their composition and their wetting properties. All these factors were shown to have an influence upon the emulsification process.

Asphaltenes and resins, by themselves and in combination, were effective emulsifying agents. Model oils containing only wax as the emulsifying agent did not form stable emulsions. But the addition of a nominal amount of asphaltenes, an amount insufficient by itself to produce emulsions, to oils containing wax lead to the formation of stable emulsions. This indicates that different emulsifying agents can synergically interact to stabilize emulsions.

The solubility/precipitation behaviour of asphaltenes in model oils follows the solubility theory as described by the Hildebrand-Scatchard equation. The use of solubility parameters can be applied to petroleum fractions and therefore, may be useful in predicting the physiochemical conditions which favour emulsification.

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