

# RHEOLOGY OF ACACIA-STABILISED EMULSIONS

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The flow behaviour of emulsions of benzene and two paraffin oils in acacia solutions has been examined. The concentration of acacia had little effect on the relative viscosity, and the viscosity of the oil none. Emulsion viscosity increased with the volume fraction of oil which also led to an increased deviation from Newtonian flow. Evidence of thixotropy was not found in these emulsions. The chemical nature of the oil has a great influence on the viscosity and the differences are explained in terms of the characteristics of the interfacial film.

THE rheology of emulsions containing moderate concentrations of oil has been studied by Richardson<sup>1</sup>, Sibree<sup>2</sup>, Toms<sup>3</sup>, Neogy and Ghosh<sup>4</sup>, and others<sup>5,6</sup>. General agreement had been found on the effect of increasing oil concentration, but differences were noted when the nature of the stabiliser or oil were changed. No work of this kind has previously been undertaken using a hydrophilic colloid as emulsifying agent. Sumner<sup>6</sup> has pointed out the need to investigate the viscosity of emulsions stabilised by agents such as acacia, which are known to produce a visible film at the oil-water interface<sup>7</sup>.

## EXPERIMENTAL

*Apparatus.* A Ferranti-Shirley cone-and-plate viscometer was used. This has been described in detail by McKennell<sup>8</sup>. The original torsion spring was replaced by a lighter one so that a full scale deflection at maximum sensitivity was obtained with a fluid of about two poises. The temperature throughout the work was approximately 25° maintained by circulating water at 25 ± 0.1° beneath the plate.

A 1 in. diameter "Dispersator" head (Premier Colloid Mills) was used on a Mitchell laboratory stirrer for making the emulsions.

### *Materials*

Potassium arabate was produced from acacia by repeated precipitation with ethanol from an aqueous solution followed by passage through an ion exchange column to produce free arabic acid. The potassium salt was made by adding Analar potassium hydroxide to the acid in solution until the pH rose to 7.0. The method was described by Shotton<sup>9</sup>; larger batches (500 g.) were prepared and the salt was precipitated with ethanol before drying under vacuum.

The benzene was of Analar quality. Liquid Paraffin B.P., and Light Liquid Paraffin B.P. were used without further purification. They were free from acid and readily carbonisable materials, and contained no unsaturated substances. They had the following physical characteristics.

	Viscosity poises	Density g./ml.
Liquid Paraffin B.P. . . . .	1.5280	0.8796
Light Liquid Paraffin B.P. . . . .	0.2910	0.8483

*Method*

*Emulsion preparation.* A solution of potassium arabate and the oil were weighed into a 250 ml. beaker and stirred for 60 seconds at about 3,000 r.p.m. Two glass rods were held against the side of the beaker to act as baffles. Emulsions of a higher volume fraction than 0.45 were made by first preparing an emulsion containing 30 per cent of oil. The remaining oil was then added in small quantities until the required volume fraction was reached. Fine emulsions were made by passing the coarse one five times through a small hand homogeniser with the valve screwed up tight.

100 ml. volumes of emulsions of each of the oils were prepared at 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6, volume fraction. Gum concentrations in the aqueous phase were 9, 10, 15, and 20 per cent w/v.

The emulsions were stored in small glass stoppered Pyrex glass bottles and the viscosity was measured after 4 days. After this period the entrapped air had been released and the interface was known to be in equilibrium<sup>9</sup>.

Three emulsions were made for each concentration of oil and gum and three flow curves were produced for each emulsion. The mean of the nine results was taken.

Before placing in the viscometer, the emulsions were remixed by carefully rotating the containers for about 3 minutes. They were then homogeneous and substantially free from air. When a diluted emulsion was examined microscopically no aggregates of oil globules could be seen. The flow curve was quickly taken by raising the shear rate in uniform steps from 0 to 1,691 sec.<sup>-1</sup>, and the shear stress read from the indicator. Sample points were observed on the down curve to investigate the possibility of thixotropy.

## RESULTS

*Effect of Concentration of Potassium Arabate in the Aqueous Phase on the Relative Viscosity of Benzene Emulsions*

Nine and 10 per cent potassium arabate solutions produced emulsions that were not so stable as those made with higher concentrations. Creaming was rapid and some large globules separated. On attempting to make emulsions of high oil concentration with a 20 per cent solution of potassium arabate cracking occurred. A 15 per cent solution produced stable benzene emulsions when the volume fraction varied from 0.1 to 0.6, and this concentration of potassium arabate was chosen for all subsequent work.

Small variations in relative viscosity were found for emulsions of the same volume fraction prepared with potassium arabate solutions of different concentrations.

*Effect of Volume Concentration of Disperse Phase, and the Nature of the Oil used on Flow Behaviour*

The flow curves were linear for a volume fraction up to between 0.2 to 0.3, but the emulsions were non-Newtonian when the oil concentration was increased above this value (Fig. 1). This deviation increased with

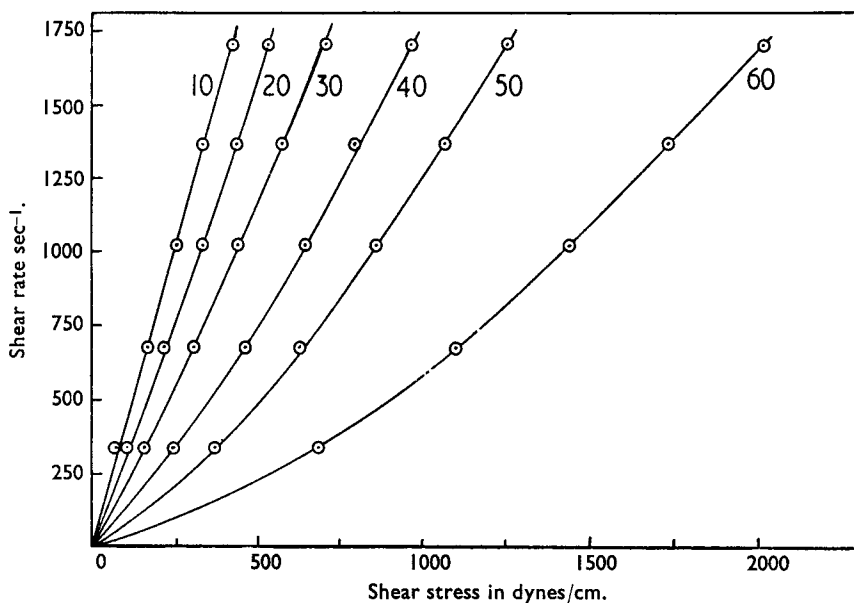


FIG. 1. Flow curves of benzene-potassium arabate (15 per cent w/v) emulsions. Figures are per cent volume concentration of oil.

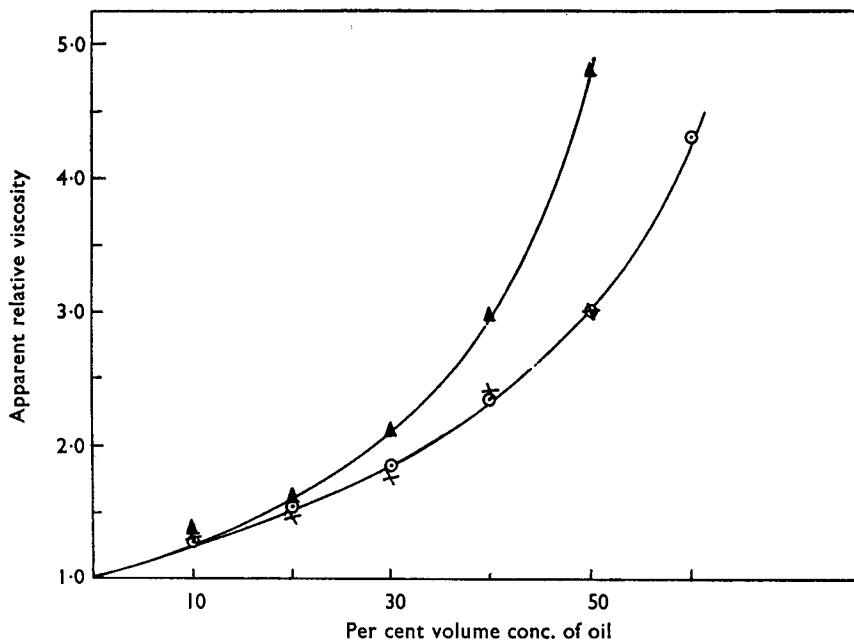


FIG. 2. Graph of apparent relative viscosity against volume concentration of oil.  
 ▲ Light liquid paraffin      X Liquid paraffin      ○ Benzene

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increasing oil concentration. No evidence of thixotropy was found even at the highest volume fraction.

Attempts have been made to represent the whole flow curve mathematically either by plotting log flow characteristics<sup>10</sup> or by using the Ree-Eyring equation for generalised flow<sup>11</sup>. However, in this instance, for comparison purposes, the apparent viscosity has been calculated from the linear portion of the plot in the manner reported by Sibree<sup>2</sup>, Richardson<sup>1</sup> and Broughton and Squires<sup>5</sup>.

A plot of apparent relative viscosity against volume concentration is almost linear to about 30 per cent volume concentration. Above this value the viscosity increases more rapidly with increase in the volume fraction as shown in Figure 2.

Benzene and liquid paraffin emulsions were similar in behaviour but light liquid paraffin emulsions were more viscous overall at any given volume fraction.

### *Homogenisation*

Homogenisation of a benzene emulsion readily caused cracking, although with care, a fine emulsion could be made. The viscosity increased only slightly. A light liquid paraffin emulsion could be homogenised without difficulty resulting in a greatly increased viscosity.

## DISCUSSION

The flow behaviour of acacia-stabilised emulsions is similar to that of emulsions prepared with synthetic stabilisers. The emulsion viscosity rises with an increase in oil concentration, and this in turn is accompanied by a greater deviation from Newtonian flow.

It appears that the viscosity of the oil has no marked effect on emulsion viscosity, a conclusion reported by others<sup>2,5</sup>. However, with acacia-stabilised emulsions the nature of the oil does influence the viscosity of the emulsion.

It may be that the droplet size distribution varies from an emulsion prepared with one oil to that prepared with another, but both Sibree<sup>2</sup> and Leviton and Leighton<sup>12</sup> found that a change in globule size did not alter emulsion viscosity.

To explain the difference in the viscosities of emulsions of the same volume fraction but of different oils, it is postulated that a substantial film is built up at the oil-acacia solution interface, and that the nature of the film depends upon the oil used. A film of substantial thickness would increase the effective volume of the globules. There would, therefore, be an increase in volume fraction, and a corresponding increase in emulsion viscosity. Reduction in mean particle size would lead to an increase in the interfacial area available for adsorbing the film. Thus, as the mean particle size is reduced, the part of the volume fraction contributed by the film would increase. A raised viscosity would follow from the effective increase in volume fraction. Homogenisation should, therefore, cause an increase in the viscosity of emulsions where the globules are surrounded by a thick interfacial film.

Shotton and Wibberley<sup>13</sup> have shown that acacia quickly builds up a multilayer at the interface, and Serrallach and Jones<sup>7</sup> found in 1931 that a film visible to the eye was formed after 4 days. Serrallach, Jones and Owen<sup>14</sup> further discovered that the chemical nature of the oil used influenced both the physical appearance and the mechanical strength of the film at the oil-acacia solution interface.

It is suggested that benzene droplets are surrounded by a comparatively weak, thin film, and light liquid paraffin droplets by one which is thicker and stronger.

Such a difference in the nature of the film would explain why benzene emulsions were less viscous than those of light liquid paraffin at the same volume concentration. It would further explain the ease of cracking of benzene emulsions when homogenisation was attempted, and the small rise in viscosity when the particle size was successfully reduced. The thicker film surrounding light liquid paraffin droplets would account for the much increased viscosity on homogenisation.

The difference in viscosity between emulsions of the two paraffin oils is probably due to a smaller mean particle size of the light liquid paraffin emulsion.

Work to test this theory is being continued on the effect of the nature of the oil, the drop size distribution, and the age of the emulsion on flow behaviour.

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After Mr. White presented the paper there was a DISCUSSION. The following points were made.

The systems under investigation behaved as Newtonian fluids, and in spite of the high shear rates used there was no hysteresis in the experimental curves.