

## The effect of emulsifier concentration on the rheological properties of acacia emulsions

E. SHOTTON AND S. S. DAVIS\*

The effect of potassium arabate concentration on the rheological properties of liquid paraffin emulsions has been examined over a range of emulsifier concentrations and volume fractions. The emulsions were of small particle size. Aggregation of the emulsions occurred when the volume fraction ( $\phi$ ) was in the region of 0.33-0.43, the exact value of  $\phi$  depending on the emulsifier concentration. The aggregated emulsions demonstrated irreversible shear thinning and hysteresis loops were obtained. The aggregation only occurred during the emulsification process and was due to a macromolecular bridging mechanism. The emulsifier concentration influenced aggregation and thereby influenced the rheological properties of the emulsions by two opposing mechanisms. It decreased the volume fraction at which aggregation first occurred ( $\phi_{\text{agg}}$ ), through its influence on particle size, but increased  $\phi_{\text{agg}}$  through its effect on the degree of contraction of the acacia molecule.

**I**NTERFACIAL films formed by hydrocolloids, such as acacia, were first described by Serrallach & Jones (1931). The build up of these films, their structure and thickness have been investigated by Shotton and his colleagues (Shotton, 1955; Shotton & Wibberley, 1959, 1960, 1961; Wibberley, 1962; Shotton, Wibberley & Vaziri, 1964). They found that the film produced by acacia at the oil-water interface was formed in about 20 sec for solutions of widely different strengths and had elastic properties. It was concluded that the first layer of acacia deposited at the interface was irreversibly adsorbed while subsequent layers were reversibly adsorbed. A film thickness of  $0.15 \mu$  was calculated. The stabilization of emulsions by hydrocolloids was dependent mainly on the coherence, rigidity, elasticity and ready adsorption of the interfacial film.

The flow curves of acacia emulsions have been described by Shotton & White (1960, 1963), who found that the emulsion viscosity increased with volume fraction ( $\phi$ ), leading to deviations from Newtonian flow but with no evidence of hysteresis. An increased viscosity caused by homogenization was attributed to the thick interfacial film formed by acacia at the oil-water interface. The concentration of acacia appeared to have little effect on relative viscosity but emulsions containing less than 10% w/v acacia were unstable.

### Experimental

#### MATERIALS

Liquid paraffin B.P.; water from an all glass still; potassium arabate prepared from acacia by the method of Shotton (1955).

#### APPARATUS

A Couette viscometer (Shotton & Davis, 1968a) was used for emulsion systems of low viscosity (<30 cP) and a Ferranti-Shirley viscometer (Van Wazer, Lyons & others, 1963) for those of higher viscosity. Measurements with the Couette viscometer were restricted to Newtonian systems

From the Department of Pharmaceutics, The School of Pharmacy, University of London, 29/39 Brunswick Square, London, W.C.1, England.

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so that results from the two instruments could be compared directly without complications due to differences in geometry. The maximum shear rate was 120 sec<sup>-1</sup>. The Ferranti-Shirley equipment was used in conjunction with an automatic flow curve recorder unit designed to provide an standardized shearing procedure. A maximum shear rate of 1692 sec<sup>-1</sup> and sweep time (upcurve) of 600 sec were chosen. The resultant flow curves were displayed on a Scientific Furnishings Ltd. X-Y autoplotted.

The particle size and particle size distribution of the emulsions were obtained using a model A (Industrial) Coulter Counter.

### PROCEDURE

The emulsions were prepared in the manner described by Shotton & Davis (1968a), by dispersing liquid paraffin in solutions of potassium arabate at arabate concentrations 0.75–12.0% w/w aqueous phase. Formulation details are in Table 1. The systems were stored for four days after preparation at 25° to allow for the release of entrapped air and the attainment of interfacial equilibrium (Shotton & White, 1960).

TABLE 1. POTASSIUM ARABATE, LIQUID PARAFFIN SYSTEMS, VISCOSITY AND PARTICLE SIZE RESULTS

Arabate conc. % w/w	$\phi$	Relative viscosity		Loop area cm <sup>2</sup> *	Particle size		Rheological behaviour
		$\eta_{lim}$	$\eta_{app}$		MVD $\mu$	s.d. $\sigma$	
0.75	0.11	1.59	—	—	4.66	2.12	N N N P/P H? P/P H? P/P H?
	0.22	2.17	—	—	5.04	2.23	
	0.33	4.20	—	—	3.57	3.76	
	0.43	7.12	7.30	—	8.35	4.85	
	0.53	9.30	10.4	—	21.5	2.01	
	0.63	13.8	18.5	—	28.3	2.13	
2.25	0.11	1.76	—	—	3.84	2.26	N N N N P/P H P/P H P/P H
	0.22	2.58	—	—	4.84	2.26	
	0.33	5.03	—	—	6.31	2.19	
	0.43	8.33	9.59	30	13.8	1.54	
	0.53	11.9	15.1	27	14.5	1.62	
	0.63	18.6	24.4	30	17.0	1.75	
4.5	0.11	1.52	—	—	4.02	2.38	N N N N P/P H P/P H P/P H
	0.22	2.37	—	—	6.04	2.18	
	0.33	5.83	—	—	5.89	2.19	
	0.43	8.84	11.7	31	13.5	1.60	
	0.53	12.5	18.1	40	12.3	1.63	
	0.63	20.6	26.9	65	13.6	1.70	
8.0	0.12	1.48	—	—	3.78	2.28	N P/P P/P P/P H P/P H P/P H
	0.23	2.40	—	—	5.27	2.05	
	0.33	5.31	6.92	—	9.91	2.28	
	0.44	8.60	11.0	54	10.3	1.65	
	0.54	13.4	19.3	115	13.6	1.62	
	0.64	20.3	30.3	155	16.8	1.74	
12.0	0.12	1.67	—	—	4.61	2.24	N P/P P/P H P/P H
	0.23	2.57	2.58	—	4.88	2.10	
	0.34	5.00	5.99	57	9.46	2.01	
	0.44	8.71	10.8	132	11.0	1.72	

N = Newtonian. P/P = Pseudoplastic. H = Hysteresis loop.  
 \* 1 cm<sup>2</sup> corresponds to 6.5 × 10<sup>3</sup> dyne cm<sup>-2</sup> sec<sup>-1</sup>.

Emulsions containing high concentrations of oil and potassium arabate could not be examined as the high viscosity of such systems presented difficulties in homogenization and the entrapping of air.

## Results

### MACRO AND MICROSCOPIC APPEARANCE

After four days storage no creaming of the emulsions was observed when the volume fraction of oil was less than 0.3. The serum turbidity of the emulsions that had creamed decreased with increase in  $\phi$ . Examination under the microscope showed that aggregation of the emulsions began when  $\phi$  was in the region of 0.33–0.43. The exact value of  $\phi$  was dependent on emulsifier concentration. The greater the concentration the lower the volume fraction for aggregation ( $\phi_{agg}$ ). For volume fractions below 0.3 the emulsion droplets were individually dispersed. The average size of the *individual* droplets decreased with increase in emulsifier concentration. The droplets in those systems containing 0.75% of arabate were larger than those in the other unaggregated systems, but there was no evidence of oil separation.

### VISCOSITY

The results of rheological analysis are given in Table 1. Newtonian behaviour was demonstrated by the unaggregated systems of low volume fraction, but non-Newtonian behaviour began in the region of  $\phi = 0.33$ –0.44. Initially this was pseudoplastic in nature but hysteresis loops were obtained as  $\phi$  rose. All the curves passed through the origin and a typical example is shown in Fig. 1. The flow curves were repeated after the sample had been allowed to rest for 10 min but there was no evidence

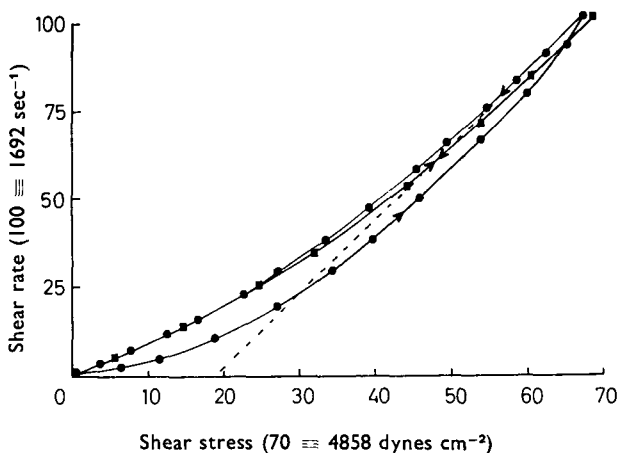


FIG. 1. A typical flow curve for a non-Newtonian arabate system (arabate concentration = 8%,  $\phi = 0.63$ ). ● Initial flow curve. ■ Repeat flow curve.

of reformation of thixotropic structure during this time (Fig. 1). The slight movement to the right was due to evaporation, an effect which prevented the emulsions from being rested for longer periods. After shearing, the emulsions were re-examined using the Coulter Counter and a reduction in aggregate size of about 50% was found. The emulsions could be described as being “irreversible shear thinning” in their

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rheological properties although it was possible that they had thixotropic structure that reformed slowly.

Limiting viscosities ( $\eta_{lim}$ ) and apparent viscosities ( $\eta_{app}$ ) for the pseudoplastic systems were calculated in the manner described by Shotton & Davis (1968a). The limiting viscosities of the hysteresis systems were obtained by measuring the gradient of the asymptote to the linear portion of the down curve (Fig. 1). The hysteresis loop areas were measured by planimeter.

The variation of the relative limiting viscosity ( $\eta_{rel}^{lim}$ ) with  $\phi$  followed the relation of Richardson (1933) at arabate concentrations 2.25–12.0% (Fig. 2)

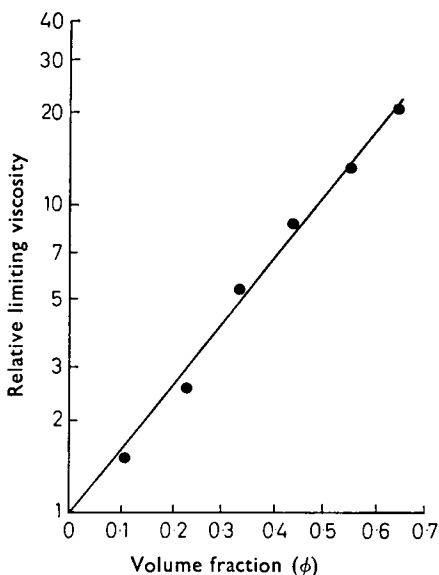


FIG. 2. The variation in relative limiting viscosity with volume fraction for potassium arabate-liquid paraffin emulsions (log plot). Mean results for arabate concentrations 2.25–12.0%.

$$\log \eta_{rel}^{lim} = k\phi$$

where  $k$  is a constant, in this case = 2.2.  $\eta_{rel}^{lim}$ , which was calculated from the slope of the linear portion of the down curve and was a measurement of viscosity when structure had been broken down, was independent of arabate concentration for  $\phi < 0.53$ . At higher values of  $\phi$  it increased with arabate concentration up to 8% after which it was again independent.  $\eta_{rel}^{app}$  was calculated from the ratio of shear stress to shear rate at the maximum shear rate, and, as a result, was greatly influenced by the shape of the pseudoplastic up-curve and therefore gave an indication of the amount of aggregation in an emulsion. Its value increased with arabate concentration from  $\phi = 0.33$  upwards and showed that for a given value of  $\phi$  the greater the arabate concentration, the greater was the aggregation. This was in agreement with the observation above that the exact value of  $\phi_{agg}$  was dependent on arabate concentration.

At and above an arabate concentration of 4.5%, the hysteresis loop area increased almost linearly with volume fraction (Table 1) and the greater the arabate concentration—the greater the area at any value of  $\phi$ . For 2.25% arabate the loop size was independent of  $\phi$ .

The analysis of Coulter Counter results for emulsions has been discussed by Shotton & Davis (1968b). The aggregates formed at high dilution were not broken down during the dilution procedure for counting and could therefore be sized in their original form. Both the aggregated and unaggregated emulsions could be represented by the log-normal distribution of particle size if allowance was made for truncation (Shotton & Davis 1968b). A plot of mean volume diameter (MVD) against volume fraction for arabate concentrations 2.25–12.0% (Fig. 3) shows that aggregation of the emulsions occurred when  $\phi$  was in the region of 0.33–0.43, the exact value of  $\phi$  varying with arabate concentration.

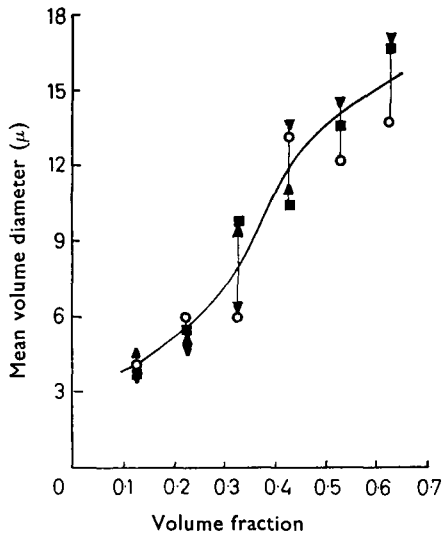


FIG. 3. The change in mean volume diameter of potassium arabate-liquid paraffin emulsions with volume fraction. Arabate concentration % (w/w). —▼— 2.25, —○— 4.5, —■— 8.0, —▲— 12.0.

#### THE EFFECT OF PARTICLE SIZE ON VISCOSITY

Emulsion homogenization was examined for both the aggregated and the non-aggregated systems ( $\phi = 0.53$  and  $0.22$ ) at arabate concentrations of 1.0, 3.0 and 6.0% w/w. Homogenization of the non-aggregated systems reduced the MVD (Table 2). At 1.0 and 3.0% arabate concentration the viscosity rose to a maximum at a MVD of 13.2 and 13.1  $\mu$  respectively, and then fell. 6.0% arabate showed a slight decrease in viscosity upon homogenization (the first homogenization in this case gave a MVD of 10.4  $\mu$ ). Aggregated emulsions also demonstrated a maximum viscosity, but only after 5–7 passages through the homogenizer. The size of the resultant aggregates decreased with homogenization but the number of

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TABLE 2. THE HOMOGENIZATION OF ARABATE EMULSIONS

Non-aggregated systems ( $\phi = 0.22$ )				Aggregated systems ( $\phi = 0.54$ )						
Arabate conc. % w/w	Homogn.	Viscosity (cP)	MVD $\mu$	Arabate conc. % w/w	Homogn.	Viscosity		Loop area cm <sup>2</sup> *	MVD $\mu$	
						$\eta_{lm}$ (cP)	$\eta_{app}$ (cP)			
1.0	1	6.43	18.3	1.0	1	16.8	20.8	4	15.1	
	2	8.05	13.2		2	22.6	27.2	18	14.4	
	3	7.77	12.9		3	23.5	28.6	17	13.8	
	4	7.40	11.8		4	23.7	28.7	17	13.0	
	5	7.19	9.7		5	24.3	29.0	16.5	12.8	
	6	6.41	8.6		6	25.3	30.4	17.5	12.5	
	7	6.11	7.6		7	24.1	29.1	14	11.7	
3.0	1	8.90	14.4	3.0	1	31.9	35.5	18	13.3	
	2	12.8	13.1		2	40.5	48.5	26	12.7	
	3	12.0	10.5		3	45.6	48.8	40	11.9	
	4	11.8	9.4		4	58.1	63.1	47	10.3	
	5	11.1	7.8		5	54.0	60.8	45	9.9	
	6	9.8	6.1		6	51.8	57.0	39	9.7	
	7	8.8	5.5							
6.0	1	14.2	10.4	6.0	1	52.7	63.6	31.5	12.8	
	2	13.7	9.3		2	78.2	99.9	58.5	12.1	
	3	13.6	6.3		3	92.3	104.0	63.0	9.9	
	4	13.4	5.0		4	86.9	114.0	63.0	8.9	
	5	13.4	4.1		5	65.7	87.4	52.5	8.2	
	6	13.1	3.5							
	7	13.1	3.2							

\* 1 cm<sup>2</sup> corresponds to  $6.5 \times 10^3$  dyne cm<sup>-2</sup> sec<sup>-1</sup>.

TABLE 3. AGGREGATION OF ARABATE EMULSION WITH TIME  $\phi = 0.53$ , ARABATE CONC. = 3.0% w/w

Time after preparation		1 min	30 min	90 min	1 day	4 days
Particle size	MVD $\mu$	12.66	12.92	12.91	12.92	13.10
Results	s.d. $\sigma$	1.56	1.55	1.55	1.55	1.55

TABLE 4. THE STORAGE OF POTASSIUM ARABATE EMULSIONS

Arabate conc. % w/w	$\phi$	Particle size results			
		4 days		3 months	
		MVD $\mu$	s.d. $\sigma$	MVD $\mu$	s.d. $\sigma$
0.75	0.11	4.66	2.12	4.53	1.97
2.25		3.84	2.26	3.52	2.38
4.5		4.02	2.38	3.97	2.40
8.0		3.30	2.37	2.92	2.36
12.0		4.40	2.16	4.40	2.56
0.75		0.43	8.38	4.86	32.8
2.25	13.8		1.54	15.08	1.62
4.5	13.5		1.60	11.27	1.57
8.0	10.34		1.59	10.88	1.62
12.0	11.88		1.62	17.00	1.79

aggregates was increased. The hysteresis loop areas showed a similar effect to the viscosity results.

### THE STORAGE OF EMULSIONS AND ITS EFFECT ON AGGREGATION

The rate of aggregation of a high volume fraction emulsion was studied by sizing samples with the Coulter Counter at different times after preparation (Table 3).

The results show that there was little change in aggregate size in the period 1 min to 4 days. Aggregation must therefore occur during, or immediately after, preparation. At the end of a three month storage period all the emulsions, except those containing 0.75% arabate, at high volume fraction, showed very little change in particle size (Table 4). There is no evidence of aggregation occurring in the originally unaggregated emulsions ( $\phi < 0.3$ ). The slight fall in particle size in some cases was probably due to bacterial growth.

## Discussion

A comparison of the results obtained in the present work is made with those of White (1961) in Table 5.

TABLE 5. THE RHEOLOGY OF ACACIA EMULSIONS

	Results for present study	White (1961)
(i) Aggregates . . . . .	Occurred when $\phi > 0.33$	Did not occur at any value of $\phi$
(ii) Hysteresis loop . . . . .	Obtained at higher values of $\phi$	Pseudoplastic behaviour only
(iii) Emulsion stability . . . . .	At arabate conc $> 2.0\%$	At arabate concentrations $> 10\%$
(iv) Increase of viscosity with $\phi$ . . . . .	For arabate conc. = 8%. $\eta_{rel}^{lim} = 1.5$ at $\phi = 0.11$ , and $\eta_{rel}^{lim} = 11.2$ at $\phi = 0.5$	For arabate conc. = 15%. $\eta_{rel}^{lim} = 1.29$ at $\phi = 0.1$ and $\eta_{rel}^{lim} = 2.99$ at $\phi = 0.5$
(v) Influence of arabate concentration	Effected value of $\phi$ at which aggregation occurred and hence value of $\eta_{rel}^{app}$	Little or none
(vi) Mean number diameter of droplets	1.0 $\mu$ (unaggregated systems)	15.0 $\mu$

The great contrast between the two sets of results may be attributed to aggregation of acacia emulsions when the particle size is small.

In the present work, homogenization of the emulsions resulted in a maximum viscosity. Shotton & White (1963) concluded that the adsorption of a thick interfacial film onto the new droplets formed in a homogenization process would raise the volume fraction of an emulsion and hence the viscosity, and this would explain the increase in viscosity for the non-aggregated systems in the present work. The reduction in particle size may also have promoted the formation of a small number of aggregates which would be broken down irreversibly by further homogenization, thereby causing a fall in viscosity. A similar effect has been reported by Sumner (1954) for the two stage homogenization of milk where the second homogenization produced a decreased viscosity that was probably due to the destruction of aggregates produced in the first homogenization.

The main contribution to the increase of viscosity for the aggregated emulsions would be the creation of an increased number of particles and thus the number of interparticulate "links". After repeated homogenization more aggregates were broken down than new aggregates formed and the viscosity fell.

The nature of these links is important. It is known that emulsions can form aggregates by a number of differing mechanisms and the interparticulate links can be formed either by electrical double layer effects

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(Derjaguin, 1940; Verwey & Overbeek, 1948) or by some physical mechanism such as film-film interaction by hydrophobic bonding (Cockbain, 1952, Shotton & Davis, 1968a) or by large molecules bridging two particles (Davies, 1964, Smellie & LaMer, 1958). The nature of the links formed by arabate and the mechanism of aggregation is now discussed.

### THE MECHANISM OF AGGREGATION

The aggregates in the arabate emulsions had a number of interesting properties: (i) the aggregates appeared to be broken down irreversibly under shear. (ii) The aggregates were not broken down on dilution, which is in contrast to soap aggregated emulsions (Shotton & Davis, 1968b). (iii) Aggregate formation was dependent on the volume fraction and particle size. (iv) Aggregates were only formed during or immediately after emulsification and non-aggregated systems did not form aggregates even when stored for long periods.

The critical volume fraction [effect (iii)] suggests that the interparticulate distance was important and that in dilute emulsions the particles were too far apart for "links" to be formed in the short period available for aggregation. The distance between particles at varying volume fraction for a given packing distribution may be obtained from the equation

$$\delta = D[(K/\phi)^{\frac{1}{3}} - 1] \quad \dots \quad (1)$$

where  $\delta$  is the interparticulate distance ( $\mu$ ),  $D$  the particle diameter ( $\mu$ ) and  $K$  the maximum packing density for the distribution. Thus the smaller the particle size the smaller will be the interparticulate distance for a given volume fraction.

For equalized spheres in rhombohedral array,  $K$  has a value of 0.74, whereas for equal spheres in random packing,  $K$  is 0.64 (Scott 1960) and for sheared suspensions  $K$  is 0.67 (Rutgers, 1962). Emulsion systems, in which the particles are polydisperse, have higher maximum packing density values. Shotton & Davis (1967) found that  $K$  has a value close to 0.74 for emulsions in random packing, a value that had been used by Sherman (1960, 1964) in calculating interparticulate distances. For the unaggregated systems in the present work a mean number diameter in the region of  $1 \mu$  has been found, so that for an initial aggregation volume fraction of 0.43 and  $K = 0.74$ , the interparticulate distance, when aggregation commences, is in the region of  $0.20 \mu$ . If for the case of the  $15 \mu$  particles reported by White we assume a critical interparticulate distance for aggregation of  $0.20 \mu$ , then the critical volume fraction for aggregation is in the region of 0.73, thus explaining the lack of aggregates in White's emulsions.

Davies (1964) considered that the aggregation of emulsions by macromolecules was due to bridge formation between the particles with the forces of interparticulate repulsion balanced by the forces of adsorption at each end of the macromolecule. Hiestand (1964) and Gillespie (1960) have discussed the flocculation of powders by this method. Smellie & LaMer (1958) found that polymer molecules formed a bridge by adsorption of a different portion of the macromolecule on to each particle and



that bridges could only be formed when the surface was partly covered by macromolecules. Polymer adsorption has been treated theoretically by Silberberg (1962) with the polymer thought of as consisting of active centres spaced along the "backbone" of the molecule. Loose ends are able to stick out into the vehicle but at equilibrium, which may be reached slowly by large molecules, these ends are adsorbed. This theory has been verified experimentally by Curme & Natale (1964).

An interesting study was made by Kragh & Langston (1962) on the aggregation of quartz by gelatin. If the particles were deflocculated and kept apart by agitation, the free macromolecule chains were adsorbed onto the deflocculated particle so that bridge formation was no longer possible and the deflocculation was irreversible.

In the present study, the aggregation of potassium arabate emulsions is explained by links which are formed by a molecular bridge mechanism with adsorption of parts of the arabate molecule onto different oil droplets. Wibberley (1963) has shown that the arabate film at the oil-water interface is formed in about 20 sec and from Smellie & LaMer's free surface requirement, bridging is therefore only able to occur in this short period. The interparticulate distance will play an important part in this type of aggregation, as only those particles that are close enough to be bridged by an arabate molecule will be aggregated. When the aggregates are sheared, the adsorbed ends of the molecule will be removed from one or both of the particle surfaces and rearrangement of the molecule (Kragh & Langston, 1962) and the "free surface requirement" (Smellie & LaMer, 1958) will prevent further bridge formation. The emulsions will thus demonstrate irreversible shear thinning. The critical interparticulate distance for aggregation from equation (1) suggests that the length of the linking molecule will be of the order of  $0.20 \mu$ . This is in agreement with the work of Veis & Eggenberger (1954) and Anderson & Rahman (1967) who have shown that the acacia molecule in solution exists as a stiff coil with a root mean square, end-to-end dimension varying from  $0.06 \mu$  at zero charge to  $0.24 \mu$  at maximum charge. At the concentrations employed in the present work the coil will be partly unfolded as a result of interparticulate repulsion between ionized carboxyl groups on neighbouring glucuronic acid residues, and an elongated molecule of  $0.20 \mu$  is quite probable.

The results have shown that the emulsifier concentration affects the value of  $\phi$  at which aggregation occurs; in general the higher the concentration, the lower the value of  $\phi_{agg}$ . In fact an increase in emulsifier concentration will influence aggregation and thus the rheological properties of an emulsion, by two opposing mechanisms. It will lead to a decrease in particle size, as demonstrated by microscopic examination and by the work of Shotton & Davis (1968b), and thus a decrease in interparticulate distance that will bring about aggregation at lower values of  $\phi$  (eqn 1). On the other hand an increase in emulsifier concentration will lead to a decreased ionization and thus a decreased length of the arabate molecule (Veis & Eggenberger, 1954). A greater volume fraction will therefore be required for initial aggregation.

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The effect of concentration on particle size will be the dominant factor as can be seen from rearranging equation (1):

$$\phi_{\text{agg}} = 0.74/(1 + \delta/D)^3 \quad \dots \quad \dots \quad \dots \quad (2)$$

The interparticulate length, i.e. the length of acacia molecule, has the limits 0.12 and 0.48  $\mu$  and a change in molecule size will only be significant when D is small. Only emulsions of small globule size and low arabate concentration will be affected by the length of the arabate molecule. In practice these systems are difficult to prepare and are unstable.

The rapid and secure adsorption of potassium arabate at the oil-water interface has yet to be explained for the arabate molecule has no groups generally recognized as being lipophilic. Kane, LaMer & Linford (1964) have had similar difficulties in explaining the way weakly anionic polymers adsorb onto strongly negative solid surfaces and cause flocculation.

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