Carbohydrate Polymers **14** (1991) 373–383

Emulsifying Behaviour of Gum Arabic. Part 1: Effect of the Nature of the Oil Phase on the Emulsion Droplet-size Distribution

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(Received 10 August 1989; revised version received 24 November 1989; accepted 15 December 1989)

ABSTRACT

The influence of the nature of the oil phase on the emulsifying behaviour of gum arabic has been investigated at neutral pH. Time-dependent droplet-size distributions are reported for oil-in-water emulsions (1% wt gum, 10% vol. oil) made with n*-hexadecane,* D*-limonene and orange oil. Three different gum samples of known analytical composition have been compared, and it is found that the gum giving the most rapid lowering of the tension at the* n*-hexadecane–water interface also gives the most stable* n*-hexadecane-in-water emulsions as well as the smallest droplets with all three oils. On the other hand, the same gum gives the poorest stability of the* D*-limonene-in-water and orange oil-in-water emulsions.*

INTRODUCTION

The traditional emulsifying and stabilising agent of flavour oils (e.g., orange oil) in the soft drinks industry is gum arabic (*Acacia senegal*). A feature of gum arabic is its ability to form an adsorbed film at the oil–water interface whose surface viscoelasticity is rather insensitive to

Carbohydrate Polymers 0144-8617/91/$03.50

dilution of the aqueous phase (Dickinson *et al.*, 1989). The formation of a thick, sterically stabilising layer around emulsion droplets enables the flavour oil emulsion to be stabilised both as a concentrate and as a diluted beverage. To produce a stable emulsion, it is necessary for enough of the gum to adsorb during emulsification to produce the requisite stabilising layer. Compared with proteinaceous emulsifiers, the surface activity of gum arabic is rather low (Dickinson, 1988); and so to compensate for this a high concentration of gum must be used — i.e., roughly 1:1 ratio of gum to oil compared with 1:10 protein to oil for a protein-stabilised emulsion.

Recently, we reported measurements of the interfacial tension, surface viscosity and emulsifying properties of samples of various *Acacia* gum species having nitrogen contents in the range from 0·1% to 7·5% (Dickinson, 1988; Dickinson *et al.*, 1988). With *n*-hexadecane as the oil phase at neutral pH, there was found to be a good correlation between the nitrogen content of the gum and its limiting long-time surface activity. The relationship between nitrogen content and emulsifying behaviour was found to be more complicated, however, because of the need to distinguish between initial droplet-size distributions (emulsifying capacity) and changes in droplet-size distribution with time (emulsion stability). Essential oils are chemically different from a hydrocarbon oil like *n*-hexadecane. We need, then, to establish whether fundamental studies on hydrocarbon emulsions are relevant to those of a pure essential oil or a commercial citrus oil.

In this paper, we compare the emulsifying properties of three different gum arabic samples with similar nitrogen contents of *c.* 0·3% corresponding to protein contents of *c.* 2% wt. Recent research has indicated (Randall *et al.*, 1988) that almost all the nitrogen content of gum arabic is associated with a high-molecular-weight fraction representing only 20–30% of the total gum, and that it is this protein-rich fraction which adsorbs strongly at the oil–water interface. Using identical homogenisation conditions, three different oils are considered: *n*-hexadecane, D-limonene and orange oil. A low ratio of gum to oil (1:10) is used here to accelerate any instabilities, thereby highlighting any potential differences between the oils or the gum samples. This ought to be a reasonable guide to relative stability behaviour at high gum concentrations, at least qualitatively if not quantitatively.

In an accompanying paper (Dickinson *et al.*, 1991), the effect of the molecular weight of the gum on its emulsifying behaviour is described. For background information on the relationship between molecular structure and functionality of gum arabic, the reader is referred to the accompanying paper. References to earlier work on the film-forming

behaviour of gum arabic are also given in a previous report (Dickinson *et al.*, 1988).

MATERIALS AND METHODS

Tables 1 and 2 give analytical data and amino acid compositions for the three gum arabic samples — I, II and III. The samples had been freeze-dried and stored at room temperature in sealed tubes. The standard analytical methods used to characterise the polysaccharide and nitrogeneous components have been described (Anderson & Brown Douglas, 1988). The AnalaR grade *n*-hexadecane and D-limonene were obtained from Sigma Chemicals; the orange oil was a commercial sample suitable for soft drink manufacture. Gums were dissolved in phosphate buffer solution (pH 7, ionic strength 0·05 M) containing 0·1% wt sodium azide as bactericide. Buffer salts and azide were AnalaR grade. Water was double distilled.

Oil-in-water emulsions were produced on a small scale (*c.* 10 ml) using the one-stage valve mini-homogeniser described previously (Dickinson *et al.*, 1987). To a 1% wt solution of gum arabic (pH 7) was added an appropriate amount of oil (*n*-hexadecane, D-limonene or orange oil) to give a premix containing 10% vol. oil. After blending, the coarse premix emulsion was homogenised at 300 bar at 25°C. The resulting emulsion was separated into two samples which were stored in a water bath at 25°C. One half was sampled immediately, and then at

TABLE 1
Analytical Data for Gum Arabic Samples I, II and III

Property	*Sample I*	*Sample II*	*Sample III*
Nitrogen content (%)	0·30	0·32	0·30
Protein content (% N × 6·60)	2·0	2·1	2·0
Intrinsic viscosity (ml g^{-1})[a]	21	18	15
Methoxyl content (%)	0·26	0·18	0·28
Neutralisation equiv. (Da)	1540	1250	1330
Uronic anhydride content (%)	12	14	13
Galactose content (%)[b]	30	43	40
Arabinose content (%)[b]	52	33	36
Rhamnose content (%)[b]	6	10	11
Specific rotation (degrees)[c]	−51	−27	−13

[a]Measured in 1·0 M NaCl solution at 28°C.
[b]After hydrolysis.
[c]In distilled water.

TABLE 2
Amino Acid Compositions of Gum Arabic Samples I, II and III (Residues per 1000 Residues)

Amino acid	*Sample I*	*Sample II*	*Sample III*
Alanine	48	25	27
Arginine	43	11	12
Aspartic acid	51	50	53
Cystine	0	0	0
Glutamic acid	36	32	33
Glycine	63	48	54
Histidine	28	46	45
Hydroxyproline	391	351	321
Isoleucine	17	15	14
Leucine	43	71	74
Lysine	22	25	24
Methionine	tr[a]	tr	tr
Phenylalanine	tr	30	31
Proline	73	61	66
Serine	74	120	126
Threonine	45	65	64
Tyrosine	41	18	19
Valine	25	32	37

[a]tr = trace.

regular intervals after thorough mixing, for droplet-size determination using a Coulter counter model TAII with a 30-μm orifice tube and 0·1 M NaCl as suspending electrolyte. The other half was inspected visually at regular intervals to record the extent of creaming and serum separation.

The time-dependent tension at the *n*-hexadecane–buffer interface (pH 7, 25°C) was monitored by the Wilhelmy plate technique (Murray, 1987). A 10^{-3}% wt gum arabic solution was made up at 25°C, and a portion was carefully poured into a thermostatted glass dish. Immediately afterwards, a volume of *n*-hexadecane was layered gently on top of the aqueous solution. The tension was determined from the pull on a mica plate over a period of 24 h to a precision of better than $\pm 0{\cdot}2$ mN m^{-1}.

RESULTS AND DISCUSSION

The droplet-size distributions of *n*-hexadecane-in-water emulsions made with gum arabic samples I, II and III are shown in Fig. 1. The three sets

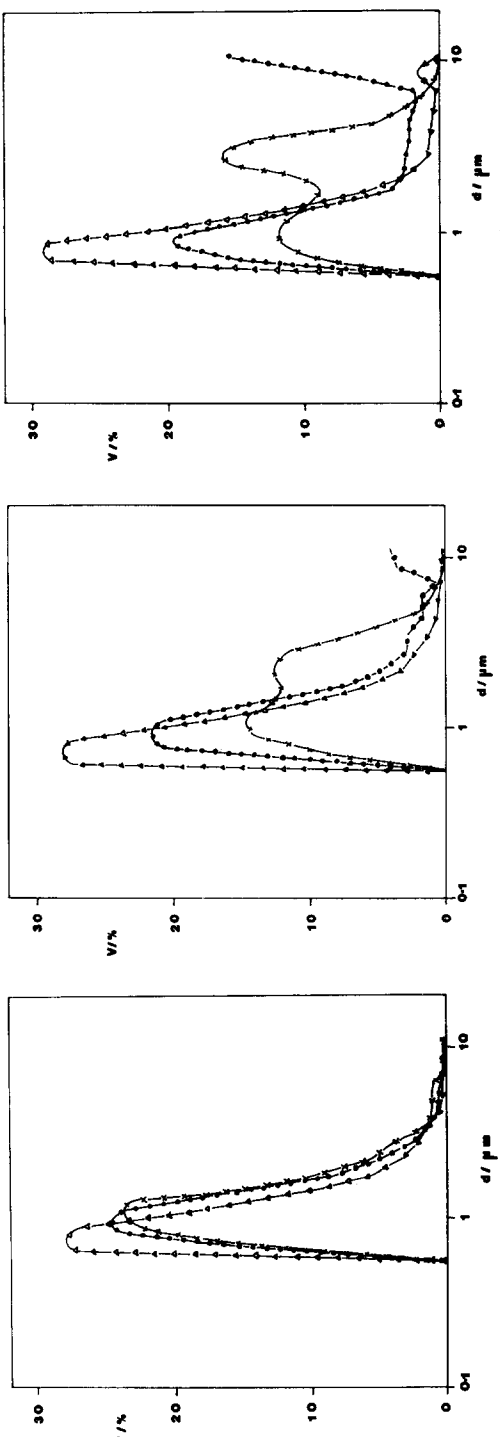

Fig. 1. Droplet-size distributions of *n*-hexadecane-in-water emulsions: (a) $t = 0$ h, (b) $t = 4$ h, and (c) $t = 24$ h. Smoothed percentage differential volume $V(d)$ is plotted against droplet diameter d for sample I (—— Δ ——), sample II (—— × ——), and sample III (——●——).

of Coulter counter distributions refer to measurements made (a) immediately after emulsion preparation ($t = 0$ h), (b) 4 h after emulsion preparation ($t = 4$ h), and (c) 24 h after emulsion preparation ($t = 24$ h). In each case the percentage differential volume V is plotted against droplet diameter d. The equivalent experimental data for D-limonene-in-water emulsions and orange oil-in-water emulsions are presented in Figs 2 and 3, respectively.

The first general point to note from Figs 1, 2 and 3 is that all the emulsions are relatively unstable as one might expect from gum arabic emulsions made with such a low gum-to-oil ratio. With each of the oils, the distribution tends to shift to distinctly larger droplets over the observational time-scale, though the rate and nature of the shift is dependent on the type of oil and the sample of gum. The way in which the droplet-size distribution changes with time is distinctly different for *n*-hexadecane compared with D-limonene or orange oil. With *n*-hexadecane, the position of the main peak in $V(d)$ remains constant at $d \approx 1$ μm, but the peak height is gradually reduced and a new peak appears at a larger value of d. (This statement applies to samples II and III, but not to sample I which gives an *n*-hexadecane emulsion with no loss of stability over 24 h.) This type of change in droplet-size distribution with time is indicative of emulsion instability proceeding predominantly by a droplet coalescence mechanism, flocculation being ruled out by the fact that sonication leads to no significant change in the distribution. In contrast, however, with the emulsions made with D-limonene or orange oil, there is a gradual shift in the position of the main peak in $V(d)$ to larger d values. This is indicative of the process of Ostwald ripening (Dickinson, 1986), which is the predominant instability mechanism with emulsions made with D-limonene or orange oil, because of the appreciable solubility of these oils in water. Ostwald ripening occurs with each of the gum arabic samples, though with sample I it appears also to be accompanied by extensive coalescence.

The relative droplet-size distributions in the different emulsions are a good guide to their relative stabilities with respect to creaming under the influence of gravity. Figure 4 shows the extent of serum separation as a function of time for the *n*-hexadecane-in-water emulsions. The height L of a distinct clear serum layer at the bottom of the emulsion samples was determined by simple visual observation. The most stable emulsion (sample I) in Fig. 4 is the one with the smallest droplets in Fig. 1, and the least stable (sample II) is the one with the largest droplets.

Gum arabic sample I produces the smallest droplets with each of the three oils investigated — see Figs 1(a), 2(a) and 3(a) — and so it has the best emulsifying capacity of the three gum samples. This is consistent

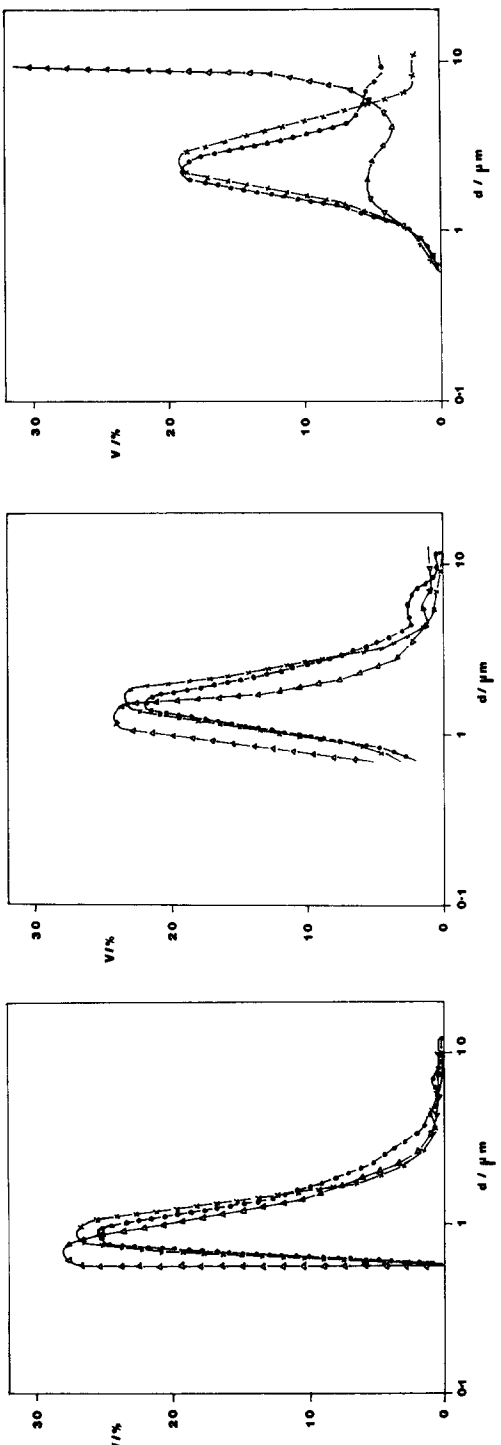

Fig. 2. Droplet-size distributions of D-limonene-in-water emulsions: (a) $t = 0$ h, (b) $t = 4$ h, and (c) $t = 24$ h. Smoothed percentage differential volume $V(d)$ is plotted against droplet diameter d for sample I (—— Δ ——), sample II (—— × ——) and sample III (——●——).

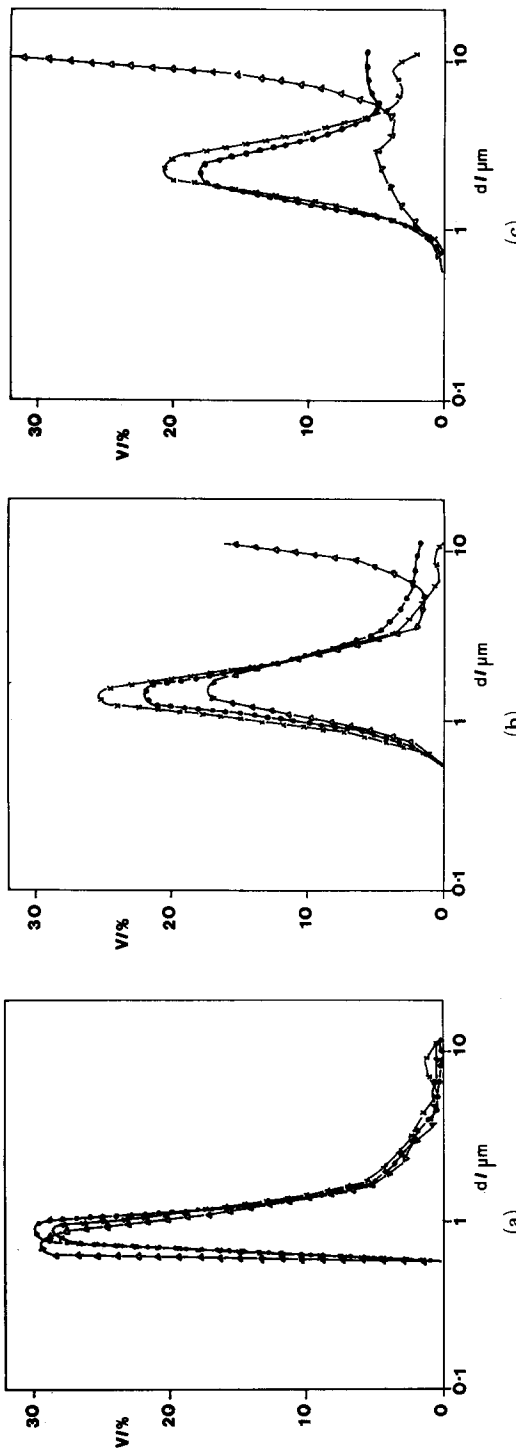

Fig. 3. Droplet-size distributions of orange oil-in-water emulsions: (a) $t = 0$ h, (b) $t = 4$ h, and (c) $t = 24$ h. Smoothed percentage differential volume $V(d)$ is plotted against droplet diameter d for sample I (—— Δ ——), sample II (—— × ——) and sample III (——●——).

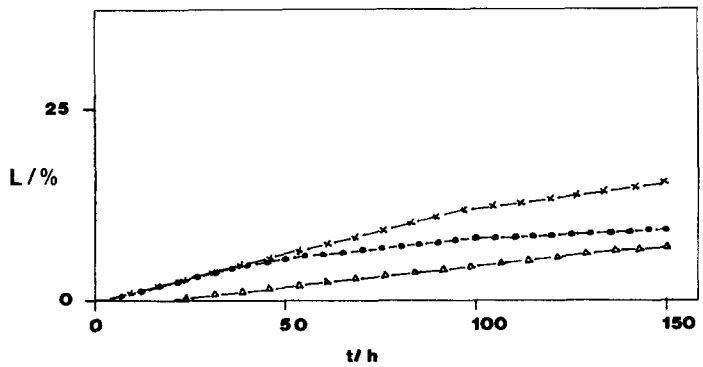

Fig. 4. Creaming stability of *n*-hexadecane-in-water emulsions. The height L of serum layer (expressed as percentage of total sample height) is plotted against storage time t for sample I (—△—), sample II (—×—) and sample III (—●—).

with its higher surface activity at the oil–water interface at short adsorption times as illustrated in Fig. 5. The time-dependent tension data plotted in Fig. 5 refer to averaged results from duplicate sets of measurements at the *n*-hexadecane–water interface. At short adsorption times from a very dilute gum arabic solution (10^{-3} %wt in pH 7 buffer), the relative surface activities lie in the order sample I > sample III > sample II, which is intuitively consistent with the relative droplet-size distributions determined immediately after emulsion preparation, and the associated stabilities with respect to creaming. This good correlation between rate of lowering of interfacial tension at the *n*-hexadecane–water interface and the emulsifying behaviour was also observed (Dickinson *et al.*, 1988) with *Acacia* gums of various origins having a wide range of nitrogen contents.

Although sample I gives the best emulsion stability with *n*-hexadecane, it is the poorest with both D-limonene and orange oil. So, while sample I is effective at preventing the coalescence of hydrocarbon oil droplets, it is much less effective at preventing the growth of essential oil droplets by Ostwald ripening. The reason for the better stabilising ability of samples II and III for citrus oil emulsions may be related to the fact that both of these samples give a greater lowering of the tension at long adsorption times than does sample I (see Fig. 5), even though the opposite is the case at short times ($t \lesssim 2$ h). Assuming that it is the high-molecular-weight proteinaceous fraction which is the most effective part of the gum sample in stabilising the essential oil emulsion, it is not unreasonable to infer that a sample giving the lowest long-term lowering of the tension, due to slow diffusion of large macromolecular entities to

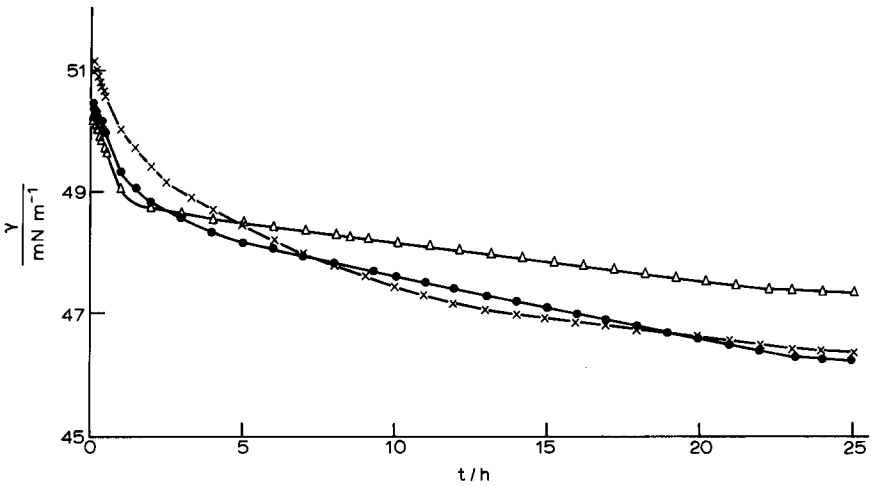

Fig. 5. Surface activity of gum arabic samples (10^{-3} %wt) at the *n*-hexadecane–water interface (pH 7, 25°C). The interfacial tension γ is plotted against the adsorption time t for sample I (—— △ ——), sample II (—— × ——) and sample III (——●——).

the interface, will also be a sample giving the best stability (i.e., slowest growth of droplet size).

Comparison of Figs 2 and 3 shows that the relative emulsifying behaviour of the gums is similar for D-limonene and orange oil. On this evidence, it appears that D-limonene is a better model system for simulating orange oil emulsions than is *n*-hexadecane. The advantage of D-limonene over orange oil for comparing the stabilising properties of different gum samples is that it provides a more reliable reference system. It is known from technological practice that different batches of orange oil can give different emulsifying behaviour with the same sample of gum arabic.

The amino acid compositions of the protein fractions of samples II and III are very similar (see Table 2), but both are substantially different from that of sample I. It is noteworthy, therefore, that samples II and III give similar long-term tensions at the *n*-hexadecane–water interface (Fig. 5) and also similar emulsion stabilities with D-limonene or orange oil. We may speculate then that, for gum arabic samples of essentially the same nitrogen content, a close match of amino acid compositions tends to be associated with a close match of emulsification behaviour. From Table 1, we can see that the only substantial difference between samples II and III is in the methoxyl content. It may be significant that sample II gives less short-time lowering of the interfacial tension than samples I and III, the

latter being more hydrophobic than the former in view of the higher methoxyl content.

In conclusion, three gum arabic samples with essentially the same nitrogen content have different emulsifying properties (especially sample I compared with samples II and III). This confirms the view that it is the nature and distribution of the proteinaceous component of gum arabic which is important — not just its overall amount.

ACKNOWLEDGEMENT

E.D. acknowledges financial support from AFRC.

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