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Emulsifying Behaviour of Gum Arabic. Part 2: Effect of the Gum Molecular Weight on the Emulsion Droplet-size Distribution

Eric Dickinson, Vanda B. Galazka

Procter Department of Food Science, University of Leeds, Leeds LS2 9JT, UK

&

Douglas M. W. Anderson

Chemistry Department, University of Edinburgh, Edinburgh EH9 3JJ, UK

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ABSTRACT

The effect of the molecular weight of the gum arabic sample on droplet-size distributions of n-hexadecane-in-water emulsions (1% wt gum, 10% vol. oil) has been investigated at neutral pH. A high-molecular-weight fraction (0·87% nitrogen) corresponding to 10% of a natural gum (0·38% N) gives initially slightly larger droplets but better emulsion stability than the low-molecular-weight fraction (0·35% N) corresponding to the residual 90% of the original gum. Samples of a different gum arabic (0·35% N) subjected to different degrees of controlled degradation give decreasing emulsion stability with reduction in weight-average molecular weight from $3{\cdot}1 \times 10^5$ *to* $2{\cdot}2 \times 10^5$ *Da.*

INTRODUCTION

This is the second of two complementary papers concerned with factors affecting the emulsifying behaviour of gum arabic, the natural exudate from *Acacia senegal*. Part 1 (Dickinson *et al.*, 1991) discusses the effect of the nature of the oil phase. This paper reports experimental data on the emulsifying behaviour of selected fractionated and degraded samples of the gum.

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Physicochemical studies of gum arabic have suggested that it consists of a mixture of high-molecular-weight charged polysaccharides in combination with a small amount of protein (*c.* 2% wt). There are six carbohydrate moieties in gum arabic: arabinofuranose, arabinopyranose, galactose, glucuronic acid, 4-*O*-methylglucuronic acid, and rhamnose. The main structural feature of the heteropolymer is a backbone of β-galactopyranose units linked through positions 1 → 3, with side-chains of 1,6-linked galactopyranose units terminating in glucuronic acid or 4-*O*-methylglucuronic acid residues (Street & Anderson, 1983). The special film-forming properties of the gum arise from its protein fraction. Amino acid compositions have been studied in detail (Akiyama *et al.*, 1984; Anderson *et al.*, 1985), and it is consistently found that hydroxyproline and serine occur in large proportions. These two amino acids are believed to be involved in covalently linking the carbohydrate to the protein to form an arabinogalactan–protein complex. The most widely accepted structural model for the arabinogalactan–protein complex is the so-called 'wattle blossom' model (Fincher *et al.*, 1983) in which several polysaccharide units (*c.* 2×10^5 Da each) are linked to a common protein core. Recent studies of the determination of molecular size differences in samples before and after the treatment of the gum with the proteolytic enzyme pronase (Connolly *et al.*, 1988) are consistent with the wattle blossom model. Published molecular weights of gum arabic samples vary between *c.* 2×10^5 Da and *c.* 1×10^6 Da (Anderson *et al.*, 1968; Fenyo, 1989), suggesting that the crude natural gum may be a mixture of arabinogalactan–protein complexes containing from one to several polysaccharide units linked to the protein core. The relative number of sugar residues given by Street and Anderson (1983) for the arabinogalactan unit suggests that the complex molecular weight would be a multiple of *c.* $1{\cdot}5 \times 10^5$ Da, which is roughly consistent with the findings of Connolly *et al.* (1988).

The protein component of gum arabic is mainly associated with a high-molecular-weight fraction representing less than 30% of the total gum (Vandevelde & Fenyo, 1985). The major fraction is of lower molecular mass and contains very little nitrogeneous material. It has been demonstrated recently (Randall *et al.*, 1988) that it is the protein-containing high-molecular-weight fraction which adsorbs most strongly at the oil–water interface, and is probably mainly responsible for the emulsifying and stabilising properties of the natural gum. This is consistent with our own experiments (Dickinson, 1988; Dickinson *et al.*, 1988), with samples of several different *Acacia* gum species with nitrogen contents in the range 0·1–7·5% (protein contents 0·5–47%),

TABLE 1
Viscosity Data and Inferred Weight-average Molecular Weight M_r for Degraded Products of Natural Gum Arabic Sample GA1 (0·35% N)

Sample	*Shear viscosity (mPa s)*[a]	*$[\eta]$ (ml g^{-1})*[b]	*M_r (10^5 Da)*[c]
GA1	36	12·0	3·1
GA2	32	11·0	2·6
GA3	30	10·5	2·4
GA4	28	10·0	2·2

[a] Measured with a Brookfield viscometer (20% wt aqueous solution).
[b] Intrinsic viscosity measured in 1·0 M NaCl at 28°C.
[c] From $[\eta] = KM_r^x$ with $K = 0{\cdot}013$ and $x = 0{\cdot}54$ (Anderson & Rahman, 1967).

which indicate a strong correlation between the proportion of protein in the gum and its surface properties at the oil–water interface.

MATERIALS AND METHODS

The gum samples GAO (0·38% N) and GA1 (0·35% N) were good quality Sudanese *Acacia senegal* samples (*not* spray-dried) which had been milled to a fine powder. Gum GAO was fractionated on a gel permeation chromatography column packed with Sephacryl S-500 and eluted with 0·3% wt NaCl solution. Using a molecular weight distribution curve based on a previously established elution profile for GAO, gum fraction GAH was an arbitrary cut intended to separate the 10% of material of highest molecular weight.† Gum fraction GAL is the material subsequently recovered after removal of GAH from GAO. Several separate runs were undertaken in order to obtain enough of the fraction GAH for emulsification studies. Gum samples GA2, GA3 and GA4 were three of a series of controlled degradation products derived from GA1 to give a range of molecular weights in order to test the simple hypothesis that high molecular weight is desirable for good functionality. Each of the samples GA1, GA2, GA3 and GA4 has a nitrogen content of 0·35%. Table 1 gives concentrated solution viscosities, intrinsic viscosities, and derived molecular weights.

Emulsions of *n*-hexadecane-in-water (1% wt gum, 10% vol. oil, 0·05 M phosphate buffer, pH 7) were prepared on a small scale (*c.* 10 ml) using

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†Fraction GAH was found to have a nitrogen content of 0·87% (i.e., 5·7% wt protein) as against a nitrogen content of 0·35% (i.e., 2·3% wt protein) for residual fraction GAL.

the one-stage valve mini-homogeniser described previously (Dickinson *et al.*, 1987). After blending, the coarse emulsion premix was homogenised at 300 bar. Each emulsion sample was stored in a water bath at 25°C; 0·1% wt sodium azide was added as bactericide. Immediately after emulsion preparation, and at regular intervals after thorough mixing, aliquots were taken for droplet-size determination using a Coulter counter model TAII with a 30 μm orifice tube and 0·1 M NaCl as suspending electrolyte.

Interfacial tensions were measured at the *n*-hexadecane–water interface (10^{-3}% wt gum, pH 7, 25°C) using the Wilhelmy plate technique (Murray, 1987).

RESULTS AND DISCUSSION

Figure 1 shows the droplet-size distributions of *n*-hexadecane-in-water emulsions immediately after preparation with gum samples GAO, GAH and GAL. While the Coulter counter distributions are not very different

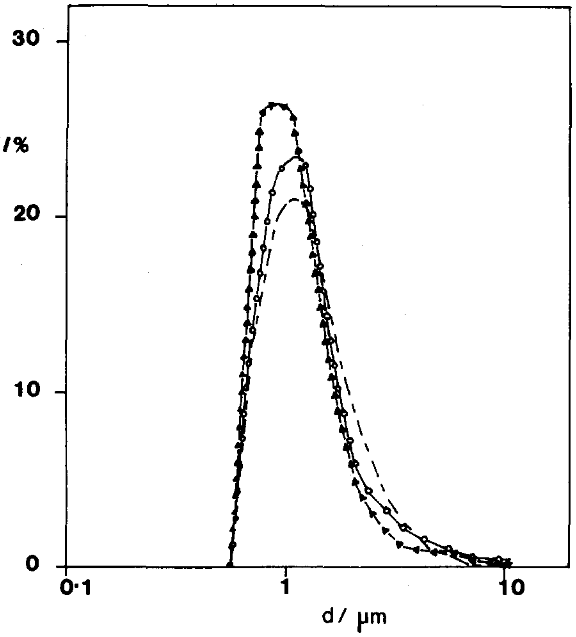

Fig. 1. Droplet-size distributions of *n*-hexadecane-in-water emulsions immediately after preparation with fractionated gum arabic samples. The smoothed percentage differential volume $V(d)$ is plotted against droplet diameter d: GAO, —○—; GAH, - - -; GAL, —▲—.

for the three samples, the high-molecular-weight fraction GAH (0·87% N) gives a coarser emulsion than the residual low-molecular-weight fraction GAL (0·35% N), with the original gum sample GAO (0·38% N) somewhere inbetween. Figure 2 shows droplet-size distributions of the same emulsions after storage for 24 h. The loss of height in the main peak of the distribution function $V(d)$ and the appearance of a second peak at larger droplet diameter d are indicative of emulsion instability via droplet coalescence. It can be seen from Fig. 2 that the most stable emulsion is the one made with the high-molecular-weight high-nitrogen fraction GAH. Results at longer storage times (not shown) indicate that the least stable emulsion is the one made with the residual low-molecular-weight fraction GAL.

The interfacial tensions of 10^{-3}% wt gum solutions at the *n*-hexadecane–water interface after 24 h lie in the order GAH < GAO < GAL. That is, the high-nitrogen fraction GAH is more surface active (by *c.* 1 mN m^{-1}) than the residual fraction GAL, with the original gum sample GAO lying somewhere inbetween. This is consistent with our earlier results (Dickinson *et al.*, 1988) which showed a good correlation

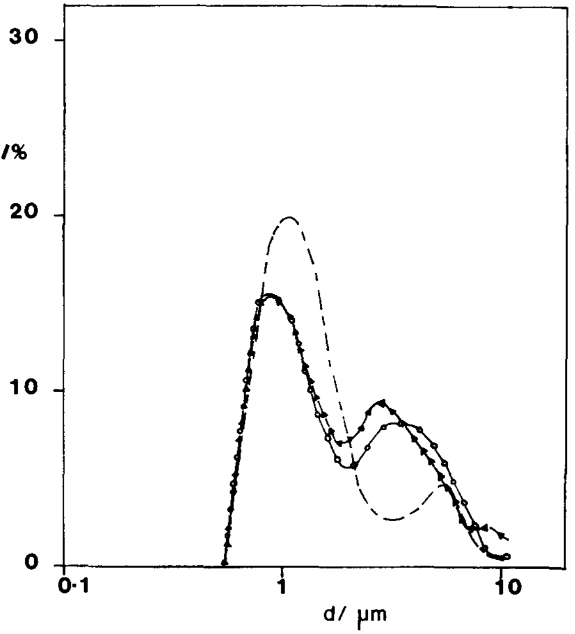

Fig. 2. Droplet-size distributions of emulsions prepared with fractionated gum arabic samples after storage for 24 h. The smoothed percentage differential volume $V(d)$ is plotted against droplet diameter d: GAO, —o—; GAH, - - -; GAL, —▲—.

between nitrogen content and limiting long-time surface activity. This difference between GAH and GAL is not apparent, however, at short adsorption times (< 2–3 h), probably because it takes a long time for the high-molecular-weight arabinogalactan–protein complexes to diffuse to the interface. So, the gum fraction GAL makes the smallest emulsion droplets even though it contains less protein because the smaller macromolecules get to the interface faster at the instant of emulsification, and are therefore able to emulsify a larger area of oil–water interface. For long-term emulsion stability, however, the larger protein-rich polymers of fraction GAH are more effective, as illustrated in Fig. 2.

Samples GA1, GA2, GA3 and GA4 corresponding to different degrees of controlled degradation give decreasing emulsion stability with increasing degradation (i.e., decreasing average molecular weight). Figure 3 shows droplet-size distributions of *n*-hexadecane-in-water emulsions measured 5 h after emulsion preparation. The finest emulsion is that made with the original gum sample GA1 having $M_r = 3{\cdot}1 \times 10^5$ Da (see Table 1), and the most coarse emulsion is that made with the most degraded sample GA4 with $M_r = 2{\cdot}2 \times 10^5$ Da. This result is consistent

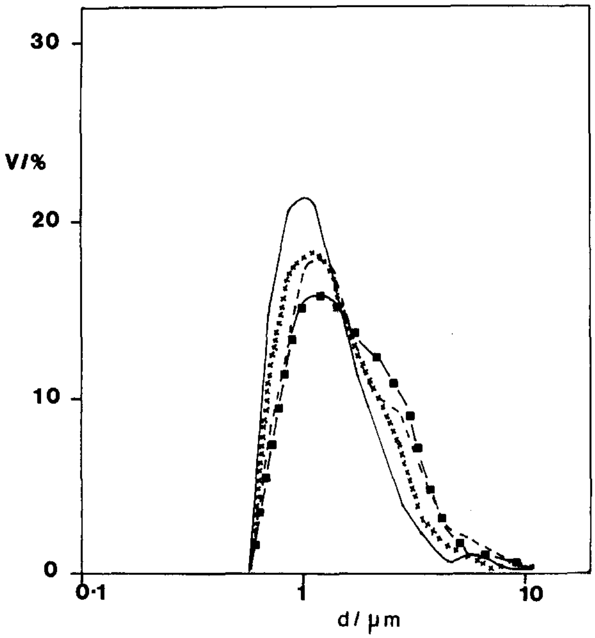

Fig. 3. Droplet-size distributions of emulsions prepared with degraded gum arabic samples after storage for 5 h. The smoothed percentage differential volume $V(d)$ is plotted against droplet diameter d: GA1, ——; GA2, xxxxx; GA3, ----, GA4, ——■——.

with the work of Nakamura (1986) who studied nearly 100 separate samples of gum arabic with M_r in the range $2\text{–}3 \times 10^5$ Da. Nakamura (1986) showed, without apparently being aware of the nitrogen content of the gum samples, that emulsion stability increases with the weight-average molecular weight of the gum. Table 1 and Fig. 3 indicate that, when the nitrogen content is kept constant, there is indeed a positive correlation between the molecular weight of the gum and its stabilising ability.

In conclusion, we note that the results reported in this paper on model *n*-hexadecane-in-water emulsions are consistent with the idea that it is the protein-rich high-molecular-weight component (the arabinogalactan–protein complex) which provides the functionality of gum arabic as an emulsion stabiliser. There is also evidence, however, that in the ideal gum sample it may be desirable to have a mixture of both small and large protein-containing macromolecules, the former providing the emulsifying power (finer droplets initially) and the latter conferring the emulsion stability (less droplet coalescence).

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