

# THE EMULSIFYING PROPERTIES OF GUM ACACIA

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The quantity of potassium arabate required to stabilise as an emulsion a known volume of a hydrocarbon oil has been determined and an estimate of the dimensions of the interfacial film made. The gum acacia remaining in the washed emulsion is held strongly at the oil: water interface and is not yielded to the bulk of the aqueous phase.

AN attempt was made to determine whether acacia is adsorbed at the oil water interface in equilibrium with the bulk solution or if it is irreversibly adsorbed. If it is in equilibrium repeated washing of the emulsion should cause the destruction of the emulsion as the gum is removed from the system.

## METHOD

Emulsions of light liquid paraffin, benzene, cyclohexane and heptane were made by mixing equal volumes of hydrocarbon oil and approximately 10 per cent w/v solution of potassium arabate, stirring with a dispersator and then passing twice through a hand homogeniser.

### *Washing of the Emulsion*

The method used was an adaption of that described by King<sup>1</sup>. A convenient volume of an emulsion was diluted to twice its volume with water and centrifuged to separate the phases. Nearly all the separated aqueous phase was removed and replaced by a similar volume of water, and after thorough mixing the emulsion was centrifuged again. This process was repeated for as many cycles as necessary.

A heptane emulsion was examined after seven such cycles and the oil content was determined by comparison of the densities of oil, water and emulsion. The surface area of the globules was calculated by measuring diameters and counting the numbers of droplets on twenty photomicrographs. The distribution of gum between the aqueous phase and the interface was found by evaporation of samples of aqueous phase and emulsion respectively.

## RESULTS

Benzene emulsions could be washed several times without obvious change but after the fourth cycle the emulsion began to crack, and thereafter each washing yielded a small volume of benzene. Cyclohexane emulsions were more stable, no sign of cracking appeared until the seventh washing, but even after the fourteenth the bulk of the emulsion remained. A heptane emulsion did not show any sign of deterioration after the seventh washing (see Table I), and a light liquid paraffin emulsion was stable after ten washing cycles. All these washed emulsions stored well but in most there was a noticeable coarsening after several weeks. The stability appears to be the same order as the resistance to washing.

## DISCUSSION

In an emulsion which has been washed until the concentration of potassium arabate in the continuous phase is virtually zero it is reasonable to suppose that the amount of gum remaining is the minimum quantity necessary to stabilise that emulsion. There is experimental evidence for the interfacial area of the oil globules, the weight, and hence the number of molecules of potassium arabate adsorbed. To calculate the thickness of, and number of layers of molecules in the interfacial film, we need to know the volume and shape of the molecule. The conclusions of Veis and Eggenberger<sup>3</sup> that the arabic acid molecule is a short stiff coil, of length slightly greater than its diameter does not seriously disagree with those of Matthews<sup>4</sup> who described the molecule as spherical, but the estimates of size cannot be reconciled. Matthews' estimate must be discounted since it was based on over-simplified structure construction of the molecule

TABLE I  
COMPOSITION OF A HEPTANE EMULSION AFTER SEVEN WASHING CYCLES

Volume composition (from density measurements) .. .. .	23.0 per cent v/v
Volume of heptane in 50 ml. of emulsion .. .. .	11.6 ml.
Weight of gum in 50 ml. of emulsion .. .. .	0.0672 g.
Weight of gum in 50 ml. of aqueous phase .. .. .	not weighable
Weight of gum per ml. of emulsion .. .. .	1.4 mg.
Weight of gum per ml. of heptane .. .. .	5.8 mg.
Interfacial area of heptane in 50 ml. emulsion .. .. .	$9.55 \times 10^{20} \text{ \AA}^2$
Number of molecules of potassium arabate (mol. wt. $3 \times 10^5$ ) <sup>3</sup> .. .. .	$1.35 \times 10^{17}$
Area per molecule .. .. .	$7.07 \times 10^4 \text{ \AA}^2$
Number of molecules of potassium arabate (mol. wt. $10^6$ ) <sup>4</sup> .. .. .	$4.049 \times 10^{14}$
Area per molecule .. .. .	$2.35 \times 10^4 \text{ \AA}^2$

whereas that of Veis and Eggenberger for molecules of molecular weight  $10^6$  and at limiting concentration represents a molecule at its maximum size. That the volume of  $7.2 \times 10^{-16}$  ml. proposed by Veis and Eggenberger is too large for real solutions is shown by their statement that solutions of independent non-overlapping molecules of that size cannot exist above concentrations of  $2 \times 10^{-3}$  g./ml.

If the concept of an isodiametric molecule be accepted it becomes possible to speculate about the dimensions of the interfacial film in the heptane emulsion. From the measured area per molecule, the film thickness is derived, and since the weight of gum is known a volume and concentration can be assigned to the interfacial film. Table II shows the results of calculations based on acacia solutions of various strengths.

One case, that of the 65 per cent w/v solution, gum of molecular weight  $3 \times 10^5$ , fits the required dimensions of a monolayer of an isodiametric molecule very well. A solution of this concentration is an elastic gel. The remaining examples although fitting the requirements much less satisfactorily, do tend to support the hypothesis of a monolayer interfacial film.

During this work, the stability of the washed emulsion was very noticeable, even when heated to about  $105^\circ$  to volatilise both phases, the emulsion did not break until the drying was nearly complete. The potassium arabate recovered from the emulsion in this way was readily soluble in

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water and did not appear to have been denatured. The mechanism by which the molecule of potassium arabate becomes so securely adsorbed at the interface in the apparent absence of a lipophilic group remains obscure but it seems the mechanism will be different to that of soaps, proteins and saponin because these either contain a lipophilic group or denature during use.

This interfacial film of acacia cannot be removed by very considerable dilution of the aqueous phase which seems to indicate the adsorption of this monolayer is not an equilibrium process such as envisaged by Gibbs.

TABLE II  
RESULTS OF CALCULATIONS BASED ON ACACIA SOLUTIONS OF VARIOUS STRENGTHS

1	2	3	4	5	6	7	8
Molecular weight $3 \times 10^5$	State of acacia solution per cent w/w or solid	Vol mol calculated ( $\text{\AA}^3$ )	Area mol measured ( $\text{\AA}^2$ )	Film thickness from col. 3 col. 4 calculated $\text{\AA}$	Film thickness from $\sqrt[3]{\text{vol mol calculated}}$ $\text{\AA}$	Fit to measured area (Col. 6) <sup>2</sup> Col. 4	Fit to calculated thickness Col. 5 Col. 6
	Solid	$0.33 \times 10^8$	$7.0767 \times 10^4$ = $(84.12)^2$	46.9	69.24	0.675	0.825
	75	$0.498 \times 10^8$	"	70.3	78.9	0.88	0.837
	65	$0.5928 \times 10^8$	"	84	84	1.00	1.00
	50	$0.826 \times 10^8$	"	116.72	93.82	1.24	1.39
	33.33 O:W:G 4:2:1	$1.494 \times 10^8$	"	211.2	114.4	1.84	2.50
$10^6$	Solid	$0.11065 \times 10^8$	$2.356 \times 10^4$ = $(153.5)^2$	46.9	47.9	0.098	0.313
	75	$0.166 \times 10^7$	"	70.3	118.5	0.21	0.775
	65	$0.2 \times 10^7$	"	84	126	0.3	0.824
	50	$0.2755 \times 10^7$	"	116.8	140.2	0.582	0.916
	33.33	$0.4978 \times 10^7$	"	211	170.8	1.89	1.15

Such a monolayer whilst sufficient to stabilise an emulsion may form a multilayer when in equilibrium with an acacia solution as used in emulsions. The substantial nature of these thick films is indicated by the behaviour of droplets of acacia solutions in oils<sup>5</sup>.

The varying degree of stability of the different emulsions to the washing process indicates that the efficiency with which the gum is adsorbed depends at least in part on the nature of the oil.

REFERENCES

1. King, *The Milk Fat Globule Membrane*, p. 4. Technical Communication No. 2 of Commonwealth Agricultural Bureaux.
2. Oakley, *Trans. Farad. Soc.*, 1935, 31, 136.
3. Veis and Eggenberger, *J. Amer. chem. Soc.*, 1954, 76, 1560.
4. Matthews, *Trans. Farad. Soc.*, 1939, 35, 1113.
5. Shotton and Wibberley, *J. Pharm. Pharmacol.*, 1959, 11, *Suppl.* 120T.

After Mr. Wibberley presented the paper there was a DISCUSSION. The following points arose.

After seven washings of a heptane emulsion, the acacia remaining could be presumed to be the minimum amount required to stabilise the emulsion as it existed. If this emulsion were to be subjected to a further homogenisation then it would probably crack because there would be insufficient acacia to stabilise the fresh interfacial area produced.