## SCIENCE PAPERS AND DISCUSSIONS

### THE INTERFACIAL TENSION OF SOLUTIONS OF ARABIC ACID

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#### INTRODUCTION

GUM acacia has been used in medicine for many centuries[1] and is still valued in pharmacy particularly as an emulsifying and suspending agent for oral preparations. Nevertheless very little appears to be known about those properties of gum acacia which are responsible for its effectiveness as an emulsifying agent. According to the more recent theories of emulsions a substance must be adsorbed at the interface in order to act as an emulsifying agent, forming a coherent film the physical properties of which will determine the type and stability of the system.

Clark and Mann[2] studied the effect of the concentration of gum acacia on the surface tension of aqueous solutions and the interfacial tension with benzene using the drop-weight and drop-volume methods of determination. They found that the surface tension increased slightly with concentration up to 0·1 per cent. and as the concentration was increased further the surface tension was decreased giving a value of 61·49 dynes/cm. for a 10 per cent. solution. The interfacial tension however was reduced as the concentration of gum acacia increased and for the 10 per cent. solution a value of 22·87 dynes/cm. was reported. Banerji[3] determined the surface tension of solutions of gum acacia with Traube's stalagmometer allowing "a fairly long time" for the formation of the drops and found that an approximately 4 per cent. solution had a surface tension of 63·16 dynes/cm. compared with 69·69 dynes/cm. obtained by Clark and Mann for a 5 per cent. solution. Banerji also found that the addition of electrolytes depressed the surface tension.

The drop-volume method was also used by Matthews[4] who determined the effect of gum acacia on the interfacial tension between water and *cyclo*hexane. Both the crude gum and the gum purified by precipitation with ethanol were used. This work was more systematic than that of the previous workers since Matthews first determined the rate of formation of the drop below which a constant drop-volume was obtained with a

given tip. This maximum rate of formation corresponded to forming a drop in 2·5 minutes and under these conditions he assumed the surface would be in equilibrium. Further, by rapidly forming the drops to practically full size, allowing them to hang for varying lengths of time and then completing their formation at the rate of one drop in three minutes he concluded that the equilibration time was one minute. From the published graph he showed that the interfacial tension of water and *cyclo*hexane was lowered uniformly as the concentration of the purified gum was increased (approximately 13 dynes/cm. by 3 per cent. of the gum) but that the crude gum showed a more rapid lowering up to about 1 per cent. concentration.

The ring method was used by Du Nouy[5] and by Boutaric and Roy[6], the latter showing that there was a decrease in the surface tension over a period of 4 hours, this decrease being greater if the solution was first boiled.

A review of the work on the chemical constitution of arabic acid has been made by Hirst[7]. The repeating unit in the molecule consisting of a branched chain.

The molecular weight of arabic acid was determined by Oakley[8] and Säverborn[9] who found it to be of the order of 290,000 and between 279,000 and 319,000 respectively. More recently Veis and Eggenberger[10] using a light scattering method found the molecular weight of arabic acid to be $1·00 \pm 0·05 \times 10^6$. With a substance of such large molecular weight it is to be expected that a comparatively long time would be necessary for the interface to reach equilibrium.

In the present work a comparison has been made of the drop-volume and the sessile drop methods for determining the effect of arabic acid on the interfacial tension of benzene and water and also the influence of time.

<div align="center">EXPERIMENTAL</div>

*Materials*

*Gum acacia.* A sample was obtained from James Laing (London) Ltd. which was used throughout this work. According to the importers this material came from the province of Kordofan through the El Obeid market and was collected between November 1947 and "early 1948."

*Distilled water.* Distilled water from a Manesty still was re-distilled from an all-glass apparatus, a little potassium permanganate being added to the water in the still. The condenser and receiver were cleaned with chromic acid and the still was run for an hour before water was collected.

*Benzene.* Benzene of Analar quality was recrystallised twice immediately before use.

*The purification of the gum acacia.* 100 g. of the gum was dissolved in 150 ml. of water, strained free from insoluble matter and 300 ml. of 95 per cent. ethanol added gradually with constant stirring. After standing for 15 minutes the supernatant liquid was removed and the residue centrifuged to separate the precipitate. The gum was precipitated twice more and the purified gum dried in a vacuum desiccator.

The product had a moisture content of 5·71 per cent. and the $pH$ of a 1 per cent. solution was 5·0.

The viscosity of a 2 per cent. solution was compared with that of the crude gum using a No. I B.S. viscometer of the Ostwald pattern. Crude gum acacia 2·060 per cent. w/v, viscosity (25° C.) 2·12 centipoise. Purified gum acacia 2·012 per cent. w/v, viscosity (25° C.) 2·15 centipoise. Purified gum acacia after 12 months storage 2·100 per cent. w/v, viscosity (25° C.) 2·18 centipoise.

These results indicate that the purification process did not materially affect the gum acacia and that it remained stable on storage. Taft and Malm[11] obtained a lower figure (1·6 centipoise for a 2·1 per cent. solution at 30° C.) but the above figures were in agreement with those of Riddell and Davies[12] (2·088 centipoise for a 1·994 per cent. solution at 20° C.).

*The preparation of arabic acid.* A solution containing about 12 per cent. of the purified gum acacia was passed through a column of cation exchange resin Zeo Karb 225 to remove the potassium, calcium and magnesium ions[13,14]. The arabic acid solution collected from the column was dried *in vacuo* over silica gel. When the initial foaming had subsided a high vacuum pump was connected and the solution frozen, the pumping being continued until a porous solid was obtained. The moisture content of the solid was determined by drying to constant weight at 100 to 110° C. and the concentration of solutions used in this work is expressed in terms of anhydrous material. The ash value showed some variation with different batches but was generally below 0·06 per cent. w/w.

*Viscosity.* The solution of arabic acid collected from the ion exchange column was diluted to about 2 per cent. and compared with a 2 per cent. solution prepared from the dried material. Solution from ion exchange column 1·896 per cent. w/v, viscosity (25° C.) 1·647 centipoise. Solution of the dried arabic acid 1·910 per cent. w/v, viscosity (25° C.) 1·793 centipoise.

A solution of arabic acid showed no change in viscosity after standing for 14 days at 25° C. Some change appears to take place in the arabic acid on drying[1] and the material was prepared at approximately 3 month intervals. One sample remained soluble for about 9 months after which time an increasing proportion swelled in water but did not dissolve.

The equivalent weight was determined by electrometric titration using a glass electrode. An approximately 10 per cent. solution of arabic acid was titrated against standard potassium hydroxide and four samples gave the following values for the equivalent weight, 1125, 1142, 1187 and 1201 (average = 1164). The shape of the curve indicating that arabic acid is a comparatively strong acid.

In a review of the literature Säverborn[9] shows that the reported values vary between 1000 and 1400, the lower results being obtained by heating the arabic acid with standard alkali and back titrating which indicates some of the carboxyl groups are combined as lactones.

*Density of arabic acid solutions.* A graph was constructed which showed the relationship between the density and concentration was linear. In the calculation of the interfacial tension the density of the solution was obtained from the graph.

## THE DETERMINATION OF INTERFACIAL TENSION

*The drop-volume method.* The method used by Gaddum[15] was adopted using an "Agla" micrometer syringe. The tips were formed by grinding down a piece of "Viridia" tubing (bore 0·2 or 0·3 mm.) to give an external diameter of about 2 mm., in the manner described by Harkins[16] and the tubing was then fused on to the adaptor fitting into the syringe barrel. The glass apparatus was cleaned with chromic acid and well washed. In order to prevent the aqueous solution from creeping up the sides of the tip it was treated with a 2 per cent. solution of Silicone DC 1107 in carbon tetrachloride to within 2 mm. of the end of the tip which was again cleaned with chromic acid. The solutions and benzene were mutually saturated by shaking together, the separated liquids being used for the experiments.

The apparatus which was finally evolved is shown diagrammatically in Fig. 1 and was enclosed in a cabinet to protect from draughts, the water in the beaker K was circulated from a constant temperature water bath at 25° C. When drops were allowed to hang from the tip for long periods of time it was found necessary to seal each end of the barrel of the syringe

TABLE I

DROP-VOLUME METHOD: THE EFFECT OF HANGING TIME ON THE INTERFACIAL TENSION (25° C.)

| Time drop allowed to hang | 5 min. | 30 min. | 1 hour | 19 hours |
|---|---|---|---|---|
| Water/benzene (dynes/cm.) .. .. .. .. .. | 34·7 | 34·4 | 34·25 | 34·25 |
| 1·025 per cent. w/v arabic acid/benzene (dynes/cm.) .. | 27·75<br>27·2 | 25·45<br>25·65 | 25·85 | — |
| 10·165 per cent. w/v arabic acid/benzene (dynes/cm.) .. | 17·8<br>19·49<br>18·6<br>18·19 | 18·19<br>18·26<br><br>18·2 | 18·26<br>18·9 | 18·9<br>18·9 |

with a little liquid paraffin to prevent evaporation which otherwise would give a high result. In preliminary experiments the micrometer head was turned by hand. A drop was formed about ¾ of its probable final volume and after hanging for some time it was then increased by rotating the micrometer head three divisions (one division = 0·0002 ml.) every ten seconds until the drop disengaged. The results in Table I show that the time the drop hung from the tip did not materially affect the value of the interfacial tension obtained. The corrections of Harkins[16] were used in calculating the interfacial tension from the drop volume. Harkins and Brown[17] found the interfacial tension between water and benzene to be 34·68 dynes/cm.

The variations in some of the results were probably due to the final additions to the drop not being made uniformly in each case and when drops were completed by larger increments at approximately 30 minute intervals the 1·025 per cent. arabic acid solution yielded drops which were approximately two thirds the previous size from the same tip.

It was concluded that the interface was not in equilibrium and in order to form drops at a uniform rate a synchronous motor (1 rev. per hour)
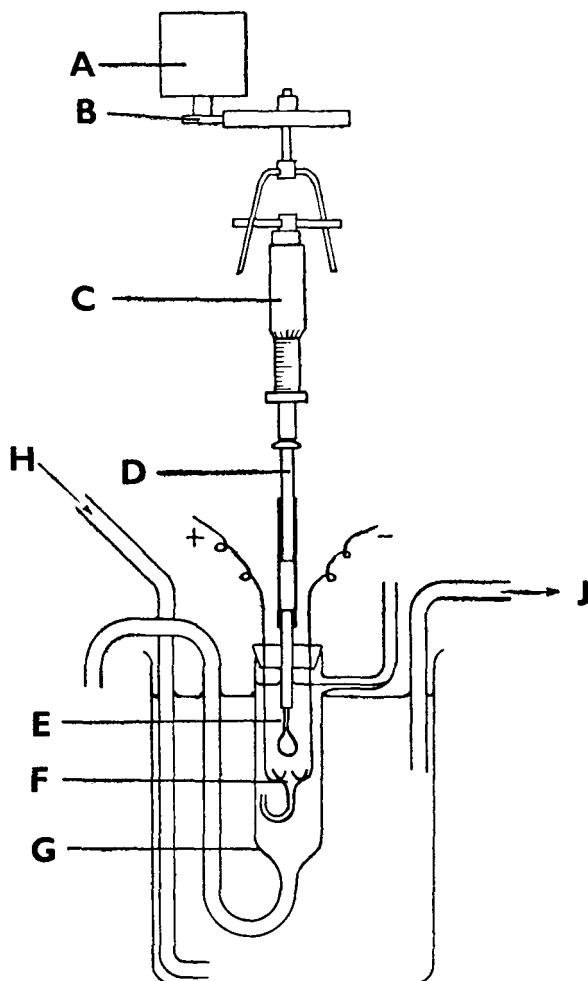
FIG. 1.   Drop-volume apparatus.

A.   Synchronous motor (1 r.p.h.).
B.   Gear drive.
C.   Micrometer screw gauge.
D.   Agla syringe (0·5 ml. capacity).
E.   Accurately ground tip.

F.   Glass funnel with Pt electrodes.
G.   Container for benzene.
H. and J.   Inlet and outlet for water at 25° C.

and gears were added to the apparatus as in Figure 1.   By this means it was possible to drive the micrometer syringe at speeds varying from 8 to 1/8 revolutions per hour corresponding to increments of 0·08 to 0·00125 ml. per hour.   When the drop fell into the small funnel F the circuit between the two platinum electrodes was closed and this caused a micro-switch to break the circuit of the synchronous motor which then stopped. The readings were then taken at a convenient time.   The results are given in Table II.

### TABLE II

DROP-VOLUME METHOD: THE EFFECT OF THE RATE OF FORMATION ON THE INTERFACIAL TENSION

| Solution per cent. w/v of anhydrous arabic acid | | Rate of formation (revs. per hour) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | By hand | 8 | 4 | 2 | 1 | ½ | ¼ | ⅛ | 1/16 |
| 1·025 | γ (25° C.) | 27·5 | — | 22·0 | 20·4 | 19·1 | 17·8 | 17·7 | 17·5 | 17·2 |
| | Time of formation | 10 min. | — | 2 hrs. 20 min. | 4 hrs. 20 min. | 7 hrs. 45 min. | 14 hrs. 26 min. | 28 hrs. 33 min. | 42 hrs. 25 min. | 55 hrs. 48 min. |
| 5·265 | γ (25° C.) | 20·5 | 17·3 | 17·1 | — | 15·0 | 15·0 | — | — | 14·3 |
| | Time of formation | 5 min. | 50 min. | 1 hr. 35 min. | — | 5 hrs. 32 min. | 11 hrs. 5 min. | — | — | 42 hrs. 12 min. |
| 10·165 | γ (25° C.) | 18·27 | — | — | 15·9 | 15·2 | — | 14·8 | 13·6 | 14·0 |
| | Time of formation | 10 min. | — | — | 2 hrs. 40 min. | 4 hrs. 45 min. | — | 18 hrs. 27 min. | 25 hrs. 10 min. | 34 hrs. 44 min. |

In an attempt to shorten the time of the experiments drops of about ⅔ of the final volume were formed immediately and completed at the rate of ⅛ r.p.h. but the results exceeded those in Table II at ⅛ r.p.h. by 3·5, 3 and 2 dynes/cm. for the 1, 5 and 10 per cent. solutions respectively.

*The sessile drop method.* In this method a drop of a fluid of suitable size is formed on a horizontal plane surface within the second fluid. The volume of any given drop is constant and changes in surface area take place only as a result of a change in shape. The shape of such a drop, which depends upon the interfacial tension, volume and the difference in density of the two phases, comes within the scope of Bashforth and Adams's treatment of surfaces of revolution. Porter[18] published a method of calculating the interfacial tension from the dimensions of a sessile drop shown in Figure 2 where r is the equatorial radius and h is the height of the vertex above the equator. The original paper should be consulted for the theory of the method.
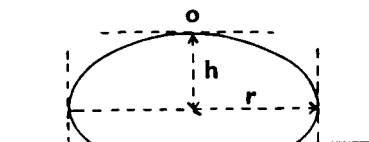


FIG. 2. Profile of the sessile drop.

r. radius of drop at the equator (maximum diameter).

h. height of drop from the equator to the vertex O.

The interfacial tension is obtained from the formula,

$$\frac{\beta^2}{r^2} = \frac{1.h^2}{2\,r^2} + \Delta \quad \text{where} \quad \beta^2 = \frac{\gamma}{g\,(\rho_1 - \rho_2)}$$

$\rho_1$ and $\rho_2$ are the densities of the two phases.

$\gamma$ = interfacial tension in dynes/cm.

The correction $\Delta$ was obtained from a curve constructed from the values published by Porter.

When $\dfrac{h^2}{r^2} = 0 \cdot 25$ the correction is zero and the size of a drop was found for each solution that gave a value for $\dfrac{h^2}{r^2}$ between 0·20 and 0·30 after 96

hours since it is in this region that the correction is known with greatest accuracy.

The apparatus is shown diagrammatically in Figure 3 and for convenience it was mounted on an optical bench. The light from the mercury vapour lamp A was passed through two filters B, Chance ON16 and Ilford 807 so that the light of the mercury green line was transmitted and illuminated the ground glass screen D.
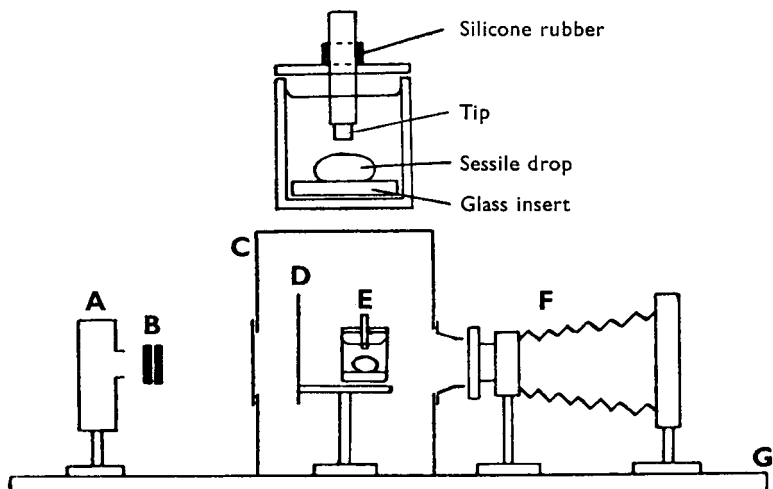


FIG. 3. Apparatus for the sessile drop method.

|   |   |   |   |
|---|---|---|---|
| A. | Mercury vapour lamp. | E. | Optical cell assembly. |
| B. | Filters: Ilford 807; Chance ON16. | F. | Camera. |
| C. | Thermostat cabinet at 25° C. | G. | Optical bench. |
| D. | Ground glass screen. |   |   |

The solution and benzene were mutually saturated at 25° C. by shaking together and allowing to stand overnight in the thermostatically controlled cabinet C. The drop was measured into the optical cell containing the benzene with a hypodermic syringe the apparatus having been maintained at 25° C. also.

The glass insert in the optical cell E was treated with a 2 per cent. solution of methyl chlorosilane in carbon tetrachloride and well washed with water to impart a water repellent surface to the glass which prevented the drop from spreading. This insert was cut from a concave mirror blank with a radius of curvature of one metre to locate the drop centrally in the cell.

The sessile drop was photographed in silhouette against the screen D through a hole in the side of the cabinet. An accurately ground tip of known external diameter was suspended in the benzene through the lid of the cell as shown so that the magnification of the image of the drop could be calculated and the actual dimensions of the drop found. Photographs were taken at intervals of 3 min., 1, 4, 8, 24, 48 and 96 hours and the resulting plates measured with a Cambridge Universal Measuring

machine which can measure in two dimensions at right angles. This machine is graduated to 0·001 cm. and estimates to 0·0002 cm. may be made without difficulty.

Figure 4 shows the effect of time on the shape of a drop and was formed by superimposing photographs of the same drop taken after 3 minutes and 96 hours. The results obtained for solutions of arabic acid are given in Figure 5 together with the results for the benzene/water interface. Facilities for conditioning and filtering the air in the laboratory were not available and manipulations were carried out as rapidly as possible to avoid extraneous contamination.

On a number of occasions contamination of the benzene occurred which resulted in a marked fall in the interfacial tension over a period of 1 hour and 4 hours as shown in Table III. These results have not been used. Recrystallisation of the benzene removed the contamination and the fall in the interfacial tension with time again followed the curves given in Figure 5. An investigation into the types of substances which can produce this effect will be undertaken later.
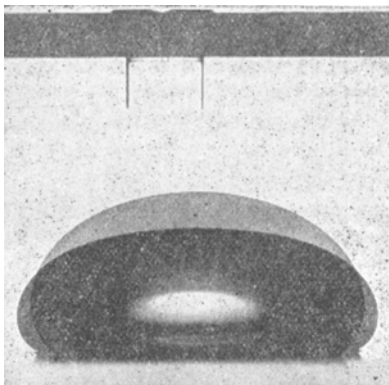


FIG. 4. The effect of time on the shape of the sessile drop. Photographs of a drop after 3 minutes and 96 hours have been superimposed to show the flattening of the drop after 96 hours.

Diameter of tip above drops is 0·4048 cm.

The solution contained 0·998 per cent. arabic acid.

TABLE III

SESSILE DROP METHOD: THE EFFECT OF CONTAMINATION IN THE BENZENE ON THE INTERFACIAL TENSION

| Solution per cent. w/v of anhydrous arabic acid | Time after formation of sessile drop | | | | | | |
|---|---|---|---|---|---|---|---|
| | 3 min. | 1 hr. | 4 hrs. | 8 hrs. | 24 hrs. | 48 hrs. | 96 hrs. |
| 0·0984 | 33·7 | 15·3 | 14·4 | — | 15·3 | 14·9 | 15·3 |
| 0·500 | 31·75 | 16·9 | 16·1 | — | 15·8 | — | 15·2 |
| 1·000 | 32·4 | — | 17·2 | 16·7 | 15·4 | 14·1 | — |
| 5·00 | 20·1 | 14·6 | 13·2 | — | 11·7 | 10·9 | 10·0 |

DISCUSSION

The ring method has been used for the determination of the surface tension of gum acacia solutions. The method was attempted in the present work using a chainomatic balance as described by Harkins[19] and although the results obtained for the surface tension of water (71·5 dynes/cm.) and of benzene (27·92 dynes/cm.) were in agreement with the
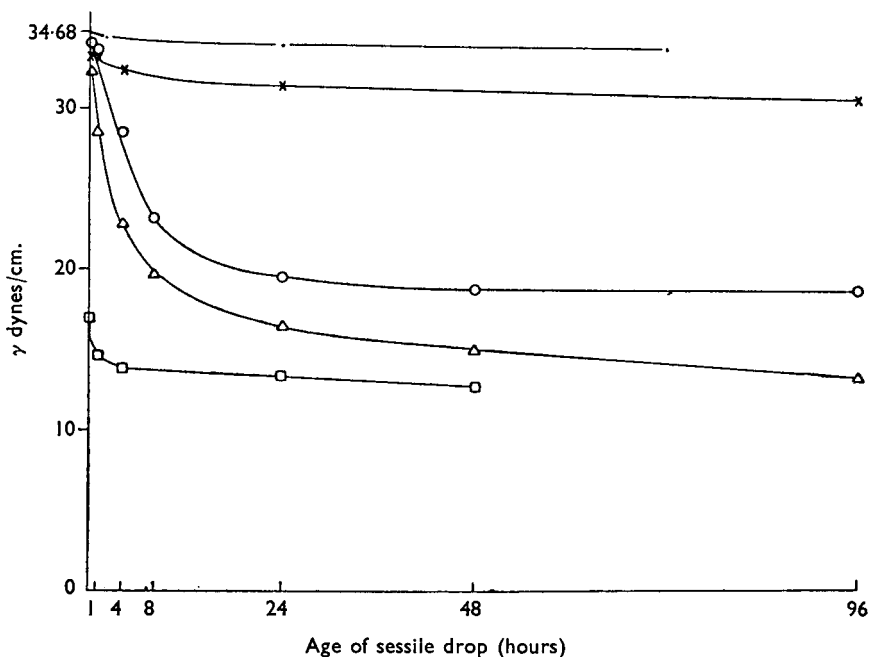
FIG. 5. Sessile drop method. The effect of time on the interfacial tension of arabic acid solutions and benzene.

× 0·01 per cent. arabic acid.　　　　　△ 1·0 per cent. arabic acid.

○ 0·1 ,, ,, ,, ,,　　　　　□ 10·0 ,, ,, ,, ,,

—·— distilled water/benzene interface.

accepted values the interfacial tension for benzene and water was approximately 1·5 dynes/cm. too low. The correction factors of Harkins[19] and the equation of Zuidema and Waters[20] were used to calculate the results and both methods showed good agreement.

The difficulty most probably arises from the ring not being in one plane and parallel to the surface so that the interface broke away from the ring first at one point. This suggests that the liquid/liquid interface is more sensitive to the adjustment of the ring than is the liquid/air surface. Hutchinson[21] experienced similar trouble.

However, as the ring is raised there is a considerable extension of the surface so that the criticisms of the drop-volume method for the determination of the interfacial tension of arabic acid solutions will apply also to the ring method.

From Figure 5 and Table II it is evident that the change in interfacial tension with time is slow but the change shows the same general form by both methods. Since the values obtained by the drop-volume method are inversely related to the rate of formation of the drop and at the slowest rate gives greater values than those obtained by the sessile-drop method it is reasonable to suppose that the surface of the drop growing on the tip does not achieve equilibrium with the bulk of the solution. This is

supported too by the determinations in which the drop was partially formed rapidly and then completed at the slowest rate of growth yielded higher values than if the drop was grown completely at the slowest rate.

The results obtained by Clark and Mann[2] show a linear relationship between the concentration and the interfacial tension, the drop being formed over a comparatively short period of time. A direct relationship was obtained by Matthews[4] using *cyclo*hexane instead of benzene although Matthews' curve had a steeper slope. The determinations being carried out by the drop-volume method in both cases.

If the values which were obtained by the sessile drop method after the drop had aged for 3 minutes are plotted against concentration the relationship is seen to be linear also. This implies that the time allowed for the formation of the drop by Clark and Mann and by Matthews was insufficient for an equilibrium to be established and also insufficient to give an interfacial tension/concentration curve of the right shape. Banerji[3] whilst apparently recognising the problem of attaining equilibrium at the surface by stating that "a fairly long time was taken for the formation of the drops" made no attempt to determine the time necessary and his results for solutions of approximately 4, 2 and 1 per cent. gum acacia showed an almost linear relationship also.



FIG. 6. Sessile drop method. The effect of the concentration of arabic acid on the interfacial pressure between water and benzene.

A static method is therefore essential for the determination of surface or interfacial tension of solutions of such substances which attain equilibrium very slowly and the sessile drop or bubble method seems to be the method of choice. A difficulty arises with the hanging drop method as a drop formed initially which is suitable for measurement may detach itself after the surface has aged for a few hours.

Even after 4 days it was not certain that equilibrium had been reached by the sessile drop method and the interfacial tension obtained was plotted against the reciprocal of the time for each concentration and the curves extrapolated to infinite time. These values were deducted from the *interfacial* tension of benzene and water obtained in the same way and the resulting value for the surface pressure ($\pi$) was plotted against the con-
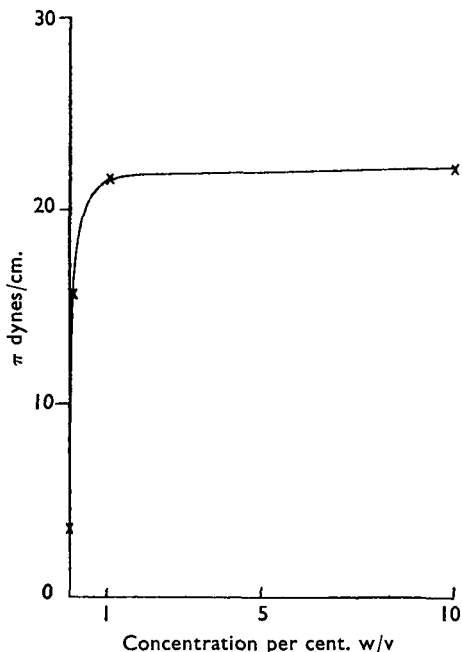
centration in Figure 6. In this way any changes occurring in the cell were allowed for and the shape of the curve was unaltered.

From the data on this curve the approximate surface excess ($\Gamma_2^v$) has been calculated using the Gibbs equation for concentrated solutions.

$$-\frac{N_1 . d\gamma . N_2}{RT \; dN_2} = \left(\frac{N_1 + N_2 . V_2}{V_1}\right)\Gamma_2^v$$

Where $N_1$ and $N_2$ are the mole fractions, $V_1$ and $V_2$ are the partial molar volumes of the components water and arabic acid and $\gamma$ is the interfacial tension. By substituting values for $N_1$, $V_1$ and $V_2$, expressing $N_2$ in terms of the concentration $C_2$ and substituting $d\pi$ for $d\gamma$ the approximate expression

$$\frac{1}{RT} . \frac{d\pi}{dC_2} . C_2 = \left(1 + \frac{C_2}{150}\right)\Gamma_2^v$$

is obtained by assuming the solid arabic acid to have a density of 1·5 and a molecular weight of 300,000.

As there are insufficient number of points on the curve in order to obtain $\frac{d\pi}{dC_2}$ the change in value for sections of the curve has been substituted, denoted by $\Delta\pi$ and $\Delta C_2$ which should give results of the right order, $C_2$ being the approximate average for the corresponding section.

| Concentrations per cent. | $\dfrac{\Delta\pi}{\Delta C_2}$ | $C_2$ per cent. w/v | $\Gamma_2^v$ moles/cm.$^2$ |
|---|---|---|---|
| 0–0·01 | $\dfrac{3\cdot4}{0\cdot01}$ | 0·005 | $0\cdot69 \times 10^{-10}$ |
| 0·01–0·1 | $\dfrac{12\cdot1}{0\cdot09}$ | 0·05 | $2\cdot7 \times 10^{-10}$ |
| 0·1–1·0 | $\dfrac{6\cdot2}{0\cdot9}$ | 0·5 | $1\cdot39 \times 10^{-10}$ |
| 1·0–10·0 | $\dfrac{0\cdot5}{9}$ | 5·0 | $1\cdot1 \times 10^{-11}$ |

The initial rapid rise in $\pi$ and concomittant rise in $\Gamma_2^v$ up to about 0·1 per cent. arabic acid is probably due to an increased adsorption of arabic acid at the interface. Further increases in concentration above 0·1 per cent. probably results in a rearrangement of the adsorbed layer and subsequently the building up of layers containing a high proportion of arabic acid immediately below the surface will account for the decrease in $\Gamma_2^v$ above about 0·1 per cent. concentration. For convenience such a structure is referred to here as a "multilayer" and with a hydrophilic substance such as arabic acid it is probable that water molecules enter into its structure. This also offers an explanation of the interfacial tension/time curves given in Figure 5.

A highly concentrated multilayer such as this should exhibit a strong lateral attraction between the molecules and be very viscous or gel-like in character. It was observed that when a drop of the 10 per cent. solution was withdrawn from the cell with a hypodermic syringe after ageing for 96 hours the drop did not shrink uniformly but collapsed without

reducing the area of contact with the glass insert and the surface became wrinkled. This also supports the view that the surface layers have gel-like properties.

From his curve for gum acacia Matthews concluded that a vaporous film was formed at the interface but his curves for dextrin and for apple and citrus pectins were similar to Figure 6 for arabic acid which he interpreted as being due to the formation of a condensed film. In the same paper he mentions that in a preliminary experiment arabic acid also gives a curve of the condensed type implying a difference in behaviour of gum acacia and arabic acid. However, in some preliminary work with the potassium and calcium salts of arabic acid it was found that the shape of the curves are similar to Figures 5 and 6 which suggests that there is no great difference between the adsorbed layers of arabic acid and its simple salts. Further work on the salts of arabic acid is proceeding.

*A Comment on the Emulsifying Properties of Gum Acacia*

If it may be assumed from the preliminary work on the salts of arabic acid that gum acacia solutions exhibit the same structure as arabic acid at the interface a hypothesis can be given to account for the stability of acacia emulsions which is in agreement with the modern theories.

An interfacial film of the type suggested which has a gel-like structure should possess the necessary physical properties, such as lateral coherence and elasticity, for the stabilisation of an emulsion. In addition, with a strong acid, it may be predicted that the system would exhibit a marked interfacial potential which appears to be necessary for the formation of oil in water emulsions. In attempting to draw an analogy with the theory of emulsions put forward for soaps by Schulman and Cockbain[22] it must be remembered that the soaps having a strong hydrophobic group in the molecule will form a monolayer. The soaps are only effective as emulsifiers if a condensed film is formed and this is achieved by forming a complex at the interface by the addition of an oil souble components and it is-this complex condensed film which has these necessary physical properties for the stabilising of emulsions.

The lowering of the interfacial tension by gum acacia is not so great as that produced by the condensed complex film formed by the soaps and this would account for the greater amount of work necessary to bring about the subdivision of oil in acacia emulsions.

SUMMARY

1. The effect of arabic acid on the interfacial tension between water and benzene has been examined by the drop-volume and sessile drop methods. The change in interfacial tension with time has been found to be very slow and the sessile drop method is the method of choice since no change in volume is involved.

2. The shape of the interfacial tension/time and the interfacial tension/concentration curves are interpreted as being due to the formation of an adsorbed "multilayer," containing a high concentration of arabic acid, possessing gel-like properties.

3. A film such as this should possess those physical properties, such as coherence, elasticity and surface potential, which would explain the emulsifying properties of gum acacia in solution.

I wish to express my thanks to Mr. R. Fitall for technical assistance.

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## DISCUSSION

The paper was presented by THE AUTHOR.

MR. J. H. OAKLEY (London) asked whether the accepted 4:2:1 and 2:2:1 ratios were the most suitable for making a primary emulsion. Were these a compromise, and was there an optimum concentration in the final emulsion? It would be of interest to learn whether the author found much variation in the acacia available on the market, and whether allowance should be made for such variation.

DR. F. WOKES (Kings Langley) referred to the plotting of the results in Figures 5 and 6, and observed that the points in the early part of the curve were very close together and those in the latter part were spread out. He asked whether plotting against the log time or some other scale would have given a more linear curve, more suitable for extrapolation.

MR. VAN ABBÉ (Loughborough) said that he was interested in the property called "lateral coherence," and in the comparison of samples of acacia and gelatin as binding agents. The only method he knew involved the use of the Bloom gelometer, and it would be interesting to know whether the type of measurements carried out by the author was likely to be of use in evaluating coherence.

MR. H. D. C. RAPSON (Dorking) commented on the very long time taken for equilibrium to be reached, and said that there were three possible explanations. The first was the slow rearrangement of the multilayer at

the interface, the second, slow diffusion of the material to the interface, and the third, the final area of contact of the drop with the substrate compared with the initial area. It would be interesting to know whether the last affected the Porter method of calculating the interfacial tension.

DR. G. BROWNLEE (London) asked whether it was true that there were only two parameters to the curve, that is, was there only one rearrangement in the forces which reached equilibrium? Was the 1 per cent. arabic acid solution achieving equilibrium so the curve was flat thereafter, or was it true as the curve suggested that it was not really reaching equilibrium. Was there a new interfacial tension being introduced by the benzene?

MR. E. SHOTTON, in reply, said that he had not examined other samples of acacia, therefore he could say little new on the question of variation. It would be observed from the curves that the fall of interfacial tension of the 10 per cent. solution was much more rapid than in the weaker solutions. In the 4:2:1 ratio a highly concentrated solution was being used which should have sufficient lowering of interfacial tension. He had tried log plots but had discarded them because they did not produce straight lines and it appeared better to give the arithmetic plots. A reciprocal of the time against interfacial tension was plotted to obtain a figure for infinite time. With regard to the term lateral coherence, its use here was confined to the lateral coherence in the surfacelayer. It was the lateral coherence of the molecules in the surfacelayer which accounted for the physical properties. Gelometers and other instruments might be of some use in the bulk phase but not in the interfaces. It seemed at first that equilibrium was not established even with the sessile drop method, but one could never be sure that some contamination might not have got into the cell. In his view rearrangement did take place but it should not take so long. Matthews had suggested that the rate of diffusion which had been published for acacia should not account for a three minutes time-lag in achieving equilibrium in his case. Mr. Shotton's own conclusion was that it must be something else and that is why he referred to it as a multilayer.