

INTERFACIAL FILMS BETWEEN BENZENE AND SOLUTIONS OF SALTS OF ARABIC ACID

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The interfacial tension between benzene and acacia, arabic acid and its salts falls rapidly for about eight hours and then more slowly. The effect on the interfacial tension is similar with the soluble salts of both monovalent and divalent metals. A tenacious film is formed in a few seconds and continues to increase in thickness with time. The evidence suggests that the film eventually formed is a substantial multilayer with many of the properties of an elastic solid. A film of this kind would account for the stability of acacia emulsions.

In 1955 Shotton¹ investigated three methods of determining the interfacial tension of benzene:arabic acid and benzene:potassium arabate systems, choosing the sessile drop method as the most suitable as it involved less change in shape and surface area of the drop during a prolonged experiment. The values obtained were lower than by the other methods, indicating the system was more likely to be in equilibrium. This method was used to study similar systems.

EXPERIMENTAL

Apparatus

The apparatus was as described by Shotton¹.

Materials

Analar benzene was distilled to remove a trace of water and purified by crystallisation. Acacia preparations were made from a selected sample purified by precipitation from solution with absolute ethanol and dried under vacuum. Arabic acid was prepared by passing an approximately 10 per cent w/v solution down a column of a sulphonic acid resin in the hydrogen form¹. From the arabic acid solution calcium and magnesium salts were prepared by the addition of the appropriate oxide until the solution was pH 7. The material was recovered by freeze drying until the moisture content was less than 15 per cent. Distilled water containing a little potassium permanganate was redistilled from an all-glass apparatus and collected in Pyrex bottles. This water and the benzene described had an interfacial tension of about 34.5 dynes/cm. This is close to the accepted value².

Method

Appropriate volumes of benzene and solution of arabic acid or its salt were prepared, a little of the other phase added and stored at 25° overnight to saturate.

An optical cell containing a slightly concave block of glass, siliconed to make it non-wettable by aqueous solutions so that a stable drop was

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formed, was two-thirds filled with purified benzene. A drop of solution was then formed beneath the benzene by expelling a measured volume from an all-glass hypodermic syringe. A lid, from which depended the glass cylinder used as a size reference, was then fitted so that drop and cylinder were co-axial. Photographs were taken as soon as possible

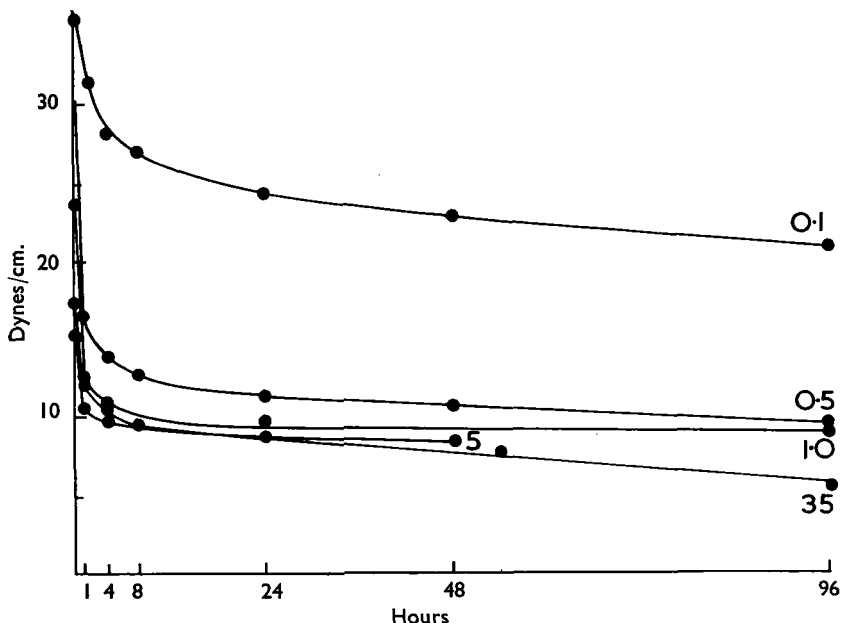


FIG. 1. Interfacial tension between benzene and solutions of natural acacia. Figures are per cent concentrations.

and at increasing intervals up to 96 hours. The image of the glass cylinder was measured and the magnification of the photograph calculated, thus making it possible to determine the actual equatorial radius of the drop and the height of the vertex above this plane. Porter's method was used to calculate the interfacial tension³.

RESULTS

The results of the determination of the interfacial tension between benzene and solutions of crude acacia, purified acacia, arabic acid, calcium arabate and magnesium arabate are summarised in Figures 1 to 4. All the materials examined showed similar behaviour. With solutions of 1 per cent w/v and over, the interfacial tension falls rapidly for a period of about 8 hours and then the rate of decrease becomes very much slower. At 96 hours equilibrium has not been attained. Over a wide range of concentration the final interfacial tension lies in a quite small range. Solutions below 1 per cent w/v show a much slower rate of fall and the final values are substantially greater. Very dilute solutions (0.01 per cent w/v) show very little effect on interfacial tension.

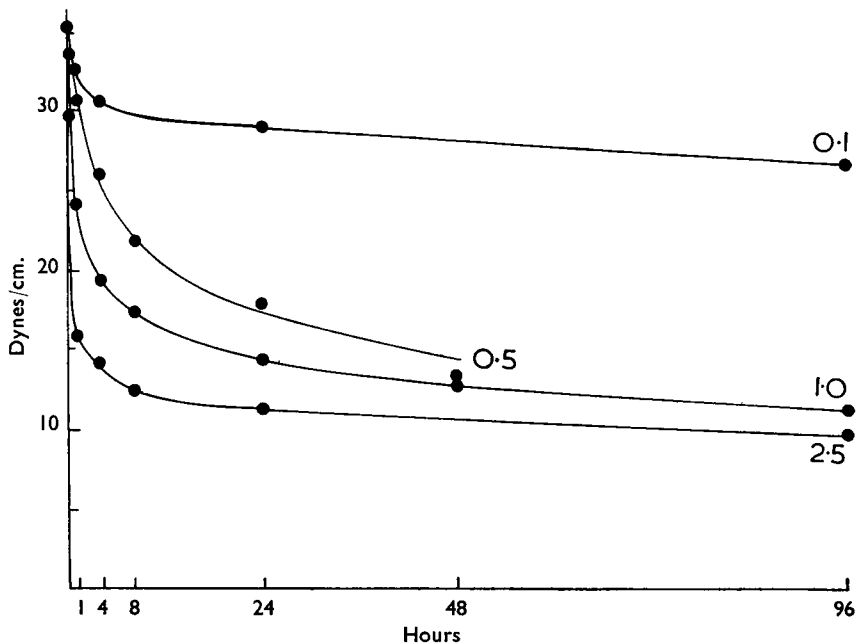


FIG. 2. Interfacial tension between benzene and solutions of purified acacia. Figures are per cent concentrations.

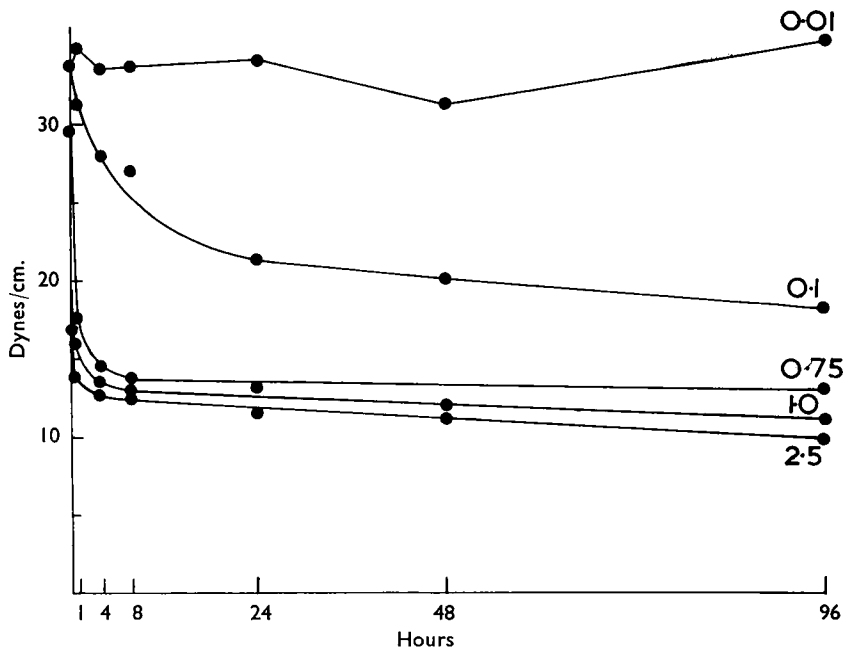


FIG. 3. Interfacial tension between benzene and solutions of calcium arabate. Figures are per cent concentrations.

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Discussion of Results of Interfacial Tension Determinations

The similarity of the interfacial tension:time curves for crude acacia, purified acacia, arabic acid and its salts shows that the orientation of the molecules at an interface is little affected by the pH of the solution or the valency of the cation. The most important feature is that there is evidence of change taking place at the interface for many hours without equilibrium being reached and it is difficult to imagine that only a molecular monolayer is being built up. This is not in accord with the findings

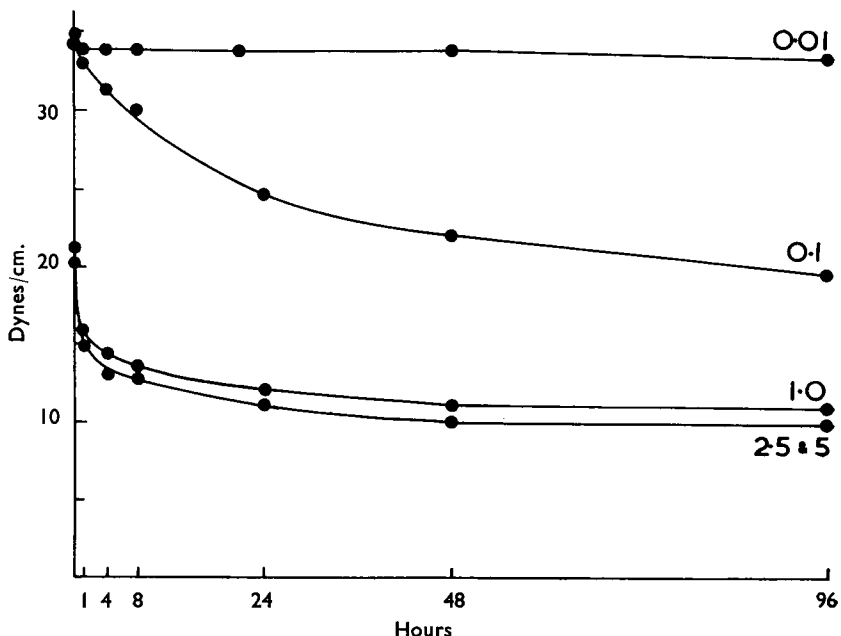


FIG. 4. Interfacial tension between benzene and solutions of magnesium arabate. Figures are per cent concentrations. The curve for 1 per cent arabic acid coincides with that for 1 per cent magnesium arabate.

of other workers⁵⁻⁷, who report equilibrium to be attained in an hour or less. It is doubtful if the complex film theory for oil in water emulsions of Schulman and Cockbain⁴ is applicable to this case as only one molecular species is present. However, since magnesium, calcium and potassium arabates are soluble and ionise in solution they will form a charged film. The film attains the necessary degree of condensation without complex formation.

Evidence and Discussion on the nature of the Interfacial Film

In 1909 Marshall⁸ reported the existence of solid films around emulsion globules but specifically stated that acacia did not produce such films. Bancroft in 1913⁹ postulated the existence of a third phase separating the oil and water phases of an emulsion. This third phase was assumed

to consist of the emulsifying agent in a hydrated form. Sellarach and Jones¹⁰ in 1931 reported the existence of interfacial films, which were visible to the naked eye, between acacia solutions and various oils. Two years later Sellarach and others¹¹ described experiments in which a wire ring was forced through these films and the force required was measured. Particular attention was drawn to the great extension of the film that took place before the film broke. We consider this implies the film may be an elastic solid.

Shotton in 1955¹ reported the appearance of wrinkles on the surface of a sessile drop 4 days old when the volume of the drop was reduced and described their slow disappearance on standing, likening it to viscous flow, but such an effect could also be ascribed to the contraction of an elastic multilayer.

Behaviour of Air Bubbles at the Interface

An attempt was made to examine the film by introducing air bubbles below the interface, in the aqueous phase. A bubble introduced into a sessile drop rose to the vertex of the drop and distorted the surface according to its size, remaining there indefinitely. Bubbles of approximately 2 mm. diameter were retained below the interface for such long periods there must be a barrier present. Such a barrier must have some of the properties of a solid since a Newtonian liquid would allow bubbles to pass by viscous flow. As this barrier was distorted by the bubble at the surface it is probable the film has elastic properties, and as it retains the bubble indefinitely it does not undergo relaxation. Elasticity also implies the existence of a tensile strength, a property usually associated with solids. This solid barrier around the drop was not visible to the naked eye by either transmitted or reflected light.

An air bubble about 2 mm. diameter introduced into a drop of 35 per cent crude acacia solution which was about 5 days old produced gross distortion of the interface. The bubble remained securely in place and did not alter materially in shape for 5 days. Subsequently the bubble burst and the upper part fell to one side remaining comparatively undamaged (Fig. 5). The fragment of the bubble must be solid in order to retain its shape. For such a structure to arise it is suggested that multilayers developed on both sides of the liquid layer enclosing the air and that the surplus solution gradually drained from between these two layers until only the solid multilayers remained, so forming a rigid structure.

Air bubbles about 2 mm. diameter passed freely through a benzene: water interface. With a 5 per cent solution of potassium arabate similar bubbles passed the interface freely for about 20 seconds after its formation. After this time the bubbles rose freely to the interface where their ascent was abruptly checked and they then moved along the curved meniscus to the wall where some remained. To account for such behaviour it is necessary to postulate the existence of a solid film at the benzene: solution interface. Solutions as dilute as 0.15 per cent potassium arabate formed these films at approximately the same speed.

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Benzene globules of about 4 mm. diameter when injected into the aqueous phase of a benzene:arabate system did not readily coalesce but remained indefinitely as an extremely coarse "emulsion". This suggests that each globule rapidly acquired a film of potassium arabate.

Behaviour of Drops of Potassium Arabate Solution in Benzene

Drops of arabate solutions falling through benzene also showed evidence of a solid interfacial film. A solution of 5 per cent potassium arabate was covered by a layer of benzene and with a wire loop samples of the solution were brought near to the surface of the benzene. The lens of solution was transparent and showed no structure but on gentle movement of the loop could be made to extend almost to a hollow hemisphere without detachment or permanent distortion which shows marked elasticity. The solution when detached from the loop immediately contracted, became opaque with a greyish surface and assumed a very irregular shape. As the drop fell the shape changed but did not approximate to a sphere during its descent. The impression is that an elastic membrane held stretched over the lens of the solution contracted immediately the restraint of the frame was removed until the interfacial layer became solid but not rigid. Inside, the liquid solution attempted to assume a spherical shape but was prevented from doing so because it was enclosed in a solid sac whose surface area was much greater than that of a spherical

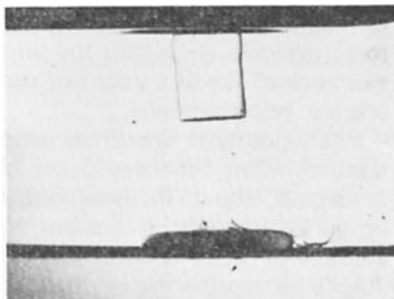


FIG. 5. Debris of rigid film formed around an air bubble at the benzene/acacia interface.

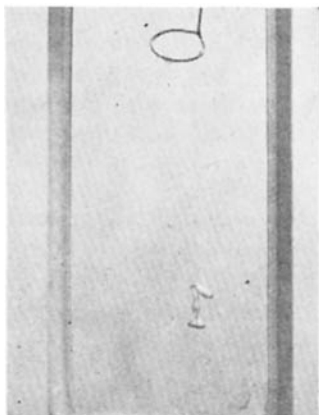


FIG. 6. Drop of potassium arabate solution, 5 per cent, falling through benzene.

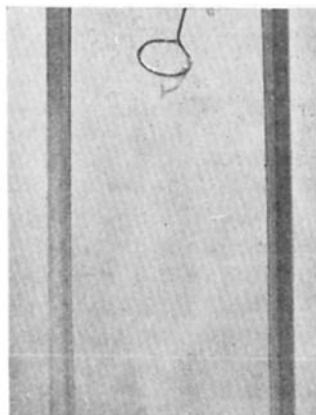


FIG. 7. Solid film of potassium arabate.

drop derived from the lens of solution held on the loop (Fig. 6). Occasionally after the detachment of the lens of solution a portion of the interfacial film was left adhering to the wire. Such a structure must be a solid (Fig. 7).

When the benzene was replaced by light liquid paraffin which is much more viscous, it was possible to manipulate the drop into any desired shape which then remained almost unchanged whilst falling through the oil. Using light liquid paraffin and water it was possible to produce spheroidal drops only.

Evidence of the existence of a tenacious or solid interfacial film may be found on interfaces only minutes old at a stage when sessile drop measurements show that the interfacial tension is still quite high. The existence of the film does not therefore depend on a very low interfacial tension being attained.

Pharmaceutical emulsions may be made with acacia in a very few minutes when benzene:35 per cent acacia systems have an interfacial tension of about 20 dynes/cm. so emulsion formation cannot depend on a low interfacial tension between the phases. The considerable amount of work needed to produce a primary emulsion confirms the interfacial tension to be high yet in the time taken to make such an emulsion a tenacious film will form around the oil globule. On standing this film will increase in thickness and behave as an elastic solid thus accounting for the great stability of acacia emulsions.

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After Mr. Wibberley presented the paper there was a DISCUSSION.