

# ON THE INTERFACIAL TENSION BETWEEN GELATIN AND SODIUM ALGINATE SOLUTIONS AND BENZENE

## PART I. EFFECT OF TIME AND CONCENTRATION ON INTERFACIAL TENSION

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A cell is described for determining both surface and interfacial tensions by the sessile drop method. The interfacial tension between gelatin solution or sodium alginate solution and benzene has been determined. Both substances lowered the interfacial tension, the gelatin attained equilibrium quickly. Both tension-concentration curves were similar in shape. It is suggested that a condensed multilayer having the physical properties required to stabilise emulsions, is built up immediately below the surface.

SHOTTON<sup>1</sup> showed that acacia solutions are slow to attain equilibrium at the interface with benzene and that a static method for the determination of interfacial tension is necessary.

The slow change in surface tension or the phenomenon of surface ageing could be due to either a slow diffusion process between the bulk and the interface which continues until the equilibrium is attained<sup>2</sup>, or a re-orientation of solute molecules at the interface. A linear molecule may re-orientate by the unfolding of the chain<sup>3</sup>.

With protein solutions adsorption takes place at the surface and they may become denatured to give an insoluble film. Johlin<sup>4</sup> considered it would appear irrational to measure the surface tensions of such solutions.

## EXPERIMENTAL AND RESULTS

### *Materials*

*Water.* Distilled water containing a very small amount of potassium permanganate was redistilled in an all glass still.

*Benzene.* Analar benzene was recrystallised.

*Gelatin.* One sample of a pharmaceutical grade gelatin (B.P.C.) supplied by Young's Gelatin Co. Ltd. was used throughout this work.

*Purification.* A de-ashed gelatin was prepared by using a method described by Holmes<sup>5</sup> and Janus, Kenchington and Ward<sup>6</sup> using a mixed bed ion exchange resin. The pH of a 1 per cent solution of the de-ionised gelatin was 6.4 at room temperature (20° approx.). *Density of solution.* The density of the gelatin solutions was proportional to the concentration. To calculate the interfacial tension of gelatin solutions the density was obtained from the graph.

*Sodium alginate.* A food grade sodium alginate supplied by Alginate Industries Ltd., under the trade name "Manucol SS/LB" of low viscosity

was used. It contained 0.4 per cent of calcium as impurity. *Purification.* The method of Black and Woodward<sup>7</sup> was used. Alginic acid was precipitated from a solution of sodium alginate with sulphuric acid and washed. This acid was then dissolved in sufficient sodium hydroxide solution to give a pH of approximately 6.7 which was the neutral point shown on the titration curve. The process was repeated and finally sodium alginate precipitated with ethanol and dried under vacuum. The equivalent weights of two batches of the purified sample were determined by electrometric titration and found to be 184 and 175.

#### *Measurement of Interfacial Tension*

The apparatus was similar to that used by Shotton<sup>1</sup>. Interfacial tensions were calculated by Porters<sup>8</sup> method.

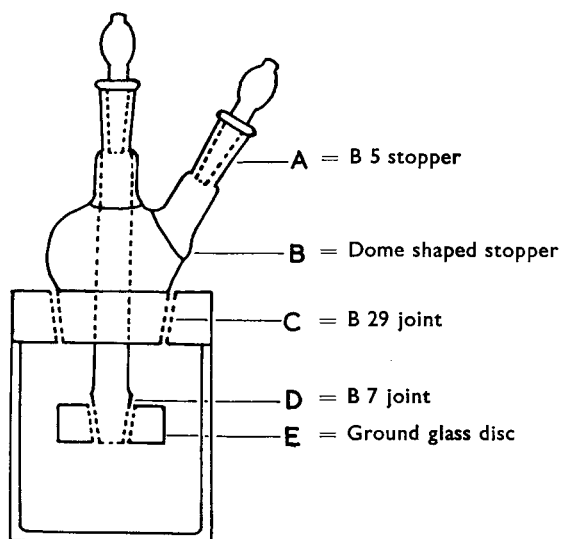


FIG. 1. The optical cell

The cell, Figure 1, was a cube of 4 cm. edge made from optically flat glass to which was cemented a glass block bored to receive a B.29 cone joint. The dome shaped stopper which fitted into the glass block had two openings, and to the central one was fixed a glass tube on which was fitted an accurately ground glass disc, 27 mm. in diameter, cut from a mirror blank with a radius of curvature of 1 metre.

The diameter of the disc was accurately measured and this was used to determine the magnification of the photographs.

Flasks containing water and benzene were mutually saturated and left at 35° in the cabinet overnight with the glass apparatus to attain temperature equilibrium. The sessile drop was formed by withdrawing a known volume of benzene from the flask and transferring it slowly through the opening in the dome of the cell, the cell having been previously assembled and filled with water. A photograph was taken after approximately 3

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minutes and thereafter at intervals of 1, 2, 4, 8, 24, 48, and 72 hours. The diameter at the equator and the height of the vertex above the equator was measured.

The change of interfacial tension of benzene:water with time as determined by each of the two methods of drop formation is given in Table I. Harkins and Cheng<sup>9</sup> obtained the value of 34.09 dynes/cm.

TABLE I  
THE CHANGE IN INTERFACIAL TENSION WITH TIME OF BENZENE:WATER AT 35° C.  
(DYNES/CM.)

Method	Time after formation							
	3 min.	1 hr.	2 hr.	4 hr.	8 hr.	24 hr.	48 hr.	72 hr.
Drop of benzene in water	34.2	33.9	33.6	33.6	33.60	33.6	33.6	33.6
Drop of water in benzene	34.2	34.0	33.8	33.7	33.7	33.6	33.6	33.6

### *Interfacial Tension of Solutions*

*Interfacial tension of gelatin solution against benzene.* The gelatin solutions were the same as those prepared by the method of Davis, Salisbury and Harvey<sup>10</sup>. Two solutions of different concentrations were used for each experiment and saturated with benzene, care being taken to prevent emulsification. A drop of benzene was formed in the solution and photographed at the intervals indicated above. The results are summarised in Figure 2.

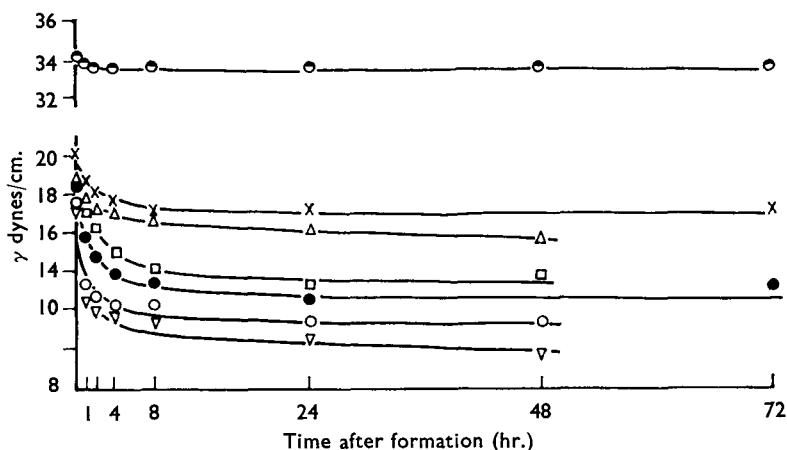


FIG. 2. The effect of time on the interfacial tension between gelatin solutions and benzene (temp. = 35°C).

Per cent, w/v.  
 ● water      × 0.05      △ 0.17      □ 0.35      ● 0.755  
 ○ 0.988      ▽ 3.825

*Effect of pH on interfacial tension.* A 1 per cent gelatin solution was prepared containing 0.3 per cent analar sodium chloride to prevent

flocculation. The interfacial tension of this solution against benzene was very little different from that of a solution of gelatin alone. The amount of sodium hydroxide or hydrochloric acid to give the required

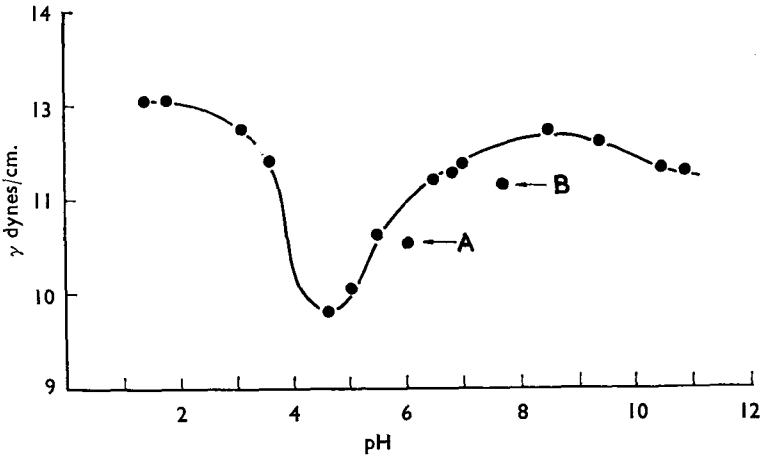


FIG. 3. The effect of pH on the interfacial tension between 1 per cent gelatin solutions and benzene (temp. = 35°C). Values taken after 24 hours. (A and B see text, p. 114).

pH was obtained from the titration curve of a 1 per cent gelatin solution. The effect of pH on the interfacial tension of 1 per cent gelatin solutions measured after 24 hours, is shown in Figure 3.

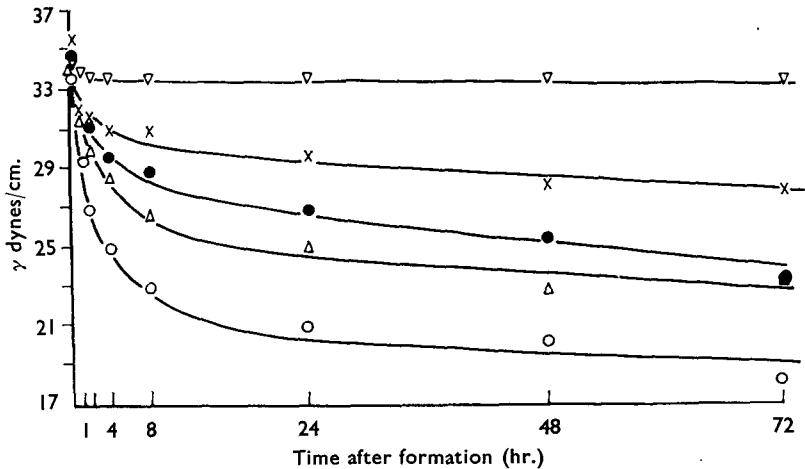


FIG. 4. The effect of time on interfacial tension between sodium alginate solutions and benzene (temp. = 35°C). Per cent, w/v.

▽ water      × 0.1 drop = solution      △ 0.1 drop = benzene  
 ● 0.25 drop = solution      ○ 0.25 drop = benzene

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*Interfacial tension of sodium alginate solutions.* The required amount of purified sodium alginate was accurately weighed allowing for the moisture content of the purified material. Solutions were prepared by dissolving the materials in distilled water, heated to 75°. The interfacial tension of each solution was determined using both methods of forming the drop, i.e., a drop of benzene in solution or a drop of solution in benzene. The two systems were photographed side by side and the results summarised in Figure 4.

### DISCUSSION

The photographs of the drop were taken without altering the focus or the distance of the cell, but the value obtained for the magnification of the disc varied within  $\pm 1$  per cent. Hence an average for the magnification factor was taken to calculate the actual dimensions of the drop. According to Porter<sup>10</sup> the correction factor ( $\Delta$ ) is known with the greatest accuracy in the region of  $h^2/r^2 = 0.25$ . The volume of the drop was adjusted so that  $h^2/r^2$  reached a value of 0.20–0.30 after 24 to 72 hours. Taking into account all sources of variation, it is considered that the results obtained using this method have an experimental error of about 3 per cent initially, reducing to about 2 per cent for the later readings.

#### *Change of Interfacial Tension with Time*

The greatest rate of fall in the interfacial tension of gelatin and sodium alginate solutions against benzene took place in the first hour and was then less rapid up to 8 hours, after which period the change was very slow.

On forming a drop of benzene in a solution a fresh surface is created and diffusion into the interface takes place causing a rapid drop in interfacial tension. The interface becomes more concentrated with time and the subsequent slow change in interfacial tension may be due to a re-orientation of the molecules in the surface layer.

According to Cheesman and Davis<sup>3</sup> the protein molecule is normally rigid due to the forces of cohesion and the van der Waals force of attraction between the non-polar groups. At an oil-water interface the cohesive energy is reduced by the penetration of the oil between the cohesive side chain, and hence the molecule tends to unfold.

In the case of sodium alginate the molecule is probably held rigid due to the repulsion between the ionised carboxyl groups and may undergo re-orientation on reaching the interface by directing the polar groups towards the water.

Reynolds<sup>12</sup> observed that the interfacial tension of 0.5 per cent gelatin solution at 18° fell from 21.0 dyne/cm. after fifteen minutes to 19.9 dyne/cm. after 24 hours, whereas a 0.35 per cent solution at 35° fell from 18.5 dyne/cm. at 3 minutes to 13.9 dyne/cm. in 24 hours. Johlin<sup>4,13,14</sup> determined the surface tension of gelatin solution using different methods and he emphasised the need for a static method.

Matthews<sup>2</sup> attributed the flattening of the curves to either slow diffusion to the interface or the formation of a condensed monolayer, however the times he allowed to attain equilibrium were too short. Shotton using

acacia suggested that phenomena was due to "multilayers" being built up at the interface. Supporting evidence has been published recently<sup>15</sup>.

#### *Effect of Concentration on Interfacial Tension*

The interfacial tension was lowered by an increase in concentration of the aqueous solution. The solutions of gelatin and sodium alginate when kept in contact with benzene became opalescent and considerable difficulty was experienced in photographing the drops and measuring them accurately. Hence the system of forming the drop was reversed, the drop being formed with the opalescent solution in benzene. The results obtained for this system were consistently and appreciably higher than those obtained by using a drop of benzene in the solution, the discussion on this apparent anomaly is given in Part II.

It is difficult to compare the above results with those of previous work as different methods and samples have been used. Holmes and Child<sup>11</sup> determined the interfacial tension by Donnan pipette and found an initial decrease in interfacial tension of gelatin solutions from 0 to 0.3 per cent, and remained constant on further increase in concentration. This could have been due to the non-attainment of surface equilibrium.

Matthews<sup>2</sup> stated that the type of  $\Delta\gamma/\text{concentration}$  curve depended upon the nature of the interfacial film which in turn depended upon the shape of the solute molecule that constitutes the film. He suggested that pectin would form a film of the intermediate type showing a tendency to form a condensed film but the lateral forces of attraction between the molecules would not be sufficient to bring this about. Alginic acid bears a structural resemblance to pectin. Pectins are regarded as poly-galacturonic acid in the form of the methyl esters and alginic acids are also poly-galacturonic derivatives. It is to be expected that these two substances will behave similarly at the interface.

#### *The Effect of pH on Interfacial Tension of Benzene:Gelatin Solutions*

The interfacial tension had the lowest value at pH 4.55, indicating that the isoelectric point of the gelatin used was in this region. At the isoelectric point the molecule is neutral and may readily form aggregates. Under these conditions adsorption at the interface is most probable and surface interfacial tension is at a minimum.

On either side of the isoelectric point the value for interfacial tension increased steadily on the addition of acid or alkali. On the acid side a maximum was reached at pH 2.5 and did not increase on further addition of acid, whereas with alkali it reached a maximum at pH 8.6 and decreased on further addition of alkali. This was probably due to the formation of sodium gelatinate which dissociated to form the electro-negative protein ions which were less readily adsorbed at the interface than undissociated molecules. The lowering of the interfacial tension above pH 8.6 could be due to suppression of the dissociation of sodium gelatinate by the presence of excess of sodium ion or, possibly, to the hydrolysis of gelatin. The results given at A and B in Figure 3 were not repeatable and it is possible that some contamination had occurred.

*The Stabilisation of Emulsions with Hydrophilic Colloids*

Emulsions were prepared using gelatin, sodium alginate and acacia solutions and 50 per cent of benzene. It was found that gelatin emulsions could be made with 0.3 and 0.4 per cent solutions by hand shaking, whereas using acacia or sodium alginate solutions, emulsions could be prepared only with a 10 per cent solution and a mechanical stirrer.

Sodium alginate emulsions were unstable, when compared with those made with acacia, the emulsification being difficult to achieve even when using a high concentration of alginate. The difference in the ease of emulsification can be probably attributed to the differences in the surface activity and the nature of interfacial film. It is suggested that emulsions formed by hydrophilic colloids are stabilised by an interfacial film having certain physical properties. Condensed multilayers which are charged by ionisation have the required properties to favour the formation of o/w emulsions.

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