A SIMPLE METHOD FOR THE STUDY OF VARIATION OF BOUNDARY TENSION WITH TIME

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Introduction

Several methods have been described in literature to measure the variation of boundary tension with time. Adam[1] has employed the maximum bubble pressure method to study the variation of surface tension with time, for a period of ten minutes, but concludes that the method is not suitable. Venkatachala[2] and Krishnappa[3] arrive at the same conclusion after employing this method to study the ageing of surfaces of aqueous solutions of wetting agents. The sessile bubble method has been used by Adam and Shute[4] for studying the variation of surface tension with time, of certain paraffin chain salts. The method seems to be free from contact angle effects but special precautions have to be taken against accidental contamination. Tartar, et al.[4a] have made a comparative study of the capillary rise and the sessile bubble methods for the determination of the variation of surface tension. They prefer the latter method and claim that it gives reproducible results.

The trough method suggested by Doss,[6] and McBain and Wilson,[7] is quite suitable for a study of the variation of surface tension with time but this method is cumbersome for the study of the variation of interfacial tension with time. The pendant drop method described by Andreas,[5] Hauser and Tucker, appears to be satisfactory for the latter purpose, but the apparatus is very complicated.

In the present method, the advantages of the pendant drop method are combined with those of the drop weight method. The method consists in forming a small drop of the solution at the end of a vertical capillary placed inside a thermostat. The drop is allowed to age, and the time required for the drop to fall, is noted. The boundary tension is calculated by applying Harkin's[8] corrections for the volume of the ideal drop.

Experimental

Reagents empolyed

(i) *Benzene.*—The benzene (Kahlbaum's pure grade) was distilled in an all-glass apparatus and the middle fraction was used.

* Part of the Thesis submitted by R. S. Subrahmanya for the M.Sc. Degree of the Mysore University.

(ii) *Congorubin.*—Congorubin was purified by the sodium acetate method of Robinson.[11] It was washed with alcohol and dried in vacuum.

(iii) *Potassium iodide, acetic acid and sodium chloride.*—A. R. quality reagents were used.

Apparatus

The stalagmometer used for the measurement of boundary tension consisted of a calibrated micro burette which had a suitable capillary tube fused on to its delivery end. The tip of the capillary was carefully ground, using fine corborundum powder,[9, 10] and finally wet talc. As pointed out by Andreas, *et al.*,[5] microscopic perfection was not necessary since the liquid tended to bridge slight irregularities. The capillary tube passed through a rubber stopper fixed to a small bottle containing benzene, so that the tip was immersed about 0·5″ below the surface of benzene. The stopper carried a sensitive thermometer and a small capillary tube, open to the atmosphere. The entire apparatus was placed in an air-thermostat at 30° C. ($\pm$ 0·05°). The radius of the capillary was 0·3402 cm.

Determination of Interfacial Tension between Water and Benzene

The stalagmometer was cleaned thoroughly with warm chromic acid and finally washed with conductivity water. It was then filled with conductivity water saturated with benzene. No grease was employed to lubricate the stopcock. The bottle was filled with benzene saturated with water, and kept in the thermostat for five to six hours. The stopcock was gently opened and a small drop of water was allowed to form in the benzene. The drop was sucked back so that the liquid meniscus was at a fixed mark on the capillary tube. The water level in the micro burette was then noted by means of a travelling microscope. The stopcock was next opened and a fresh drop of water in benzene, was allowed to form slowly. The time of formation of each drop was about five minutes. After the drop fell off from the tip, the water was once again sucked back to the mark, and the stopcock closed. The microburette was then read and the volume of the drop determined. Within the limits of experimental error, it was noticed that the volume of the drop of water was independent of the time of formation of the drop. Evaporation of water from the microburette was minimised by attaching to its open end a fine capillary. The reproducibility in the formation of drops can be gauged from the following values obtained in an experiment:—0·3903 c.c., 0·3909 c.c., 0·3903 c.c., 0·3887 c.c.—mean value 0·3901 c.c. The interfacial tension γ was calculated from the following formula:—

$$\gamma = \frac{V (D_2 - D_1) g}{2R\phi},$$

where, R = radius of tip of capillary,

$\quad\quad V$ = volume of drop,

$\quad\quad D_2$ = density of water,

$\quad\quad D_1$ = density of benzene,

$\quad\quad g$ = acceleration due to gravity.

$R/V^{1/3}$ being known the value of ϕ was ascertained from data furnished by the Harkins and Brown.[8] Using the above formula, the interfacial tension was calculated. The mean value for the benzene-water interface was 34·29 dynes per cm. which agrees with the standzard value of 34·34 at 30° within the limits of experimental error (about 0·3%).

Determination of the Variation with Time of the Interfacial Tension between Benzene and Aqueous Solutions of Rubin

As pointed out already, the chief difficulty in the determination of the variation of interfacial tension with time, was the maintenance of the interface in an undisturbed condition during the entire period, over which the measurement extended. In the present investigation, this difficulty was overcome by employing the principle of the pendant drop method. The following procedure was adopted :—

After cleaning, the stalagmometer was filled with the rubin solution saturated with benzene, while the bottle was filled with benzene saturated with the rubin solution. After the attainment of temperature equilibrium, a drop of known volume was produced in four to five seconds at the end of the capillary tube. The drop was allowed to hang on at the tip of the capillary when it was noticed that the semi-spherical shape of the drop gradually changed to that of an elongated sphere until finally the drop fell into the benzene. The interval between the formation and the falling of the drop was noted. The aqueous solution was sucked back to the mark and the final volume of the drop determined. The interfacial tension at the time of falling of the drop was determined by Harkin's method, as already described. It was noticed that for a given concentration of rubin, the time of falling of a drop was a function of the volume of the drop. The intervals for the falling of drops having various volumes were noted and the corresponding values of interfacial tensions calculated. Fig. 1 represents the variation of interfacial tension with time for different concentrations of rubin solution. The rubin solution (0·005%) was then mixed with a few drops
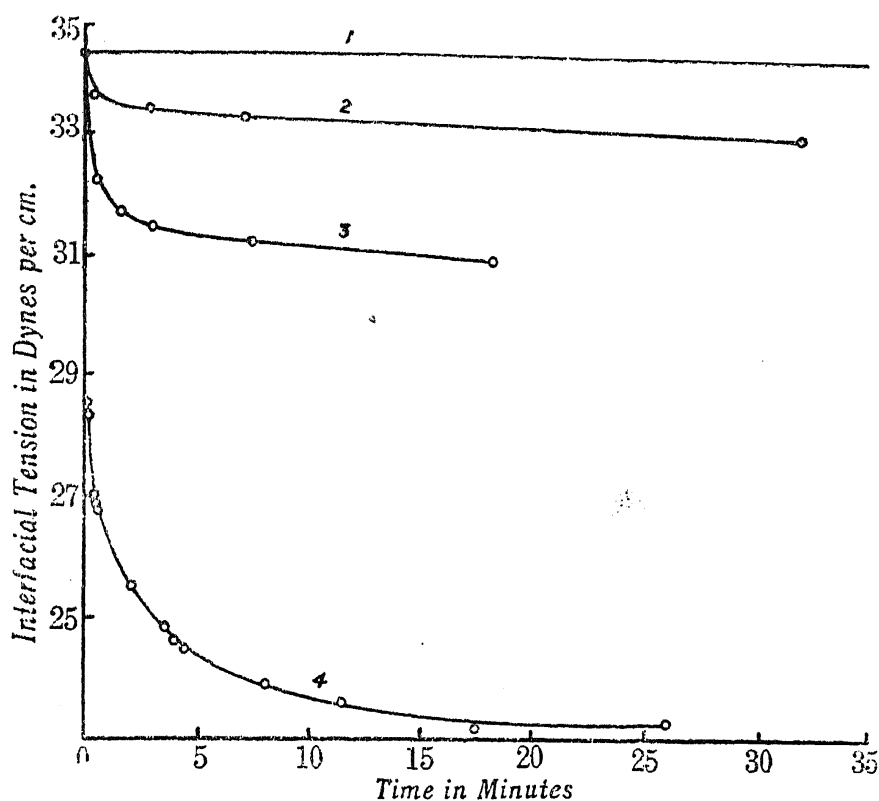
FIG. 1. Effect of concentration on the variation of interfacial tension, with time, of Congorubin solution at benzene interface.

Concentration of congorubin pertaining to curve $1 = 0 \cdot 00005\%$, curve $2 = 0 \cdot 0005\%$, curve $3 = 0 \cdot 005\%$, and curve $4 = 0 \cdot 05\%$.

of dilute acetic acid to lower the pH to $3 \cdot 8$ and fresh measurements made with the solution. From the results obtained (Fig. 2) it is clear that a lowering of pH greatly diminishes the interfacial tension.

Effect of Salts on the Variation of Interfacial Tension with Time

Evans[13] and Guest[14] have shown that salts of the type of sodium or potassium chloride increase the interfacial tension between aqueous solutions and an inert organic liquid, while potassium iodide decreases the tension. It was of interest to examine if sodium chloride and potassium iodide have the same effect on the interfacial tension between congorubin solution and benzene and how the interfacial tension varies with time. $0 \cdot 005\%$ rubin solution was employed. The salt concentration was $0 \cdot 1$ molar. The results obtained are indicated in Fig. 3. It will be noticed that both the salts considerably lower the interfacial tension, the effect being greater with the iodide. With time, the interfacial tension decreases in both the cases.

Measurement of Surface Tension

It was found necessary to prevent evaporation of water from the pendant drop, by having in the bottle some of the rubin solution, 1 to 2 mm.
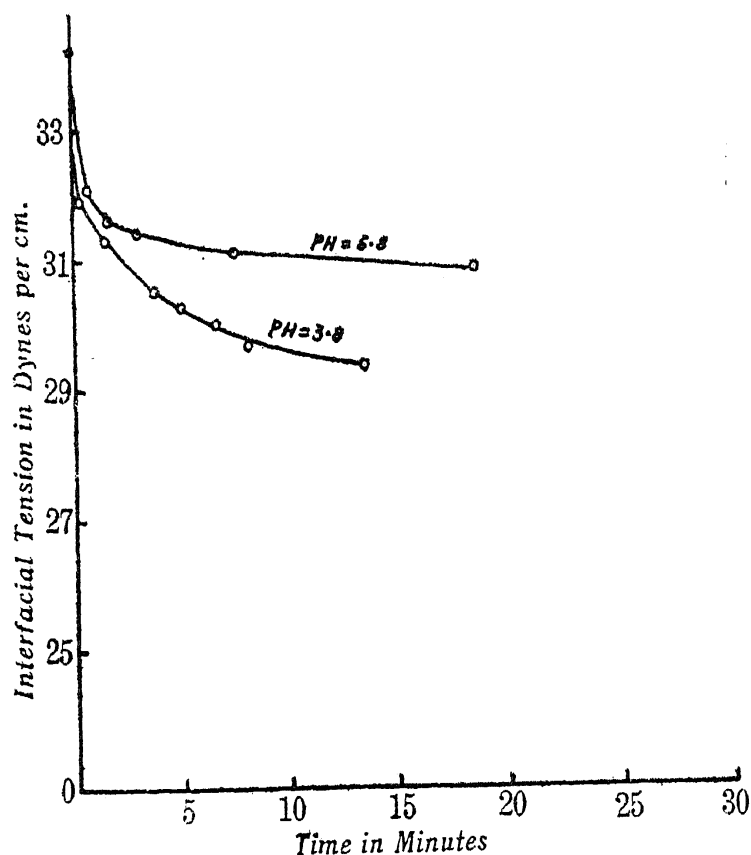
FIG. 2. Effect of pH on the variation of interfacial tension, with time, of Congorubin solution (0·005%) at benzene interface.

below the drop. The variation of surface tension with time for the rubin solution was also determined by the trough method. The results obtained by the two methods are given in Fig. 4. The agreement between the values obtained by the two methods is very satisfactory.

DISCUSSION

Variation of Surface Tension with Time

Investigations by the present method, on the variation of surface tension with time, using 0·2% solution of congorubin in water, confirm the results obtained by the trough method. The present method can be employed for a study of surface tension at different temperatures more easily than the trough method. Another advantage of the method is that only small quantities of solutions are required. The slow variation of surface tension with time shows that the accumulation of the rubin molecules at the surface of the solution is of the activated type and is a slow process (cf., Doss,[15] McBain, et al.[16]).

Variation of Interfacial Tension with Time of Aqueous Rubin Solutions at Benzene Interface

The effect of concentration of rubin on the variation of interfacial tension with time is quite marked. At very low concentrations (0·00005%) of
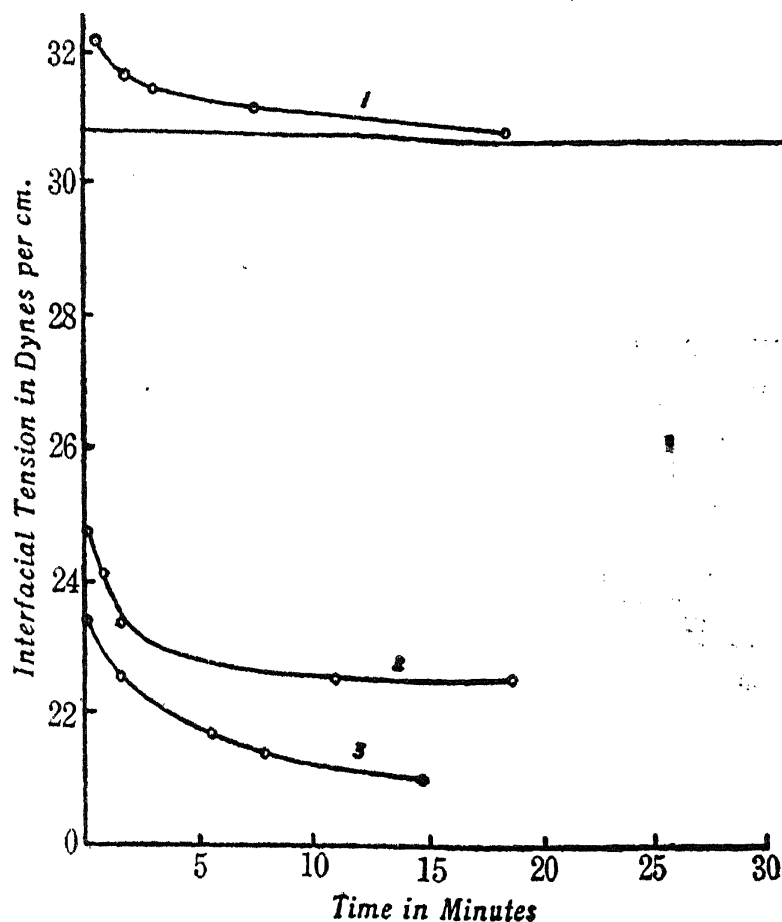
FIG. 3. Effect of Salts on the variation of interfocial tension, with time, of Congorubin solution at benzene interface.

Composition of aqueous solution :—

Curve 1   0·005% dye

,,   2   ,,   + 0·1 N sodium chloride.

,,   3   ,,   + 0·1 N potassium iodide.

,,   4   0·1 N potassium iodide.

(*Note.*—As with potassium iodide solution, there was no change in interfacial tension with time, in the case of 0·1 N sodium chloride).
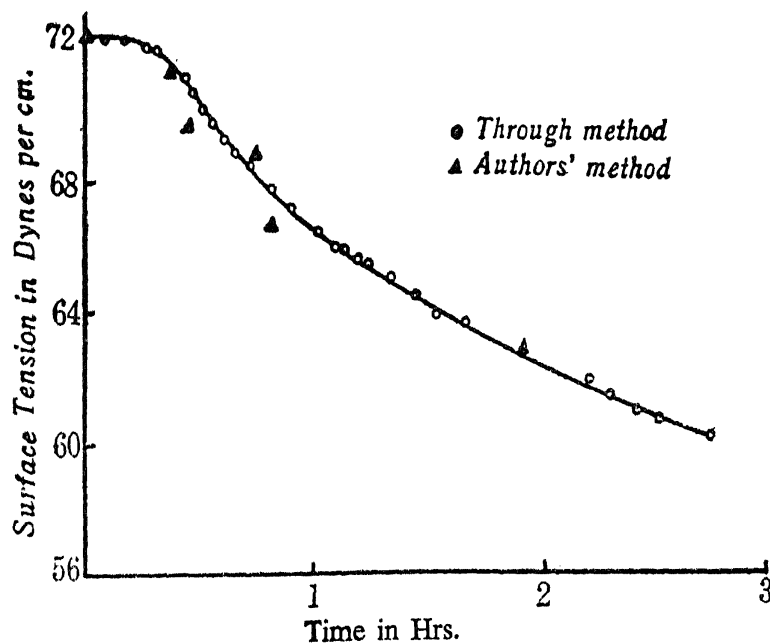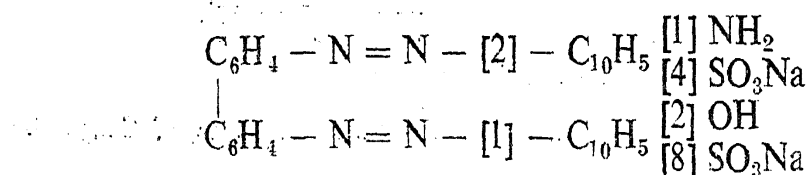

FIG. 4. Variation of surface tension with time of 0·2% Congorubin solution,

rubin, the interfacial tension will be practically the same as that between water and benzene. There is scarcely any change with time. But at concentrations of the order of 0·0005% and above there is not only a fall in the interfacial tension but also a variation in the tension with time. This change is rapid in the beginning but gradually falls off. At the air-solution interface on the other hand, there is no variation in surface tension during the first 20 minutes (Fig. 4). The tension then begins to diminish and we finally get a practically constant value which is characteristic of a condensed film. Lower concentrations (< 0·2%) of rubin cannot be employed for the study of surface tension owing to very slow accumulation. In studying interfacial tension, however, solutions of far lower concentrations (0·05%) can be used. A fall in interfacial tension with time is noticed in such solutions. The film in this case is of the gaseous type as can be gathered from the nature of the curve, while the corresponding film for the air-solution interface is of the condensed type. The difference can be explained thus:—

Congorubin has four hydrophilic groups as shown by its constitution.—

$$C_6H_4 - N = N - [2] - C_{10}H_5 \begin{array}{l} [1]\ NH_2 \\ [4]\ SO_3Na \end{array}$$
$$C_6H_4 - N = N - [1] - C_{10}H_5 \begin{array}{l} [2]\ OH \\ [8]\ SO_3Na \end{array}$$

As shown by Doss[12] for benzopurpurin, the slow surface accumulation of rubin may be due to the extra activation energy required to eject two of the hydrophilic groups into the air. Thus the activated molecule will have the hydrophobic group and also the hydrophilic group pointing out towards air. This explains the formation of the condensed film at the air-water interface. But when air is replaced by benzene there will perhaps be no tendency for the two hydrophilic groups to come out. On the other hand the hydrophilic groups will all be pointing out towards water while the hydrophobic portion will get oriented towards benzene, as in the case of sodium oleate solutions.[5] Hence the only force that retards the rate of accumulation at the benzene interface is the electrical double layer formed at the interface due to accumulation of rubin molecules. Owing to the potential of the electrical double layer, the concentration of the capillary active ion, in the region just beneath the surface layer, will be very much suppressed and will be equal to[15]

$$c \times e^{-\frac{\epsilon \psi_0 x}{kT}}$$

where c = bulk concentration of the solution,

e — charge on the electron,

ψ_0 — potential due to the surface fully covered by the solute molecules,

x — fraction of the total surface covered,

k — Boltzmann constant,

T — absolute temperature.

Thus, accumulation at the surface occurs from a region of low concentration. Hence the rate of accumulation will be proportional to

$$ e^{\frac{e\psi_0 x}{kT}}. $$

Examination of this equation shows that the rate of accumulation should be very high at the start (*i.e.*, for small values of x). As the surface gets enriched with respect to the solute molecules (*i.e.*, x increasing) the rate of accumulation goes on diminishing exponentially. Thus the rate of fall in interfacial tension will be high to begin with, but rapidly diminishes with time.

Andreas[5] and others have determined the variation of surface tension with time, using sodium oleate solutions. They have also determined the variation of the interfacial tension between these solutions and mineral oil. Unlike congorubin, sodium oleate gives the gaseous type of films both at the air-water interface and at the water-mineral oil interface. Evidently, the accumulation of the sodium oleate is mainly governed by the electrical double layer at the two interfaces. Adam and Shute[4] have come to similar conclusions by working with cetyl pyridinium bromide and sodium dodecyl sulphate solutions.

The rapid fall of interfacial tension (*i.e.*, the high rate of accumulation of the rubin at the interface) in presence of electrolytes needs some explanation. Adam and Shute[4] have noticed similar effects with cetyl pyridinium bromide at the air-water interface. They state that the rapid accumulation is due to micelle formation. But the actual mechanism proposed is that the high negative charge on the micelles drives very rapidly the molecular species of the pyridinium bromide, to the interface. In the case of the congorubin solution-benzene interface the effect can be ascribed to the diminution in the value of ψ_0 (Zeta-potential) with an increase in the concentration of the electrolyte, in the rubin solutions. The rate of accumulation which is proportional to $e^{\frac{e\psi_0 x}{kT}}$ gets enhanced with the decrease in the value of ψ_0. Hence the interfacial tension falls rapidly when the concentration of the electrolyte is increased. The effect of pH on the variation of interfacial tension with time can also be explained on the basis of the diminution of

the zeta potential. An increase in hydrogen-ion concentration reduces the zeta potential and thus increases the rate of accumulation (Fig. 2).

SUMMARY

1. A new method for the determination of variation of interfacial and surface tensions with time, has been described. In this method, the advantages of the pendant drop method are combined with those of the drop weight method, thus simplifying the experimental technique.

2. Variation of interfacial and surface tensions with time has been investigated for congorubin solutions. The rubin solution yields at the air-liquid interface a solid film and at the solution-benzene interface a gaseous type of film.

3. The effect of concentration of rubin on the variation of interfacial tension with time has been studied. At concentrations of rubin higher than $0 \cdot 0005\%$ the fall in the interfacial tension will be large.

4. Salts like sodium chloride and potassium iodide lower considerably the interfacial tension between rubin solution and benzene. Lowering of pH also brings about a fall in interfacial tension.

5. The slow variation of interfacial tension has been accounted for, on the basis of changes in zeta-potential.

REFERENCES

1. Adam, N. K.   .. *The Physics and Chemistry of Surfaces,* 2nd Edn. General.
2. Venkatachala   .. *M.Sc., Thesis,* 1941, *Mys. Uni..* p. 35.
3. Krishnappa   .. *Ibid.,* 1943, *Mys. Uni.,* p. 38.
4. Adam and Shute   .. *Trans. Far. Soc.,* 1938, p. 758.
4 *a.* Tartar, Sivertz and Reitmeier   *J. Am. Chem. Soc.,* 1940, **62,** 2381.
5. Andreas, Hauser and Tucker..   *J. Phy. Chem.,* 1938, **42,** 1001.
6. Doss   .. *Proc. Ind. Acad. Sci.,* 1936, **4,** 97.
7. McBain and Wilson   .. *J. Amer. Chem. Soc.,* 1936, **58,** 379.
8. Harkins and Brown   .. *Ibid.,* 1919, 499.
9. Eversole and Dallas S. Dedrick   *J. Phy. Chem.,* 1933, 1205.
10. Dallas and Maurice H. Hanson   *Ibid.,* 1933, 1215.
11. Doss   .. *Kolloid Z.,* 1938, **84,** 138.
12. ————————   .. *Ibid.,* 1939. **87,** 272.
13. Evans   .. *Trans. Far. Soc.,* 1937, **33,** 794.
14. Guest   .. *Proc. Roy. Soc.,* 1939, **170 A,** 501,
15. Doss   .. *Kolloid Z.,* 1939, **86,** 205.
16. McBain, Ford, Mills   .. *J. Am. Chem. Soc.,* 1940, **62,** 1319.