AGEING OF SURFACES OF SOLUTIONS—I.

The Study of Variation of Surface Tension of Solutions with Time by the Ring Method.*

By K. S. Gururaja Doss
and
Basrur Sanjiva Rao.
(From the Department of Chemistry, Central College, Bangalore.)

Received June 2, 1936.

The effect of the age of a surface on its surface tension was first noticed by Dupré.[1] It has since been studied by a number of workers.[2,3,4,5,6,7,8,9,22,23,24] The suitability of the ring method for such studies has been investigated in the present paper.

Experimental.

For studying the variation of surface tension with time the ring method is usually taken to be one of the best suited. *Cf.* Freundlich.[10] The technique of the ring method has been developed in full by Harkins and his co-workers.[11,12] The maximum pull exerted by a liquid on the ring when it is slowly withdrawn from the liquid surface, is measured by means of a chainomatic balance by Harkins and a torsion balance by du Noüy. Both these methods are too cumbersome to be worked in an isolated system. So, it was thought advantageous to use a quartz spring for the purpose.

An automatic device has been developed for the construction of helical springs of quartz. The quartz fibres were drawn in the usual way by pulling apart a quartz rod heated in the middle to the required temperature by means of an oxy-gas flame. When long and fine fibres were required, the heated rod was pulled out quickly by means of a falling weight. *Cf.* [13] By this method it was possible to get uniform fibres ten to twelve feet in length.

A silica tube about 1·2 cm. in diameter was given a screw motion by attaching it to the screw of a travelling microscope, which was moved by an electric motor geared down to give one revolution in three minutes. An oxy-air-gas flame played vertically down against the topmost portion of the tube. The fibre was fed horizontally through a capillary, the necessary

* Part of thesis on "Studies in Adsorption" submitted by K. S. G. Doss, in partial fulfilment of the requirements for the Degree of Master of Science of the Mysore University.

tension being given by a hanging weight. By this method one could readily get cornerless springs. In the case of the finest fibres the speed could be increased up to one turn per minute without any danger of overlapping.

The springs so prepared were calibrated by adding known weights and noting the extension through a vernier microscope reading to 0·01 mm. Within the range studied, Hooke's law was found to hold perfectly.

Four du Noüy rings were available; the best of them was selected. The circular stirrup was bent down to make it more or less elliptical. The stirrup was manipulated in such a way that the plane of the freely suspended ring remained perfectly horizontal; the presence of any tilt was detected by suspending the ring over a mercury surface and looking in between the ring and its image obtained by reflection at the mercury surface (Harkins has used a levelled gilt table). The ring was flamed before use.

The radii of the wire and the ring were measured by means of a Hilger "Photo-measuring Micrometer" reading to 0·001 mm. (kindly lent by Professor Venkatesachar of the Mysore University). The mean of twelve even diameters was chosen as the correct value.

The maximum pull was determined by making use of the apparatus shown in Fig. 1. It consisted of a U-tube with two bulbs. One of the limbs contained the spring carrying the ring. The liquid level in the limb was adjusted by suction or pressure through the other limb. The maximum pull was measured by means of a vernier microscope reading to 0·01 mm.

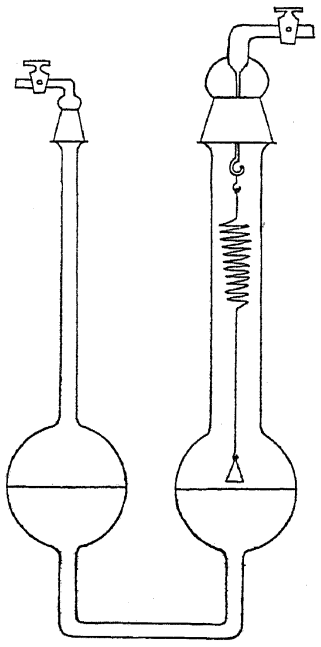

FIG. 1.

In order to standardise the procedure, the surface tension of toluene was determined. In calculating the surface tension from the value of the maximum pull the theories proposed by Cantor,[14] Lohnstein,[15] Lenard,[16] Tichanowsky,[17] and MacDougall,[18] are found to be unsatisfactory. Harkins and his co-workers[11,12] have determined the empirical corrections to be applied to the ring method. Freud and Freud[19] have given theoretical support to the empirical procedure. There has been a great deal of controversy as to whether one should make any allowance for the weight of the drops of the liquid, which cling to the ring, after the ring detaches itself from the liquid.[12,18,20] No such allowance has been made by Harkins in working out the corrections

to be applied. As long as one uses the corrections suggested by Harkins one should not make any allowance for the adherent drops. A value of 27·32 dynes per cm. was obtained for the surface tension of toluene at 30° C., while the value given in the *International Critical Tables* is 27·3 ± 0·1.

Variation of Surface Tension with Time.

A few alterations in the apparatus were necessary to study the variation of surface tension with time. As the surface of the liquid is to be disturbed to the least extent possible two modifications are found to be necessary: (*a*) The maximum pull should be determined without actually detaching the ring from the surface of the liquid; this was effected by employing a spring of smaller sensitivity (about 3 cm. per gm.). (*b*) The liquid level should be maintained very near the point of maximum pull so that the value

TABLE I.

Variation of Surface Tension with Time of an Aqueous Solution of Benzopurpurin (0·002 *Molar*).

Time in mins.	Extension for maximum pull in cm.			
	Exp. 1	Exp. 2	Exp. 3	Exp. 4
0	..	..	1·723	1·763
5	..	1·737	1·704	..
10	..	1·700	1·687	..
15	1·729	1·683	1·676	..
20	1·724	1·673	1·674	..
25	1·720	..	..	..
30	1·713	..	..	..
35	1·708	..	..	..
40	1·705	..	..	..
45	1·695	..	..	..
50	1·685	..	1·658	..
55	1·670	..	..	..
60	1·661	..	..	..
65	1·657	..	..	..
70	1·650	..	..	..
75	1·639	..	..	..
80	1·631	..	..	..
85	1·625	..	..	..
116	..	..	1·639	..
600	..	..	..	1·582

NOTE.—The reading corresponding to zero minutes is the one taken as quickly as possible after the formation of a fresh surface.

Extension of the spring per gram = 3.083 cm.

TABLE II.

Variation of Surface Tension with Time of Aqueous Solutions of Brilliant Green (0·0002 *Molar*).

Time in mins.	Extension for maximum pull in cm.			
	Exp. 1	Exp. 2	Exp. 3	Exp. 4
0	..	1·171	1·242	..
1	1·124	1·153	1·219	..
3·5	1·116	..	..	..
4·5	..	1·145	1·198	..
7	..	..	1·194	..
8	..	..	..	1·207
9	1·116	.	..	..
10	..	1·144	..	..
13	..	..	1·189	..
16	1·114	..	1·192	..
20	..	..	1·193	..
35	1·117	1·143	..	1·200
40	..	..	1·180	..
60	..	..	..	1·187
66	1·116	..	1·177	..
75	..	1·13	..	..
98	..	..9	..	1·185
144	..	1·135	..	1·177
183	..	..	..	1·174
273	..	1·125	..	..
296	..	1·129	..	..
348	..	1·127	..	..
468	..	1·119	..	..
600	..	..	1·137	..

NOTE.—Extension of the spring per gram = 2.366 cm.

for the pull is obtained by a very small movement of the liquid; for this purpose, a constant-head blow off was used to maintain the desired difference in level of liquid in the two arms of the U-tube. With this arrangement the liquid level could be maintained for several hours 0·1 mm. below the position of maximum pull without the least danger of the ring breaking off the liquid. Tables I and II illustrate the nature of the variation of the surface tension of aqueous solutions of benzopurpurin and brilliant green.

Water, benzene, toluene, and benzene soultions of (*a*) phenyl phenacyl ester of stearic acid and (*b*) sudan III did not show any change of surface tension with time. The liquids did not also exhibit the contact angle effect

(which is described later). It is found that the values for the maximum pull were not dependent to any appreciable extent on the speed at which the liquid was withdrawn from the ring.

Discussion.

The tables show that the results on the variation of surface tension with time are not reproducible. It was noticed that *the maximum pull differed according as the adjustment of levels was done by the advancing or the receding method.* This difference would exist only if the liquid has an angle of contact with platinum and the receding contact angle differs from the advancing angle. The existence of a contact angle is supported by the fact that the ring had a strong tendency to float on the solution. Moreover, a ring which was not completely immersed in the solution gave a reading of 1·197 as against 1·278 obtained when the ring was fully wetted by the liquid, both the readings being taken quickly. This difference (which is well beyond the limits of experimental error) shows clearly that the solution makes a contact angle with the material of the ring. The existence of a contact angle complicates the study of the effect of time on the surface tension. For, the absolute value of surface tension of a liquid having a contact angle cannot be easily computed (as the theory of the ring method becomes too complicated presenting certain mathematical difficulties in the calculation). Secondly, the angle of contact itself may change with time. For, if one expects a change in free energy with time of the liquid-vapour interface there is no reason why this should not be true of the solid-liquid interface. The ring method is usually taken to be one of the best suited for studying the variation of surface tension with time.[6,10,21,22] Johlin,[5] however, raises an objection on the grounds that a film of liquid is pulled out by the ring, leading to uncertainties in the measurements. But, as Harkins[12] has pointed out, this phenomenon in no way affects the measurements if one measures *the maximum pull.* Our own results show that one of the most serious objections for the use of the ring method in the study of variation of surface tension with time, is the existence of indefinite contact angles in such systems.

Summary.

An automatic device for the construction of quartz helical springs is described. The surface tension of toluene has been determined by the ring method employing a quartz helical spring for measuring the maximum pull. The effect of time on surface tension of several liquids has been studied and the results discussed. It is shown that the ring method is not suitable for the measurement of variation of surface tension with time.

We wish to thank Mr. M. R. Aswathanarayana Rao for his co-operation in the preparation of quartz springs.

REFERENCES.

1. Dupré .. .. *Theorie Mechanique de la Chaleur,* Paris, 1869.
2. Rayleigh .. .. *Proc. Roy. Soc.,* 1890, **47**, 281.
3. Berczeller .. .. *Intern. Z. Physic. Chem. Biol.,* 1914, **1**, 124.
4. Du Noüy .. .. *Phil. Mag.,* 1924, **48**, (6), 264.
5. Johlin .. .. *J. Phys. Chem.,* 1925, **29**, 1129.
6. Ghosh .. .. *Ibid.,* 1932, **36**, 1916.
7. Bigelow and Washburn .. *J. Phys. Chem.,* 1928, **32**, 353.
8. Milner .. .. *Phil. Mag.,* 1907, (6), **13**, 96.
9. Davis, Salisbury and Harvey *J. Ind. Eng. Chem.,* 1924, **16**, 161.
10. Freundlich .. .. *Colloid and Capillary Chemistry,* 1926, p. 21.
11. Harkins, Young and Cheng .. .. *Science,* 1926, **64**, 333.
12. Harkins and Jordan .. *J. Am. Chem. Soc.,* 1930, **52**, 1751.
13. J. S. Tapp .. .. *Canadian J. of Research,* 1932, **6**, 584.
14. Cantor .. .. *Wied. Ann.,* 1892, **47**, 399.
15. Lohnstein .. .. *Ann. Physik.,* 1908, **25**, 815.
16. Lenard .. .. *Ibid.,* 1924, **74**, 395.
17. Tichanowsky .. .. *Physik. Z.,* 1924, **25**, 300; 1925, **26**, 523.
18. MacDougall .. .. *Science,* (N. S.), 1925, **62**, 290.
19. Freud and Freud .. *J. Am. Chem. Soc.,* 1930, **52**, 1772.
20. Klopsteg .. .. *Science,* 1924, **60**, 319.
21. Adam .. .. *Physics and Chemistry of Surfaces,* 1930, p. 329.
22. Ghosh and Dutt .. *J. Ind. Chem. Soc.,* 1929, **6**, 903.
23. Harkins and King .. *Kans. State Agr. Coll., Tech. Bull.,* No. 9.
24. Harkins and McLaughin .. *J. Am. Chem. Soc.,* 1925, **47**, 2083.