361. *On the Vaporous State of Myristic Acid Films on Aqueous Solutions.*

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Traube, as a result of measurements on the lowering of the surface tension of water by soluble capillary-active substances, concluded that the relationship between the surface concentration Γ and the lowering of the surface tension F could be expressed by the equation $F/\Gamma = RT$ or $FA = RT$ where $A = 1/\Gamma$. The resemblance between this equation and the analogous equation for a perfect gas $PV = RT$ led Traube (*Annalen*, 1891, **265**, 27) to the hypothesis of the applicability of the kinetic theory to surface films. Langmuir (*J. Amer. Chem. Soc.*, 1917, **39**, 1883) modified this concept by suggesting that insoluble films fail to show this "gas" pressure owing to a marked lateral attraction between the hydrocarbon chains which are long enough to cause insolubility. Such films resemble liquids rather than gases. Langmuir observed that surface liquids might be expected to exert a vapour pressure. The consequences of the applicability of the kinetic theory to surface films were examined in detail by Schofield and Rideal (*Proc. Roy. Soc.*, 1925, *A*, **109**, 57), who showed that the departures of FA/RT from unity for large values of F could readily be accounted for on the same basis as is advanced for the inapplicability of the Boyle–Charles law to compressed gases and of the van 't Hoff law to strong solutions.

For small values of F, the proportionality between F and Γ has been established in numerous cases for the surface phase of soluble capillary-active substances, and no extended interpolation is required to show that at infinite dilution FA/RT does indeed attain the value of unity as is required by theory. For the long-chain acids, C_8 and C_{10}, which, from the data of Frumkin and the analysis by Schofield and Rideal, we conclude are gaseous films, the interpolation required is more extended but still reasonable. Films of the acids C_{12} and C_{14} resemble liquids, the liquid expanded phase of Adam ("The Physics and Chemistry of Surfaces"), rather than vapours. The fluid character of these films within the region of their existence may readily be observed from the resemblance of the curves of the FA/RT–F characteristics to those for the isothermals of carbon dioxide below its critical temperature. The existence of a true vaporous phase for these substances, postulated by Langmuir and by Schofield and Rideal, has been shown experimentally to exist by Adam. The pressures, however, are so low at ordinary temperatures that accurate measurements of the F–A characteristics are unattainable with the ordinary trough devised by Langmuir even with the modifications introduced by Jessop and Adam (*op. cit.*) and by Gorter (private communication). In order to complete the analogy between surface films and three-dimensional matter, it appeared desirable to determine with some accuracy the F–A relationship for such vaporous films. Whilst it is to be anticipated that a direct proportionality might hold between F and Γ or $1/A$ analogous to that between P and $1/V$ for a highly rarefied gas, it is by no means certain, especially in the light of the observations of Langmuir noted above, that the molecules of the long-chain acids exist as single unassociated molecules even in extreme two-dimensional dilution. If they were associated with an invariant molecular number in the complex over the existence of the phase the equation applicable would be $FA = xRT$, where $1/x$ represents the association factor.

A modified trough was designed by Marcelin (*Ann. Physique*, 1925, **3**, 481) and employed by Delaplace (*J. Physique*, 1928, **9**, 111) as well as by Guastalla (*Compt. rend.*, 1929, **189**, 241); the last took great precautions against leakage, a defect of the earlier apparatus. He examined films of oleic acid over a range of molecular area from 45 Å.^{2} to 30,000 Å.^{2}. This substance is rather prone to autoxidation on aqueous surfaces but it is worth noting that he failed to obtain a consistent value for x, which varied from $1/20$ for the region 500 Å.^{2} to 5000 Å.^{2} and with increasing area rose towards the value $x = 1$ on extended interpolation at 30,000 Å.^{2}.

EXPERIMENTAL.

The apparatus, depicted in Fig. 1, consists essentially of a shallow rectangular brass trough divided into two sections by means of a brass strip through its middle. This strip is broken at its centre and a floating barrier is placed at right angles through the gap. The float itself, depicted in Fig. 1*a*, consists of a waxed copper wire suspended in the middle by a phosphor-bronze torsion wire in a tube rigidly attached to the trough by means of a girder. Barriers consisting of fine silk threads coated with vaselin are fastened by means of wax to the two ends of the float AA' and to thin brass strips (B) suspended from the upper structure. When the upper structure is fastened to the trough these metal strips press lightly against the sides of the trough, thus preventing leakage. To the two central terminations (C,C') and to the sides of the central brass strip vaselined silk threads are attached in addition.

In this manner the trough is cut up into four sections and is so divided by the movable barrier that a film placed on the water surface in W can pass freely from W to Z but the surfaces X and Y are kept uncontaminated by the vaselined silk barriers. The float and upper structure with the torsion wire are easily removable for the purpose of cleaning. Between the float and the torsion wire is an aluminium post E to which is attached horizontally a fine glass fibre (F).

The end of the fibre presses against a mirror suspended by a silk thread (*G*). Movement of the mirror is recorded on a scale by means of a reflected beam of light.

On the underside of the float just beneath the post *E* is a small steel bearing which rests on the points of a gramophone needle which is suspended from the upper structure. This prevents any forward or backward motion of the float. Both the gramophone needle and the torsion wire can be raised or lowered so that the point just touches the bearing and the minimum friction is obtained when the float is just resting on the surface of the liquid. The torsion wire is set in a head which can be rotated for the purpose of centring the float. Near each end of the float is soldered a vertical iron post (*H* and *H'*) of about the same diameter as the wire of the float. The post *H* rests between the jaws of a clamp fastened to the upper structure. This clamp when open prevents the float from swinging too far and breaking the barriers. It can also be closed tightly to facilitate the removal of the upper structure for cleaning purposes. The other post (Fig. 1*b*) just touches a micrometer screw head which indicates the amount of movement of the float. The whole apparatus is mounted on a brick pier in a cellar maintained at 17°, and is enclosed in a housing constructed of insulating wood provided with the necessary observation and control windows.

FIG. 1.

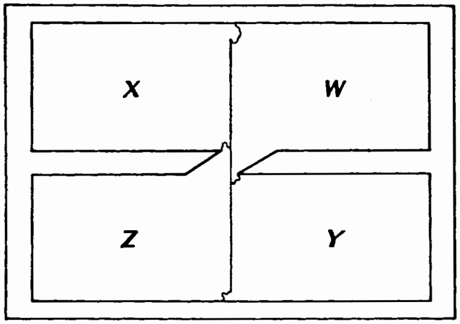


FIG. 1*a*.

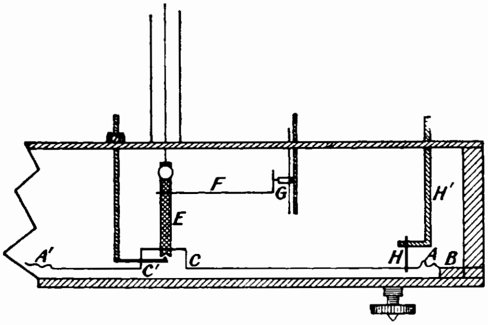


FIG. 1*b*.
Micrometer Screw Head.

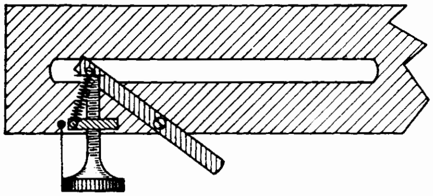
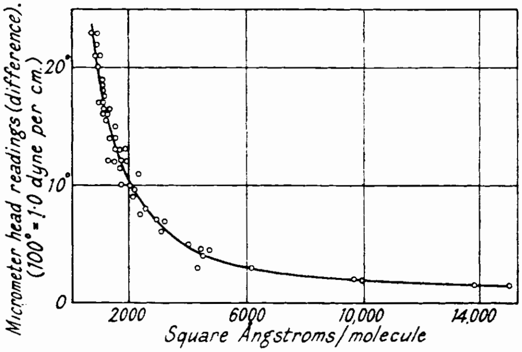


FIG. 2.
Myristic acid at 17°.



To determine a film pressure, the float is centred by means of the torsion head, and time is given for the torsion wire and float to attain true equilibrium. When a slight jarring produces no change in the position of the spot of light from the mirror, equilibrium has been reached. The micrometer head is then screwed up until it just touches the post *H'*. The exact position of contact is noted by the first movement of the light spot. Next, the micrometer head is released and all four surfaces are cleaned by means of waxed glass slides. When the cleaning of sections *W* and *Z* produces no change in the position of contact of the micrometer head, the surface is considered clean. The micrometer head is read and released, and a drop of solution in light petroleum is placed by means of an " Agla " micrometer syringe in either section *W* or *Z*. After a few minutes the head is again brought in contact with *H'*. The head is then released, and a second drop added and the procedure repeated. The difference in head readings indicates the film pressures.

Great care must be taken thoroughly to wash the " Agla " pipette with light petroleum before each run; otherwise, small amounts of myristic acid, left on evaporation of the solvent in the needle, change the reading appreciably.

To calibrate the instrument, the float clamp is removed, and a bar magnet brought near the iron post *H*. The deflexion caused is recorded by the micrometer head and the distance from the magnet to the post *H* is carefully measured. This is repeated for different positions of the magnet, and a curve of deflexion–distance is obtained. The iron post is then removed from the float and weighed in a balance. The same magnet is placed over it and the loss in weight recorded for various distances. From these two sets of measurements the micrometer head readings are converted into dynes/cm.

In Fig. 2 are given the micrometer head readings and the two-dimensional pressures obtained for films of myristic acid at 17° on water as a function of the apparent molecular area. This curve, within the experimental limits of accuracy, is a rectangular hyperbola, thus obeying the equation $FA = K$. If $K = xRT$ at 17°, we find $xR = 4{\cdot}18 \times 10^7$ ergs/degree, whence $x = 0{\cdot}5$. It would appear possible that, for these long-chain fatty acids below the critical temperature, the molecules exist in an associated state in the two-dimensional vaporous phase, and that there are two molecules of acid in each associated complex. From the constancy of the product FA, even at large areas, it is clear that the complex is extremely stable.

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