Menisci at a Free Liquid Surface: Surface Tension from the Maximum Pull on a Rod

BY J. F. PADDAY,* A. R. PITT AND R. M. PASHLEY

Research Division, Kodak Limited, Headstone Drive, Harrow HA1 4TY

Received 4*th October*, 1974

The maximum force on a vertical rod supporting a stable meniscus, at equilibrium, formed at the free surface of a liquid, is shown to be a characteristic property of the system. This maximum force depends only on the rod radius, the density of the liquid, the gravitational acceleration and the surface tension.

The maximum force represents the product of the maximum volume of liquid held above the general level, the gravitational acceleration and the density. The maximum volume of the meniscus has been derived theoretically as a function of rod radius in the form of a parametric equation with a table of coefficients. Thus from the measured rod radius and maximum force, the surface tension is derived.

The surface tensions of water and of other liquids have been measured using this method and are found to agree very well with other methods given in the literature. However, this method is believed to be accurate to ± 0.1 mN m^{-1}, and it is an absolute method in that it requires no arbitrary end corrections involving a prior knowledge of the surface tension.

It is important that the rod should be level and have a radius not so large that the angle of contact became a limitation on the maximum force measurable.

The method does not involve detachment of the rod from the surface. It is an equilibrium method the position of which may be approached from both directions.

Gay-Lussac,[1] attempted to determine the surface tension of a liquid by the measurement of the maximum force exerted on a horizontal plate as it was pulled away from the free flat surface of a liquid. He realised it was necessary to use a large plate (118.4 mm diameter) and he assumed that the meniscus formed at the edge of the plate approached that of cylindrical symmetry: in fact he assumed that the angle of the meniscus with the underside of the plate was zero.

These experiments captured the attention of Young,[2] Laplace,[3] Poisson,[4] Kirchoff,[5] Cantor,[6] Lohnstein,[7] Gallenkamp,[8] Quincke, [9] Ferguson,[10] Bouasse [11] and Bakker,[12] all of whom attempted to obtain a relation between the force on the rod or plate, the radius of the plate and the surface tension of the liquid. Of these studies only that of Lohnstein reveals the understanding necessary to obtain this relation.

The measurement of surface tension with solids of other shapes, such as the Du Nouy ring [13] has been studied by Freud and Freud,[14] and Harkins and Jordan,[15] and the sphere has been studied by Huh and Mason [16] and Scheludko.[17] The sphere problem also arises in flotation studies,[18, 19] and equations used in these studies are identical with those used in surface tension measurement.

However, despite this extensive area of previous investigation it appears that the solution to the rod or plate problem has not been established previously.

In this study we attempt to set out the physical conditions that govern the maximum pull on a rod as it is drawn from the free surface of a liquid to form a stable meniscus. We then show that the force reaches a stable maximum value well before breakaway occurs, and that this maximum, expressed as a volume, is a characteristic property of the system. In this respect we differ from the previous studies as we are interested only in the maximum force and not the force at the point of rupture. The relation between the maximum volume and the radius of the rod is derived by numerical analysis and the results are given in the form of an equation. Finally we determine the surface tension of some pure liquids from the maximum force on a rod and find excellent agreement with literature values obtained by other methods.

FORCE ACTING ON A ROD IN A FREE SURFACE

Consider the meniscus of fig. 1, produced by withdrawing the rod, A, of radius, X,

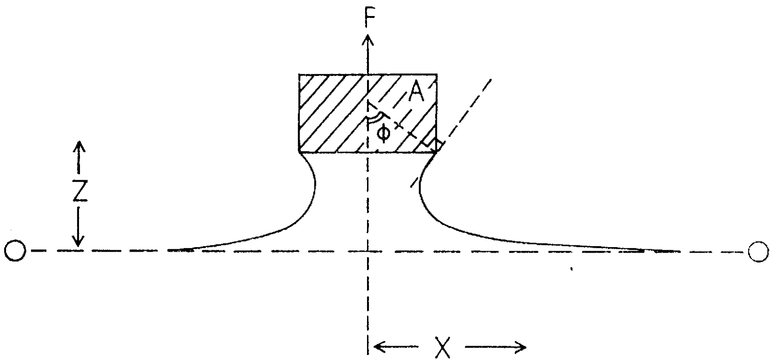

FIG. 1.—Rod-in-free-surface meniscus formed with a circular disc.

a distance, Z, above the free surface positioned along the horizontal, OO. The rod is perfectly wetted on its underside but is not wetted along its walls; a condition easily obtained experimentally when pure liquids are used.* The force, F, in excess of the weight of the rod is exactly equal to the weight of liquid raised above the general level.

From simple physical laws

$$F = \pi X^2 Z\rho g + 2\pi X\gamma \sin\phi, \tag{1}$$

where ρ is the density difference between the liquid and its surrounding fluid, g the gravitational acceleration, γ the surface tension of the liquid against its surrounding fluid, and ϕ the angle of the meniscus with the horizontal at the junction with the plate (ϕ is *not* the angle of contact given by Young's equation).

The first term represents the pressure on the underside of the plate due to the hydrostatic pressure of the liquid, and the second term the force in consequence of the surface tension pull around the edge of the plate. The force F divided by (ρg) represents the volume, V, of the meniscus above the general level of the liquid surface.

Here we shall reduce units to dimensionless ratios by dividing linear dimensions by the meniscus coefficient, k, where

$$k = (\gamma/\rho g)^{\frac{1}{2}}, \tag{2}$$

so that eqn (1) becomes

$$V/k^3 = \pi X^2 Z/k^3 + (2\pi X \sin\phi)/k. \tag{3}$$

At equilibrium V is related to X, Z, k and ϕ through the Young–Laplace equation;

$$\frac{d^2z/dx^2}{[1+(dz/dx)^2]^{\frac{3}{2}}} + \frac{k\sin\phi}{x} = z/k. \tag{4}$$

* It was found that some solutions of surfactants wetted the sides of the rod and gave rise to some error.

To solve eqn (3) it is necessary to integrate eqn (4). Eqn (4) cannot be integrated in closed form though the previous studies cited above attempted various approximations.

Numerical integration of eqn (4) applied to rod-in-free-surface menisci, has been carried out by Tallmadge [20] (corrected by Hildebrand and Tallmadge [21]), Huh and Scriven,[22] and Padday, [23-25] using modern high-speed computers. However only these last studies give the required volume data though some of the volume data is available in Freud and Freud's [14] analysis of the Du Noüy ring.

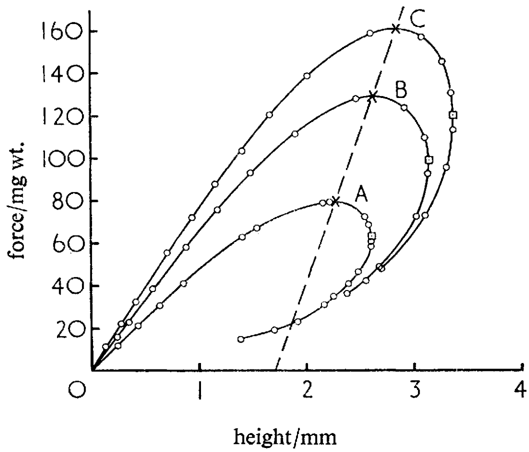

FIG. 2.—Force on a rod as a function of height from a free liquid surface. Radius of rods A, 0.141 65 cm; B, 0.203 92 cm; C, 0.239 17 cm; where $\rho = 0.998$ cm^{-3}; $g = 981.2$ cm s^{-2}; and $\gamma = 72.5$ mN m^{-1}. $\times$, position of maximum force; $\boxdot$, position of maximum height.

In fig. 2 the forces acting on each of three rods of different radius are plotted as a function of the height of the rod above the surface. The data were obtained from the tables of the properties of rod-in-free-surface menisci.[24] It is immediately obvious that the force increases with height, reaches a maximum, and then decreases to the point of rupture where the maximum height is reached. At this point the meniscus spontaneously breaks away as shown by the stability studies of Padday and Pitt.[26] It is to be stressed that the maximum volume is not that measured at the point of breakway of the meniscus. The maximum volume of this study is a stable property of the meniscus that can be approached from both sides of the equilibrium.

Only Lohnstein [7] attempted to solve eqn (3) and (4) by setting dV/dZ equal to zero. All other investigators supposed wrongly that the volume could be derived from the volume at maximum height $dz/dV = 0$. As will be shown later, Lohnstein's approximation was the only one that came near to predicting the maximum volume as a function of rod radius.

METHOD FOR OBTAINING THE TABLE RELATING X^3/V AS A FUNCTION OF X/k AND ITS USE

The maximum volume of a meniscus formed by a rod at a free surface of liquid may be obtained from the author's tables [24] as used for constructing fig. 2. This method is however tedious; so instead we have used the envelope construction technique, used previously to obtain stability data [26] as the best method for obtaining accurate data.

The envelope construction technique involves simply plotting the volume as a function of the radius for each of several profiles of given shape factors. The volume is thus plotted for all values between $\phi = 90°$ and $\phi = 0°$ for each profile (ϕ is defined in fig. 1) by starting with data at $\phi = 90°$ and integrating step-by-step until $\phi = 0°$ is reached. Further functions for other profiles are plotted on the same graph until a sufficient number of curves are present to allow the enveloping curve to be constructed.

An envelope construction curve of the type used in this study is shown in fig. 3. Here values of X/k between 7.0 and 9.0 are plotted as a function of X^3/V. The points represent successive values at 1° intervals for each of six profiles and the enveloping curve is found to be almost a straight line.

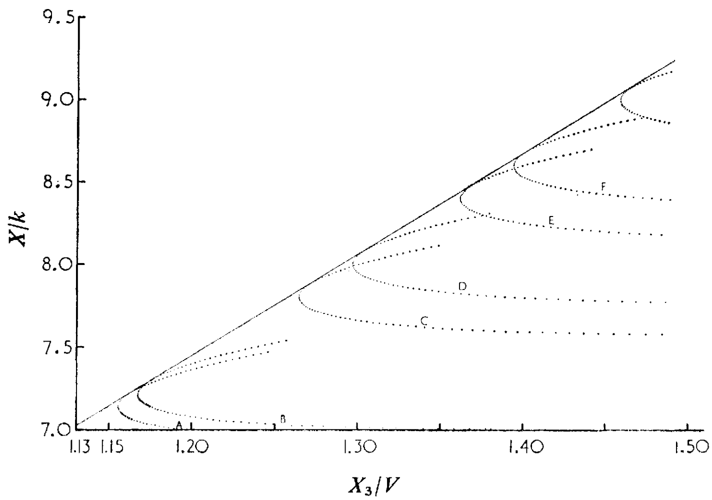

FIG. 3.—Envelope constructed curve of X/k as a function of maximum volume expressed as X^3/V. A,$\beta' = 48.08$; B,$\beta' = 49.07$; C,$\beta' = 57.51$; D,$\beta' = 60.48$; E,$\beta' = 66.66$; F,$\beta' = 69.86$; where $\beta' = [X(90°)/k]^2$.

The data were plotted with a Hewlett Packard 9100A computer, a 9125 plotter and a 9101A extended memory, with the integration procedure previously described.[23] The envelope curve was then constructed by drawing with a flexible curve and pencil.

Fig. 3 is one of 14 graphs constructed to obtain X/k as a function of X^3/V covering the whole range with sufficient accuracy. For small rods ϕ approaches 90° and for very large rods or plates ϕ approaches 0°. As is shown later approximate relations between X^3/V and X/k in these regions may be used with sufficient accuracy for general experiments.

In this study we obtained values of X^3/V in the range 0.010 0 to 1.86 corresponding to a range of X/k from 0.250 to 11.500 and it was possible to express the relationship between X^3/V and X/k using the equation

$$X/k = a_0 + a_1(X^3/V) + a_2(X^3/V)^2 + a_3(X^3/V)^3 \tag{5}$$

but with the coefficients varying according to the range of X^3/V. The simplest way to express these data was simply to calculate the value of X^3/V from experimental results and then derive X/k from eqn (5) using the coefficients given in table 1. These coefficients were obtained from the numerical integration procedure and subsequent curve fitting.

By decreasing the increment $\delta\phi$ to improve accuracy in the integration process we find that the relationship is changed only in the fifth figure which is sufficient for the accuracy of this study. Although the data of table 1 are given to six figures, this is only for computational purposes. The final value of X/k so obtained is only accurate to four figures.

TABLE 1.—VALUES OF THE COEFFICIENTS OF EQN (5) USED TO CALCULATE X/k FROM VALUES OF X^3/V

range X^3/V	a_0	a_1	a_2	a_3
0.01-0.02	$9.075\,78\times10^{-2}$	$2.073\,80\times10^{1}$	$-4.464\,45\times10^{2}$	$6.235\,43\times10^{3}$
0.02-0.03	$1.151\,08\times10^{-1}$	$1.643\,45\times10^{1}$	$-2.001\,13\times10^{2}$	$1.631\,65\times10^{3}$
0.03-0.04	$1.062\,73\times10^{-1}$	$1.692\,46\times10^{1}$	$-2.048\,37\times10^{2}$	$1.573\,43\times10^{3}$
0.04-0.05	$6.342\,98\times10^{-2}$	$1.883\,48\times10^{1}$	$-2.203\,74\times10^{2}$	$1.437\,29\times10^{3}$
0.05-0.07	$1.563\,42\times10^{-1}$	$1.230\,19\times10^{1}$	$-6.969\,70\times10^{1}$	$2.938\,03\times10^{2}$
0.07-0.10	$2.216\,19\times10^{-1}$	9.313 63	$-2.394\,80\times10^{1}$	$5.962\,04\times10^{1}$
0.10-0.15	$3.110\,64\times10^{-1}$	6.979 32	$-3.589\,29$	0.0
0.15-0.20	$3.672\,50\times10^{-1}$	6.266 21	$-1.321\,43$	0.0
0.20-0.30	$4.405\,80\times10^{-1}$	5.605 69	$1.631\,71\times10^{-1}$	0.0
0.30-0.40	$4.473\,85\times10^{-1}$	5.630 77	0.0	0.0
0.40-0.50	$4.725\,05\times10^{-1}$	5.399 06	$4.245\,69\times10^{-1}$	0.0
0.50-0.60	$3.780\,00\times10^{-1}$	5.800 00	0.0	0.0
0.60-0.80	$5.721\,10\times10^{-1}$	5.156 31	$5.338\,94\times10^{-1}$	0.0
0.80-1.00	$2.990\,48\times10^{-1}$	5.862 60	$7.834\,55\times10^{-2}$	0.0
1.00-1.20	$6.764\,15\times10^{-1}$	5.162 81	$4.012\,04\times10^{-1}$	0.0
1.20-1.40	$4.086\,87\times10^{-2}$	6.203 12	$-2.407\,52\times10^{-2}$	0.0
1.40-1.60	$2.531\,74\times10^{-1}$	5.903 51	$8.142\,59\times10^{-2}$	0.0
1.60-1.85	$-1.300\,00\times10^{-2}$	6.200 00	0.0	0.0

Experimentally one measures the maximum force on the rod and its radius, X; k is unknown. The volume, V, is found by dividing this force by ρg, and then the ratio X^3/V is calculated. The value of X/k corresponding to this value of X^3/V is obtained using eqn (5) with the coefficients of table 1 and, from X again, k is found. Finally γ is calculated from k using eqn (2).

EXPERIMENTAL

MATERIALS

Benzene was of spectroscopic grade; n-hexane was an Eastman chemical; chlorobenzene and n-butyl alcohol were of AnalaR grade. These liquids were used without further puri-

TABLE 2.—PHYSICAL PROPERTIES OF LIQUIDS USED

liquid	source	density as a function of temperature* A	B	C	surface tension/ mN m^{-1} (20°C)	surface tension temperature coefficient/ mN m^{-1} K^{-1}
water	twice distilled	[taken directly from ref. (27)]			72.75±0.05 [29]	0.150 [29]
n-hexane	Eastman Chemical	0.6769	—0.8486	—1.084	18.42 [28]	0.103 [28]
chlorobenzene	B.D.H.	1.127 82	—1.0664	—0.2463	33.28 [28]	0.116 [28]
n-butyl alcohol	M and B	0.823 90	—0.699	—0.32	24.58 [28]	0.084 [28]
benzene	AnalaR	0.900 05	—1.0636	—0.0376	28.88 [28]	0.130 [28]

* ($\rho_T = A + 10^{-3}\,BT + 10^{-6}\,CT^2$).[30]

fication. Water was first distilled in Pyrex then passed through a column of activated charcoal and finally distilled under nitrogen. The physical properties of the liquids were obtained from literature sources and are given in table 2.

APPARATUS

The apparatus used for measuring the maximum pull of a meniscus on a vertical rod is shown in fig. 4. The force acting on the rod was measured with an Oertling R20 single pan analytical balance with an accuracy of $\pm 0.000\,1$ g. The rods or plates were made of stainless steel and every attempt was made to machine the sides and bottom face to within $\pm 10^{-3}$ mm. Before measurement the undersurface of the rod was carefully ground with carborundum (particle size to pass 250 mesh) by means of a Vee-block and face plate, but the sides of the rod were left highly polished and therefore not very wettable.

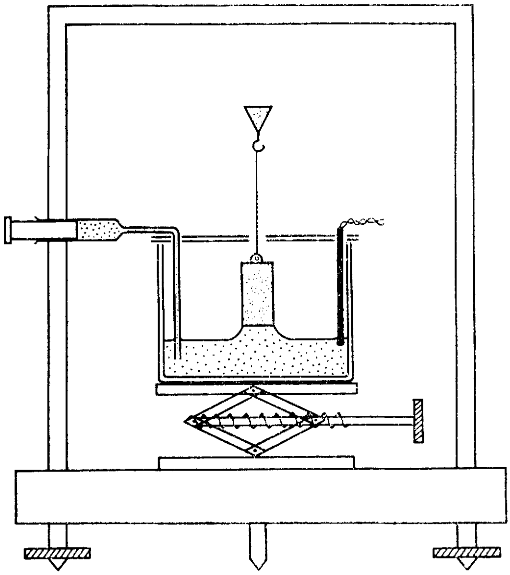

FIG. 4.—Experimental set up for measuring force on a rod.

The diameter of each rod was measured many times using a special microscope fitted with a large micrometer—adjusted table which supported the rod. The mechanical movement enabled the edge of the rod to be located within ± 0.001 mm. At the same time the surface was inspected for rounding of the edges and for blemishes which, if found, were removed by further grinding. The standard deviation of the measured radius varied from rod to rod and so is presented in table 3. Two of the rods, f and g were fitted with three screws mounted radially at the upper end so that accurate levelling was achieved.

The displacement of the balance beam per unit weight was relatively small and led to no errors at all. Larger displacements, such as are obtained with spring balances, were unsatisfactory because they rendered the system unstable very near the position of maximum volume.

The liquid was placed in a 72-cm diameter crystallising basin supported on a platform that could be raised or lowered. This platform was used for coarse adjustments of the liquid level and finer adjustments were made with a micrometer controlled syringe. The temperature was measured constantly with a thermistor measuring to ± 0.005°C and evaporation losses were prevented by covering the basin with two sheets of glass with suitable gaps for the syringe needle, the thermistor and the wire supporting the rod. When covered the temperature at the surface was found to be equal to that of the bulk, and the whole system was maintained to ± 0.02°C. Such temperature control enabled the densities of the liquids to be accurate to $\pm 2 \times 10^{-5}$ g cm^{-3}.

PROCEDURE

All apparatus was carefully cleaned and treated with chromic-sulphuric acid cleaning mixture and copiously rinsed in distilled water. The rods were similarly treated. The liquid was placed in the basin and the apparatus was set up as shown in fig. 4. The force on the rod was measured continuously as the liquid level was lowered, first by lowering the platform and then using the syringe. At some point the force was found to reach a maximum value. The apparatus was then left for several minutes after which the maximum value was approached several times from each side of the equilibrium. The junction between the meniscus and the rod was examined with a travelling microscope to ensure that the sides of the rod remained unwetted.

TABLE 3.—DIMENSIONS OF RODS

rod	mean radius mm	standard deviation / mm	weight in air/ g	height/ mm	levelling screws
a_1	3.1500	0.0015	6.5265	25	no
a_2^*		0.0022	6.5260	25	no
b	4.7397	0.0055	9.9360	15	no
c	4.9926	0.0023	9.7985	15	no
d	5.2542	0.0059	10.4800	15	no
e	7.4808	0.0031	22.2860	15	no
f	7.4208	0.0025	34.0470	22	yes
g	9.9968	0.0034	72.5650	29	yes
h	10.0045	0.0089	38.8920	15	no
i	12.5358	0.0065	60.2797	15	no
j	7.8462	0.0062	15.8980	8	no

* Rod a_1 with reground edge.

The temperature and force were noted simultaneously and the force due to the meniscus was obtained by subtracting the weight of the unwetted rod. This force was then converted into a volume by dividing by appropriate values of ρ and g according to table 2. The quantity X^3/V was then calculated from the experimental quantities and then X/k was obtained using eqn (5). From k, γ was derived with the use of eqn (2).

The gravitational acceleration for the room in which the measurements were made was 981.18 cm s^{-2}, and was derived from the value for a weather station nearby applying height corrections.

RESULTS AND DISCUSSION

The surface tensions of the liquids of table 2 were measured by this method with several different sized rods for each liquid. The results are shown in table 4 together with comparable literature values obtained from the data set out in table 2. The results indicate quite clearly that, except for measurements with very small or very large rods, all values are accurate to 0.2 mN m^{-1} if not better.

Organic liquids are very much less likely to acquire aerial contamination that lowers the surface tension; hence their values tend to be more reliable. n-Hexane is rather volatile and errors were encountered because the increased vapour density gives an additional buoyancy. To overcome this difficulty the force on the " dry " rod was found by measuring its weight when only 3 mm above the free liquid surface. During this measurement it was necessary to ensure that the rod was at the same temperature as the liquid so as to avoid errors arising from vapour condensing on the cold rod. Using rods of radius 6-10 mm under the best possible conditions we find we are able to measure surface tension with a reproducibility of $\pm$0.015 mN m^{-1}.

Except for two determinations, all measured values for water were lower than literature values. Also the errors with rods a and b, the smallest, were much larger

TABLE 4.—COMPARISON OF SURFACE TENSION MEASUREMENTS WITH LITERATURE VALUES

rod	temp/°C	γ(measured)/mN m^{-1}	γ(literature)/mN m^{-1}	error/mN m^{-1}
		(*a*) water		
a_2	21.83	71.99	72.47	0.48
a_2	21.00	72.12	72.60	0.48
a_2	20.83	72.25	72.69	0.44
b	23.77	71.95	72.17	0.22
b	23.67	71.95	72.19	0.24
b	23.72	71.95	72.18	0.22
b	23.74	71.95	72.17	0.22
c	19.80	72.75	72.78	0.03
c	20.32	72.66	72.70	0.04
c	22.36	72.39	72.39	0.00
c	21.08	72.61	72.58	−0.03
c	20.17	72.74	72.72	−0.02
d	20.67	72.65	72.65	0.00
d	21.18	72.57	72.57	0.00
e	20.86	72.41	72.62	0.21
e	20.86	72.41	72.62	0.21
h	19.72	72.16	72.79	0.63
h	21.27	71.98	72.55	0.57
a_1	21.45	72.33	72.53	0.20
a_1	20.58	72.47	72.64	0.17
		(*b*) other liquids		
		n-hexane		
c	21.28	18.25	18.29	0.04
c	21.68	18.20	18.25	0.05
f	18.88	18.48	18.53	0.05
f	18.17	18.56	18.61	0.05
f	18.19	18.56	18.59	0.03
g	19.70	18.41	18.44	0.03
g	19.75	18.39	18.43	0.04
g	19.38	18.44	18.48	0.04
a_1	21.47	18.19	18.26	0.07
		chlorobenzene		
c	21.98	33.07	33.05	−0.02
c	21.73	33.09	33.08	−0.01
		n-butyl alcohol		
c	21.58	24.49	24.45	−0.04
c	21.71	24.46	24.44	−0.02
d	21.62	24.42	24.44	0.02
a_1	21.96	24.31	24.42	0.11
g	22.30	24.27	24.40	0.12
		benzene		
d	19.73	28.90	28.91	0.01
d	19.53	28.95	28.94	−0.01
a_1	20.53	28.57	28.80	0.23
g	20.88	28.65	28.75	0.10
a_2	19.03	28.92	29.00	0.08
a_2	19.17	28.92	28.99	0.07

than those with rods c, d, f and g. This was because the smaller rods were more difficult to machine and the grinding process which was necessary to ensure wettability may have caused a submicroscopic rounding of the edge of the rod. The very large rods, on the other hand, appeared to produce menisci that broke away unevenly. We attributed the large errors found with rod h to the fact that the base of the rod was not parallel to the free liquid surface.

Rods f and g when first used were found to hang out of the vertical line and initial surface tension measurements were about 0.4 mN m^{-1} too low. These rods were drilled radially at their upper end and three grub screws were inserted into each rod. The rods were then suspended over a pool of mercury and the screws adjusted until the lower face was seen to be level. Subsequent measurements showed greatly reduced errors, as seen in table 4(*a*). The level of the underside of the rod, particularly large ones, was of great importance.

Though reasonable precautions were taken to prevent aerial contamination reducing the surface tension of water, there was inevitably the possibility of this happening in the set-up used. Only by rigorous exclusion of room air can it be certain that no contamination occurred. Even so repeated cleaning of a surface after measurement showed that the surface pressure due to contaminants was not greater than 0.03 mN m^{-1}, after ageing.

Vibration was a minor source of error and it was found expedient to conduct experiments when the surface of the liquid was free of ripples. After preliminary experiments we mounted the balance on a large paving slab supported by four rubber bungs. This successfully insulated it from gross vibrations from the structure of the building. Errors were unlikely to arise from temperature variations within the cycle of the thermostat, because the temperature coefficients of the surface tensions of the liquids were always less than 0.2 mN m^{-1} $°C^{-1}$. Densities were equally reliable.

An analysis of errors shows that the main source arises from an uncertainty in the diameter of the rods. The measurement of the force acting on the rod added to this error but other errors arising from small temperature variations and uncertainty in densities and the gravitational constant were insignificant in comparison.

The error in measurement arising from all sources could be as large as ± 0.3 mN m^{-1} but the reproducibility in measurement with a given rod was very much better, ± 0.03 mN m^{-1}. It was thus evident that the main source of error arose from some factor associated with rod to rod variations.

According to eqn (3) the volume of liquid supported by a rod is given by two terms, the first term being a pressure term and the second a surface tension term. For small rods the surface tension term predominates and the value of ϕ approaches 90°. Under such conditions sub-microscopic rounding of the edges of the rod could cause the errors that were found. For very large rods the pressure term of eqn (3) predominates because now ϕ approaches 0°. Under these conditions the force on the rod (perhaps more appropriately a plate) becomes very sensitive to any tilt of the lower surface that is in contact with liquid. Such tilt can only diminish the force from its maximum value. For these reasons we believe the rods of intermediate size (c, d, e and f) suffered from neither disadvantage excessively and therefore gave better results. To achieve a final accuracy of ± 0.01 mN m^{-1} on a surface tension of 50 mN m^{-1} the rod will have to be fabricated and measured within a tolerance of $\pm 0.000\,025$ cm on a diameter of 1 cm, a tolerance not reached in these experiments.

The surface tension of binary liquid mixtures of methyl or ethyl alcohol with water again agreed well with published values (i.e., ± 0.02 mN m^{-1}).[29] The surface tension of solutions of a number of surface-active agents were measured by this method and compared with results obtained with the Wilhelmy plate.[31]

It was found that the rod or plate method described here was not suitable for measuring the surface tensions of solutions of cationic surface-active agents, because adsorption on the underside of the rod rendered it insufficiently wettable. In this event the meniscus broke away before the maximum force was reached. The surface tensions of solutions of anionic and non-ionic surface active agents could be measured by this method but ageing effects rendered the method slow to operate. The ageing arose from the solution wetting the sides of the rod when it was first brought into contact with the liquid. As the rod was raised the wetting film drained away albeit slowly. Errors arising from this form of ageing can be as large as 0.5 mN m^{-1}. Measurements were made with glass rods, but, as they tended to become chipped at the edges during the grinding process, errors arose from an uncertainty in radius. Ageing effects from a wetting film on the sides of glass rods again produced errors with solutions of surface-active agents.

The main features that come out of these data is that the method is reliable and reproducible when used with rods of intermediate size. It is also a fundamental method for measuring surface tension in that no previous knowledge of surface tension values is required in order to calibrate or to estimate errors. The method appears to be simple to use, quick to operate and easy to clean. The apparatus is also robust.

COMPARISON WITH APPROXIMATE SOLUTIONS

In the earlier studies referred to, approximate equations were used to relate the surface tension to the experimentally measured quantities, namely the maximum force on the rod, the radius of the rod, the density difference between the liquid and its surrounding fluid and the gravitational acceleration. As all these quantities were easily measured accurately, the method appeared very attractive to these early experimenters.

All these early relations, except that of Lohnstein, were developed on the incorrect assumption that the force reached some maximum value when the distance of the rod from the free surface was greatest, that is at the point of instability and breakaway. For very large rods the maximum force does approach asymptotically the value of the force at maximum height and therefore the equations are relevant.

In chronological order the equations for large rods were:

Young (1804) $$V = \pi X^2 Z \approx 2\pi X^2 k; \tag{6}$$

Laplace (1805) $$V = 2\pi X^2 k[\cos\phi/2-(k\cos\phi/2)(1-6\sin\phi/2+5\sin^3\phi/2)/3X]; \tag{7}$$

when $\phi = 0$ $$\approx 2\pi X^2 k(1-k/3X); \tag{8}$$

Poisson (1831) $$V = 2\pi X^2 k(1-k/3X); \tag{9}$$

Lohnstein (1908) $$V = 2\pi X^2 k(1-k/3X+35k^2/18X^2-83k^3/216X^3); \tag{10}$$

Ferguson (1913) $$V = 2\pi X^2 k(1-k/3X-\sqrt{2}k^2/3X^2); \tag{11}$$

Bakker (1928) $$V = 2\pi X^2 k[\cos\phi/2-k(3X\cos\phi/2)^{-1}(1-\sin^3\phi/2)]; \tag{12}$$

Neumann (1928) $$\approx 2\pi X^2 k(1-k/3X); \tag{13}$$

and for small rods were:

Kirchoff $$V = 2\pi X^2 k[k(2\sqrt{2}+5)/6X-1\sqrt{2}]; \tag{14}$$

Poisson $$V = 2\pi X^2 k[(X/2k)(\log 4k/X-0.577\ 21)+k/X]. \tag{15}$$

The symbols of the above authors have been standardised to those of this paper.

In fig. 5 a comparison is made between the numerical results of this study and the equations cited above. However, to test those derived by Laplace and by Bakker, it was first necessary to obtain the value of ϕ at maximum volume as a function of X/k. This function is shown in fig. 6. The data for it were obtained to the nearest 2° interval by interpolation in the tables for rod-in-free-surface profiles.

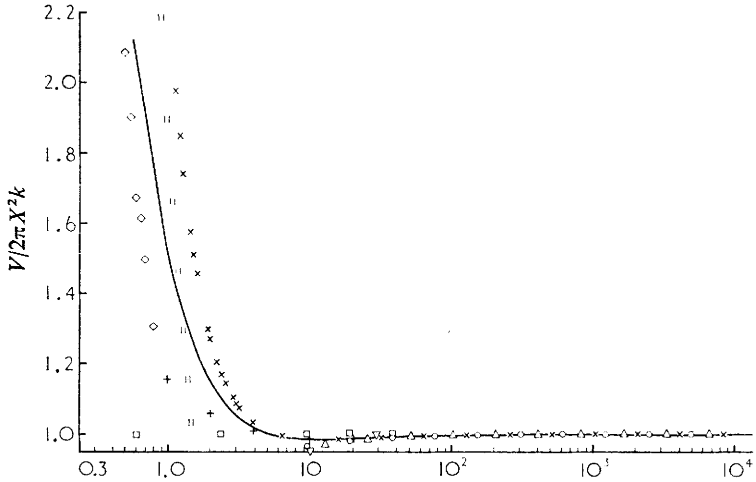

FIG. 5.—Maximum volume expressed as $V/2\pi X^2k$ as a function of rod radius X/k. ○ Poisson's equation (9) for large rods; △, Ferguson's equation (11); ×, Lohnstein's equation (10); □, Young's approximation equation (6); +, Laplace's equation (7); ▽, Bakker's equation (12); |·|, Kirchoff's equation (14) for small rods; ◇, Poisson's equation (15) for small rods.

The most important feature to emerge from this comparison is that the asymptotic solutions for large plates and where ϕ is not known can only be applied when $X/k >$ 20. For water $k \approx 2.7$ mm therefore $X \approx 55$ mm. Although Gay-Lussac used rods or plates approached this radius, we find that the problems associated with levelling and with weighing small differences of a large heavy plate render the method impracticable with such plates.

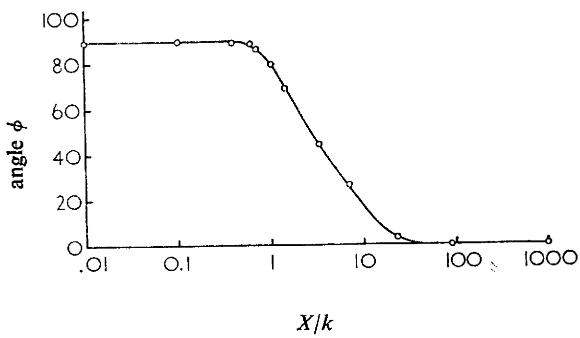

FIG. 6.—Meniscus angle ϕ for maximum volume conditions, plotted as a function of rod radius X/k.

For small plates where $X/k < 1.0$, Kirchoff's equation does not seem to fit at all; but judgement on the accuracy of the equation comes from Gallenkamp's reporting of Kirchoff's work and not from the original reference. Poisson's equation, though still in serious error between $0.5 < X/k < 1.0$, appears to approach the numerical curve when $X/k < 0.1$ as is seen in fig. 5. Clearly the only equation that follows the general shape of the curve derived from numerical data is that due to Lohnstein who was the sole worker who understood the true nature of the problem. Had Lohnstein taken further terms in his approximations, he might well have obtained a better fit at lower rod radii. As it is, his equation produced values that were too inaccurate for normal experimental use.

In fig. 7 we have replotted the data of fig. 5 but on a double logarithmic scale in order to reveal values at lower rod radii. Also plotted are the contributions of the pressure term and of the surface tension term of eqn (3) to the total volume of the meniscus. The pressure term represents the cylindrical volume of liquid between plate and free surface, and the surface tension contribution the volume of liquid outside this cylinder.

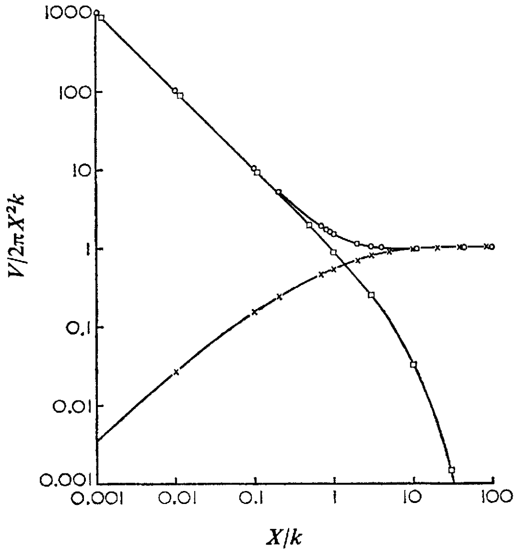

FIG. 7.—Contributions to the total volume as a function of rod radius. ×, surface pressure contribution; ⊡, surface tension contribution; ⊙, sum of all contributions.

This plot shows that when $X/k < 0.1$

$$V = 2\pi X k^2 \tag{16}$$

within an accuracy of ± 0.5 %

and when $X/k > 10$

$$V = 2\pi X^2 k \tag{17}$$

within an accuracy of ± 2.0 %

Between this range, approximate solutions are not accurate and the data should be obtained from eqn (5).

[1] N. F. Gay-Lussac, *Oeuvres*, 1880, **4**, 467.
[2] T. Young, *Miscellaneous Works* (Peacock Edn., London, 1855, originally published 1804), **1**, 418.
[3] P. S. Laplace, *Méchanique Céleste*, *2nd Suppl. to volume X* (Gauthier-Villars Paris, 1912, originally published 1806), p. 48.

[4] S. D. Poisson, *Nouvelle Theorie de L'Action Capillaire* (Bachelier, Paris, 1831), p. 226.
[5] G. Kirchoff, *Mechanik*, 1877, 147 (via Gallenkamp [8]).
[6] M. Cantor, *Ann. Physik*, 1892, **47,** 399.
[7] T. Lohnstein, *Ann. Physik*, 1893, **48,** 207; 1908, **25,** 807.
[8] W. Gallenkamp, *Ann. Physik*, 1902, **9,** 475.
[9] von G. Quincke, *Ann. Physik*, 1903, **10,** 453.
[10] A. Ferguson, *Phil. Mag.*, 1913, **26,** 925.
[11] H. Bouasse, *Capillarite Phénomènes Superficiels* (Delgrave, Paris, 1924), p. 210.
[12] G. Bakker, *Handbuch der Experimental Physik*, (Wien u. Harms, Leipzig, 1928), vol. 6, p. 149.
[13] L. Du Noüy, *J. Gen. Physiol.*, 1919, **1,** 521.
[14] B. B. Freud and H. Z. Freud, *J. Amer. Chem. Soc.*, 1930, **52,** 1772.
[15] W. D. Harkins and H. F. Jordan, *J. Amer. Chem. Soc.*, 1930, **52,** 1756.
[16] C. Huh and S. G. Mason, *Postgraduate Research Report* 52 (Pulp and Paper Institute of Canada, Montreal, 1973); *J. Colloid Interface Sci.*, 1974, **47,** 271.
[17] A. D. Scheludko and A. D. Nikdov, *Kolloid Z.*, in press.
[18] A. D. Scheludko, B. Radoev and A. Fabrikant, *Annuaire Univ. Sofia*, 1968/69, **63,** 42.
[19] C. W. Nutt, *Chem. Eng. Sci.*, 1960, **12,** 133.
[20] J. A. Tallmadge and D. A. White, *J. Fluid Mech.*, 1965, **23,** 325.
[21] J. A. Tallmadge and M. A. Hildebrand, *J. Fluid Mech.*, 1970, **44,** 811.
[22] C. Huh and L. E. Scriven, *J. Colloid Interface Sci.*, 1969, **30,** 323.
[23] J. F. Padday, *Phil. Trans. Roy. Soc. A*, 1971, **269,** 265.
[24] J. F. Padday, *Tables of Profiles of Axisymmetric Menisci* (published by the Author and Kodak Ltd in the form of a set of microfisches, 1972); *J. Electroanal. Interfacial Electrochem.*, 1972, **37,** 313.
[25] J. F. Padday and A. Pitt, *J. Colloid Interface Sci.*, 1972, **38,** 323.
[26] J. F. Padday and A. Pitt, *Phil. Trans. Roy. Soc. A*, 1973, **275,** 489.
[27] *Handbook of Physics and Chemistry* (Chemical Rubber Co. Cleveland, 1955-56), p. 1971.
[28] J. Timmermans, *Physico-chemical Constants of Organic Compounds* (Elsevier, Amsterdam, vol. 1, 1950 and vol. 2, 1965).
[29] *International Critical Tables* (McGraw-Hill, New York, 1928), vol. 4, p. 463.
[30] ref. (29), vol. 3, p. 27.
[31] J. F. Padday, *Proc. IInd Int. Congr. Surface Activity* (Butterworth, London, 1957), vol. 1,