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Measurement of surface tension by pulling a sphere from a liquid

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With 4 figures and 2 tables

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Introduction

The forces which counteract the pull of a wettable rigid sphere from the surface of a liquid are of great interest as a well defined and simple model for the adhesion between two phases.

In this sense in ref. (1) and (2) the force required for detachment of a sphere from a liquid surface has been estimated as a measure for the adherence of particles onto the interface liquid/gas in the flotation process.

Essential part of the problem of adhesion of a sphere is the problem of wetting of a cylinder. For this reason, exact calculation of the adhesive forces became possible after tabulation in (3), (4), and (5) by a computer of the problem for the shape of the liquid surface around vertical wettable cylinder partially immersed into the liquid. The numerical solutions showed that the earlier proposed analytical approximations in (6) and (7) for wetting of a cylinder are not exact.

In this work we make use of the exact solution for the wetting of a cylinder for calculation of the surface tension from the maximum force of pulling a sphere from the liquid. It is a modification of the methods of *Du Noüy* (8) and of *Wilhelmy* (9) where the ring or the plate, respectively, are replaced by a sphere. Recently in (10) it has been theoretically well-founded that at pull of a ring (with an infinitely great radius) from a liquid – the force passes through a maximum. That circumstance gains an essential advantage for the ring method over the plate method. However, for the present, mathematical difficulties restrict the solution for the ring within the limits of full wetting and other approximations (11). As it is shown here a maximum of the force is also present at pulling out a sphere and, moreover, it is possible the angle of wetting to be taken into account and the problem to be solved almost completely. It is even more important that if the sphere is obtained through melting of a vitreous material, a very regular form and homogeneous surface can be obtained which is hardly possible with a ring or a plate. Thus better reproducibility can be expected.

Furthermore, with a sphere, the angles characterising the crossing of the liquid and the solid surfaces at the maximum force are expressed through the central angle α only (fig. 1). The latter is measured most accurately using the geometry of the sphere.

When the plate or the ring are replaced by a sphere, the force of pulling is smaller, particularly with small spheres, where the homogeneity of surface and the regularity of form are greater. So the requirements for sensitivity of the balance, measuring the force of pulling, increase. Moreover, for the steady measurement of the force maximum, the balance must measure without deflection of the balance beam. The contemporary feed back electric balances answer these requirements. By using small spheres the method of measuring the surface tension becomes almost microscopic with respect to the size of the liquid surface. This is an important advantage when it refers to determination of the surface tension in unstable situations.

The circumstances given above will be further explained in more details.

Theory

In fig. 1 a solid sphere partly pulled from the liquid is shown. The most important angles for the analysis of the situation are: α the central

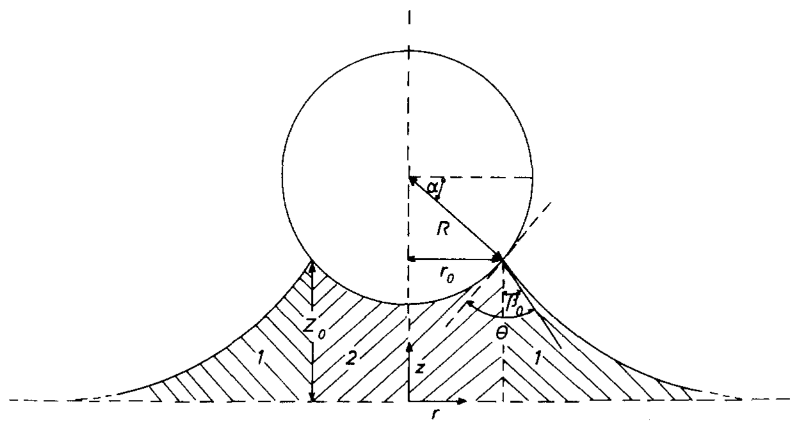

Fig. 1

angle, β_0 the effective angle of wetting of a cylinder of a radius r_0, equal to the radius of the perimeter of wetting and θ the actual angle of wetting of the sphere by the liquid. The parameters of the perimeter of wetting that belong also to the profile of the liquid surface, are denoted by an index "0". The three angles are related by the condition

$$\alpha + \beta_0 = \theta. \qquad [1]$$

The weight P of the raised liquid can be presented as consisting of two parts

$$P = P_1 + P_2. \qquad [2]$$

The part P_1 corresponds to the weight of the raised liquid on the surface of an effective cylinder of radius r_0 and angle of wetting β_0 (weight of the body "1"). It is concentrated upon the perimeter of wetting and for this reason it is equal to the vertical component of the surface tension $\sigma \cos\beta_0$ along that line

$$P = 2\pi r_0 \sigma \cos\beta_0. \qquad [3]$$

The expression [3] gives in an integral form the equilibrium of the capillary and hydrostatic forces over the surface of the meniscus, i.e. integral of the *Laplace*'s equation

$$\sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = z\varrho g \qquad [4]$$

where R_1 and R_2 are both main radii of curvature in every point of the surface, and z is the current ordinate in the same point; ϱ is the difference in densities of the liquid and of the fluid above it and g the gravity acceleration. This can easily be shown by differentiating [3] along r, putting $P = V_1 \varrho g$. Here V_1 is the volume of the meniscus "1" and $dV_1/dr = z\varrho g/\sigma$. With that we obtain

$$\cos\beta/r + d\cos\beta/dr = z\varrho g/\sigma \qquad [5]$$

coinciding with [4], since $R_1 = r/\cos\beta$ (positive in the case) and $R_2 = dr/d\cos\beta$ (negative here) at current abscissa r and β angle with the ordinate in every point of the surface. In this way the eq. [3] is well-founded.

The part P_2 is formed by the weight of a cylinder "2" with basis πr_0^2 and height z_0 minus the weight of the immersed part of the sphere (fig. 1)

$$P_2 = [\pi r_0^2 z_0 - \tfrac{2}{3}\pi R^3 \times (1 - 1.5\sin\alpha + 0.5\sin^3\alpha)]\,\varrho g. \qquad [6]$$

As it is seen P_1 is obtained directly, while in order to calculate P_2 it is necessary to know the solution of [5] for defining the maximum rise of the liquid z_0 at given r_0 and β_0.

We are confining ourselves to the treatment of the case of a moderate pull, shown in fig. 1, where the narrowest part of the profile of the liquid bridge, connecting the sphere with the liquid, coincides with the perimeter of wetting i.e. $\beta_0 \geqq 0$. When $\beta_0 < 0$, under the perimeter of wetting a narrower region appears, according to the solution of eq. [7].

The solution of [5] in (3), (4), and (5) is related to a meniscus with cylindrical symmetry at which the main radii of curvature have opposite signs. This saddle-shaped form does not allow reducing the problem to tabulated solutions for a meniscus in a cylindrical tube or for sessile or pendant drop (where the main radii of curve have the same signs), for instance to the tables of

Bashforth and *Adams* (12). We shall make use of the tables from [3], which are solution of the differential equation

$$\frac{d^2y/dx^2}{[1 + (dy/dx)^2]^{3/2}} + \frac{dy/dx}{x[1 + (dy/dx)^2]^{1/2}} - y = 0 \quad [7]$$

This equation is a dimensionless form of the eq. [5], in which

$$r = x\sqrt{\sigma/\varrho g} \quad \text{and} \quad z = y\sqrt{\sigma/\varrho g} \quad [8]$$

and $\cos\beta$ is expressed through x and y. In the tables from [3] the data for x and y are given for different

$$\varphi = 90° - \beta. \quad [9]$$

When solving the problems for interaction of a sphere with a liquid surface it is important to estimate the correlation between P_1 and P_2. For this purpose it is useful to take under consideration that the second term of P_2 in eq. [6] reduces it. Ignoring that term we shall obtain overestimated values for P_2. Substituting $\pi r_0^2 z_0 \varrho g$ for P_2 and using [8] we get the estimation

$$P = P_1(1 + x_0 y_0/2\cos\beta_0) \quad [10]$$

where x_0 and y_0 refer to given $\varphi_0 = 90° - \beta_0$.

The correction $x_0 y_0/2\cos\beta_0$ is calculated with the tables (3) in dependance of x_0 for $\beta_0 = 0$ and $\beta_0 = 45°$. The result is given in fig. 2 up to values of correction of about 10%.

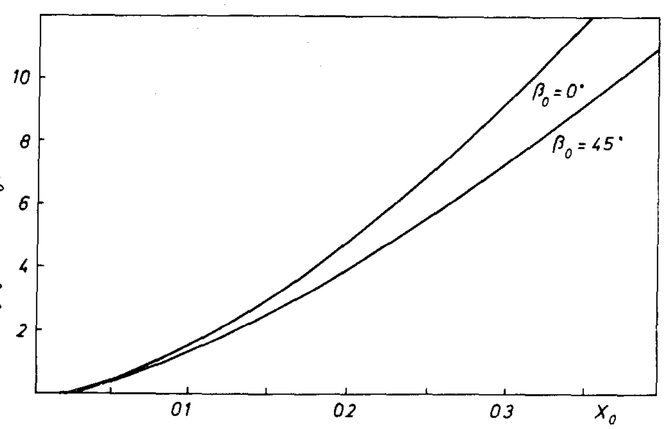

Fig. 2

It can be seen that the effect of β_0 is small. For $x_0 < 0.1$ the correction is below 1%. Since $r_0 < R$, for spheres of radius $R < 0.1\sqrt{\sigma/\varrho g}$, i.e. for $R < 2.28 \cdot 10^{-2}$ cm at $\sigma = 50$ and $\varrho g = 10^3$ or for spheres of diameter smaller than 450 μ, the weight of the deformed liquid (acqueous solution) can be given with sufficient accuracy by

$$P = P_1 = 2\pi r_0 \sigma \cos\beta. \quad [2']$$

Thus this approximation, accepted ad hoc in (1) and (2) at the analysis of the flotation attachment of a sphere to a liquid surface, is now well-founded, as the flotation is effective for particles smaller than 200 μ. By this approximation in (1) and (2) and taking under consideration the eq. [1], it was shown that P has maximum P_m at

$$\beta_{0m} = \theta/2 \quad [11]$$

and respectively

$$\alpha_m = \theta/2, \quad r_{0m} = R\cos(\theta/2)$$

and

$$P_m = 2\pi\sigma R\cos^2(\theta/2). \quad [12]$$

The maximum of P will also be preserved at greater spheres, but will be displaced to greater α and deformed.

The requirements for precision at measuring the surface tension make necessary P_2 to be taken into account. The obtained approximate result indicates where the maximum should be sought for.

The exact calculation requires the use of the complete expression for P, which according to [2], [3], and [6] has the form

$$P = 2\pi r_0 \sigma \cos\beta_0 + \pi r_0^2 z_0 \varrho g - \tfrac{2}{3}\pi R^3(1 - 1.5\sin\alpha + 0.5\sin^3\alpha)\varrho g. \quad [13]$$

Making use of the condition that $r_0 = R\cos\alpha$ and with [8] we get

$$P = 2\pi R\sigma[\cos\alpha\cos\beta_0 + 0.5x_0 y_0 \cos\alpha - x_0^2(1 - 1.5\sin\alpha + 0.5\sin^3\alpha)/3\cos^2\alpha] \quad [14]$$

with $x_0 = R\sqrt{\varrho g/\sigma}\cos\alpha$, $\varphi_0 = 90° - \beta_0$ and y_0, calculated from tables (3) for given x_0 and φ_0.

The maximum value $P = P_m$ will correspond to the maximum of $P/2\pi R\sigma$. After the differentiation on α of the expression in the square brackets in eq. [14], by using the condition [1] we get

$$f_{(\alpha)} = d(P/2\pi R\sigma)/d\alpha = \sin(\theta - 2\alpha) + x_0\left(0.5\cos\alpha\frac{dy_0}{d\alpha} - y_0\sin\alpha\right) + 0.5x_0^2\cos\alpha. \quad [15]$$

The function $f_{(\alpha)}$ can be calculated for given $R\sqrt{\varrho g/\sigma}$ and θ with the help of trigonometric tables and tables (3). Here the derivative

$$\frac{dy}{d\alpha} = \frac{dy_0}{dx_0}\frac{dx_0}{d\varphi_0}\frac{d\varphi_0}{d\alpha} = \frac{dy_0}{dx_0}\frac{dx_0}{d\varphi_0}$$

since $d\varphi_0/d\alpha = 1$ according to [1] and [9]. The transition radians-degrees gives to [15] the form

$$f_{(\alpha)} = 0.017453 \times \left[\sin(\theta - 2\alpha) + x_0\left(28.6533\,\frac{dy_0}{d\alpha}\cos\alpha - y_0\sin\alpha\right) + 0.5x_0^2\cos\alpha\right]. \qquad [15']$$

The range of the used α is several degrees over $\theta/2$ and the obtained $f_{(\alpha)}$ are very close to straight lines with constant slope. With $f_{(\alpha)}$ for given $R\sqrt{\varrho g/\sigma}$ and θ, α_m is found graphically very accurately from the cross of $f_{(\alpha)}$ with the abscissa ($f_{(\alpha)} = 0$). With this α_m and with the used θ, from [1] β_{0m} is calculated. Thus the dependence of β_{0m} on α_m at given $R\sqrt{\varrho g/\sigma}$ is obtained. These dependences for three values of $R\sqrt{\varrho g/\sigma}$ and for range of θ from zero to about 20° are given on the nomograph in fig. 3. As it is seen the influence of $R\sqrt{\varrho g/\sigma}$ is not strong, so that a sure interpolation for $R\sqrt{\varrho g/\sigma}$ between 0.36 and 0.40 is possible[1]).

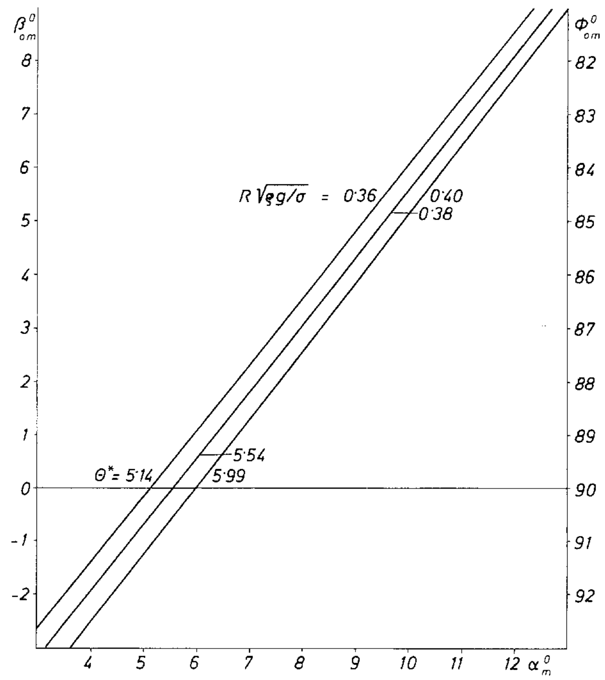

Fig. 3

Since the product $\cos\alpha_m \cos\beta_{0m}$ has the main contribution in P and, as it will be shown, $\sin\alpha_m$ is measured, a nomograph in the corresponding scales is given in fig. 4 for the three chosen

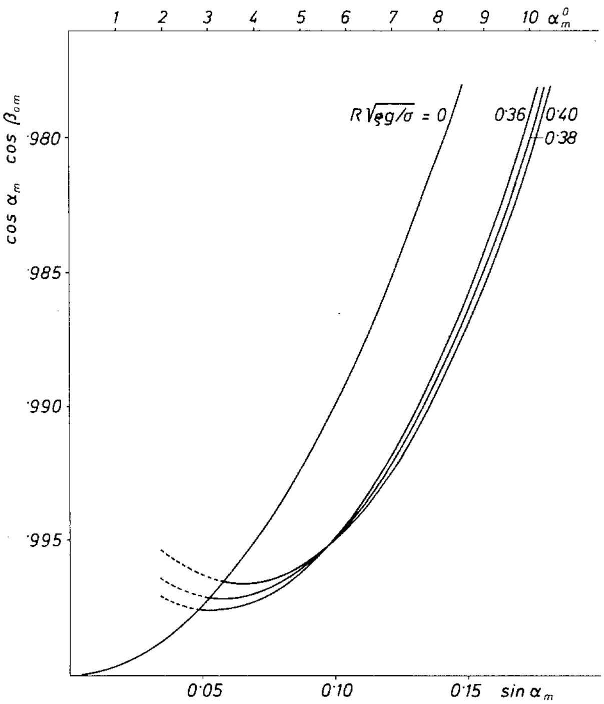

Fig. 4

values of $R\sqrt{\varrho g/\sigma}$. The fourth curve corresponds to $\cos^2\alpha_m$. The values of $\cos\alpha_m \cos\beta_{0m}$ for $R\sqrt{\varrho g/\sigma} > 0$, corresponding to angles of wetting $\theta > 0$ lie to the right of this curve. With all this we have excluded β_{0m}.

For the determination of σ from eq. [14], applied for the maximum of P, we obtain the equation

1) For the calculated cases β_{0m} in dependence of α_m lay on straight lines within the limits of accuracy of tables (3) so that the data from fig. 3 can also be written in the form $\beta_{0m} = A\alpha_m - B$; with A and B from the table. Respectively $\theta = \alpha_m + \beta_{0m} = \alpha_m(A+1) + B$; $A = 1$, $B = 0$ at $R\sqrt{\varrho g/\sigma} = 0$.

$R\sqrt{\varrho g/\sigma}$	A	B
0.36	1.245	6.395
0.38	1.255	6.957
0.40	1.282	7.680

$$\sigma = \sigma_0/\psi \quad [16]$$

with

$$\sigma_0 = \frac{10^{-3}g}{2\pi R}\left[G_m + \frac{2.10^3}{3}\pi R^3 \varrho \times (1 - 1.5\sin\alpha_m + 0.5\sin^3\alpha_m)\right] \quad [17]$$

where $G_m = 10^3 P/g$ is the maximum weight given in mlgr. and R is in cm and

$$\psi = \cos\alpha_m \cos\beta_{0m} + 0.5 x_0 y_0 \cos\alpha_m. \quad [18]$$

The "zero" approximation σ_0 is calculated directly from the measured G_m, $\sin\alpha_m$, R and ϱ. After that σ is found through successive approximations as

$$\sigma_n = \sigma_0/\psi. \quad [19]$$

For this purpose $R\sqrt{\varrho g/\sigma}$ is calculated with $\sigma = \sigma_0$, and from the nomograph (fig. 3) φ_{01} is obtained vs. α_m. With $x_{01} = R\sqrt{\varrho g/\sigma_0}\cos\alpha_m$ and φ_{01}, by the tables (3), y_0 is found and the second term of [18] is calculated. The first term is found from the nomograph fig. 4 for $R\sqrt{\varrho g/\sigma_0}$ vs. the measured $\sin\alpha_m$. By this ψ_1 is obtained and after substitution in [19] σ_1 is found. With σ_1, analogically σ_2 is found etc. until it comes to σ_n with an accuracy corresponding to this of the measurement of G_m and $\sin\alpha_m$.

The consecutive approximations of β_{0m} are found from the nomograph in fig. 3 and with eq. [1] the approximations θ_n for the angle of wetting are calculated.

The curves from fig. 3 show that the sum $\alpha_m + \beta_{0m} = \theta$ decreases with the decrease of α_m. At $\theta < \theta^*$, where $\theta^* = \alpha_m$ for $\beta_{0m} = 0$, the angle β_{0m} becomes negative and, as it has already been noted, the treatment used here is no longer valid. The smallest angle θ^*, limiting the proposed solution, depends on $R\sqrt{\varrho g/\sigma}$ and for $R\sqrt{\varrho g/\sigma} = 0.36$ to 0.40 has the values from 5.14° to 5.99°, according to fig. 3. The angle θ^* decreases with the decrease of $R\sqrt{\varrho g/\sigma}$, respectively of R.

The case $\theta < \theta^*$ will not be treated here. On one hand, when $\beta_{0m} < 0$, as it will be shown, the measurement of $\sin\alpha_m$ becomes inaccurate. On the other hand, when $\beta_{0m} < 0$, the realization of P_m may become impossible because of instability of the system. The analysis of this instability requires additional considerations about the movement of the perimeter of wetting, which are beyond the limits of the fundamental *Laplace*'s equation used up to now.

The limitation of the proposed method of measuring the surface tension for angles of wetting $\theta > \theta^*$ is not fatal. Reducing R to reasonable limits θ^* can be decreased to very small values. Thus α_m and β_{0m} at θ close to θ^*, approach zero and the approximation

$$\sigma = \frac{10^{-3}g}{2\pi R}\left(G_m + \frac{2\cdot 10^3}{3}\pi R_\varrho^3\right)\Big/\left(1 + 0.5 x_0 y_0\right) \quad [20]$$

for $\alpha_m = 0$, $\beta_{0m} = 0$ ($\varphi_0 = 90°$) becomes sufficiently accurate. On the other hand, the preservation of $\theta > 0$ is preferable, since at complete wetting the situation e.g. with the film which covers the bare surface of the sphere, becomes indefinite.

Measurements

For the measurement of the maximum weight, the electric balance Beckmann LM 600 was used. The weight G_m was determined as a difference between the maximum weight at the pull of the sphere from the liquid and its weight before the immersion.

The glass sphere was obtained by melting the tip of a *Thüring* glass fibre, of diameter about 0.3 mm, in a special burner. Through the fibre the sphere was connected with the balance hanging, mounted onto the arm in the manner recommended by the firm-producer of the balance. The most regular sphere, having a diameter about 2 mm, was chosen through microscopic observation from among twenty spheres. The radius of the suspended sphere was accurately measured by photographing from below with appropriate magnification. The equator of the sphere turned out to be without defects, having an average radius $R = 0.1009$ cm at ellipticity less than 0.1%.

The sphere was immersed into the measured solution contained in a teflon bath of diameter about 5 cm. The bath was raised and descended with the help of a micrometric screw, commanded manually or automatically. In order to remove the electrization, the solution in the bath was grounded by a platinum electrode. The whole set was kept in a box with optical windows for side observation, photographing and illuminating the sphere. In order the sphere and the meniscus around it to be visible, the bath was filled until the formation of a convex surface.

The set for the measurement of the central angle, consists of a photocamera with an objective Reichert Neupolar $f = 10$ cm installed on a cathetometer for adjustment, illuminating mercury microscopic lamp HBO 50 with an appropriate condenser and a monochromatic filter. Fine-grained spectral photo plates 6 by 9 cm were used. From the pictures of the profile of the sphere at $G = G_m$ by the help of a spectral photometer the elevation of the equator of the sphere over the perimeter of its wetting and the radius of the sphere were measured in relative units. The ratio of the former to the latter gives $\sin\alpha_m$.

The radius of the sphere was chosen in such a way that G_m would be enough to feel thousandths of dyn/cm for σ. Correspondingly to that the chosen values of the constant $R\sqrt{\varrho g/\sigma}$ from 0.36 to 0.40 in the nomographs of figs. 3 and 4 cover the range of σ for acqueous solutions from 78 to 62 dyn/cm.

As it is known the accuracy and the reproducibility of the data on surface tension are confined not only by the possibilities of the method of measuring but also by the properties of the liquid. The problems of the purity of the water and the surfactants used and the additional complications, connected with the changes in time of the surface tension, go beyond the limits of this work. It is sufficient for the check of the method the angle of wetting of the sphere by the solution to be small enough, but there must be no noticeable hysteresis and the surface tension must be constant during the time of measurement. Aqueous solution of capryc acid 4.10^{-6} mol/l and 10^{-2} mol/l HCl was suitable. That choice was dictated also by other considerations which should not be discussed here. The measurements were carried out at 22 ± 0.2 °C. Since special precautions for purity were not taken, the values obtained must not be considered as absolute data.

The initial data for the calculation of the surface tension of the selected solution are: $G_m = 50.010$ mlg, $\sin\alpha_m = 0.103$ (respectively $\cos\alpha_m = 0.9947$ and $\alpha_m = 5°55'$), $R = 0.1009$ cm, $\varrho = 1.0160$ [according to (13)] and $g = 980.22$ (for Sofia).

The "zero" approximation $\sigma_0 = 80.176$ is calculated according eq. [17]. The accuracy is only limited by the accuracy of measurement of G_m as the sensitivity of the correcting addendum of σ_0 (about 5%) to $\sin\alpha_m$ is small. The approximations σ_1, σ_2 etc. are obtained through dividing σ_0 by ψ_1, ψ_2, etc., according to eq. [19]. The calculation of σ_1 is carried out with ψ_1 in eq. [18], tables (3) and the nomographs of figs. 3 and 4 in a way described at the end of the second part of this paper. With σ_1 obtained, σ_2 and ψ_2 are calculated etc. The results are given in table 1.

The calculations are carried out with the accuracy of tables (3) (up to the fifth sign), which goes beyond the accuracy of measurement of G_m and of $\sin\alpha_m$, in order to show the convergence of the approximations. It is seen that it gives for σ tenths of dyn/cm at $n = 2$, hundredths at $n = 3$, and thousandths at $n = 5$. The tables (3) turned out to have too large step for linear interpolation and their extra specification in the used interval is necessary. So, for instance, interpolation along $x_0 y_0$, which is better linearized vs. x_0 was used. The angle of wetting θ, is faster obtained with accuracy to minutes – already at $n = 3$. The influence of the accuracy of the measurement of $\sin\alpha_m$ on σ was estimated, by calculations with a higher value, $\sin\alpha_m = 0.10424$ instead of 0.103, respectively with $\alpha_m = 5°59'$ against $5°55'$. At that $\sigma_5 = 71.5275$ was obtained against 71.5202. So in that case the change of α_m with 1′ corresponds to a change of σ of 2.10^{-3} dyn/cm. This means that the measured values of G_m and $\sin\alpha_m$ are obtained with coordinated accuracy giving for σ a few thousandths of dyn/cm.

Table 1

n	$R\sqrt{\varrho g/\sigma}$	β^0_{0m}	θ^0	φ^0_0	$\cos\alpha_m \cos\beta_{0m}$	x_0	$\frac{x_0 y_0 \cos\alpha_m}{2}$	ψ	σ dyn/cm
1	.35565	1.20	7.12	88.80	.9946	.35375	.11548	1.11008	72.2251
2	.37471	0.65	6.57	89.35	.9946	.37237	.12545	1.12005	71.5822
3	.37639	0.60	6.52	89.40	.9946	.37440	.12634	1.12094	71.5253
4	.37654	0.60	6.52	89.40	.9946	.37454	.12641	1.12101	71.5209
5	.37655	0.60	6.52	89.40	.9946	.37456	.12642	1.12102	71.5202

The approximate expression $P = P_1 = 2\pi R\sigma$ gives ≈ 80 for σ, which is about 10% higher than the real value, in accordance with the curves of fig. 2.

The given example responds to the requirement $\theta > \theta^*$. Indeed, in this case $R\sqrt{\varrho g/\sigma} \approx 0.37$, and according to fig. 3 the angle $\theta^* \approx 5.34°$, smaller than the measured $\theta = 6.52°$ (table 1).

It was interesting to check up the accuracy of the approximate formula [20] in that case. For it, with the used initial data (and putting $\alpha_m = 0$, $\beta_{0m} = 0$ and $\varphi_0 = 90°$), we obtain $\sigma_0 = 80.6958$ and the successive approximations for σ, shown in table 2.

Table 2

n	$\psi = 1 + 0.5 x_0 y_0$	σ dyn/cm
1	1.11756	72.2070
2	1.12778	71.5523
3	1.12865	71.4976
4	1.12872	71.4932
5	1.12872	71.4932

As it is seen, now the result (σ_4) is lower than the exact value 71.5202 from table 1 by 0.0270 only. This fact shows that by decreasing θ and θ^* (the latter by using smaller R), a range of accuracy of the approximate formula [20] ensuring thousandths of dyn/cm can be reached without measuring α_m. In that sense, the use of smaller spheres and more precise balance is very perspective. By that the lower limit of $\theta = \theta^*$ can be lowered to almost complete wetting.

Yet, several more notes can be made over this. During the pull of the sphere over its "bare" surface and over its holder eventually remains a film whose weight adds to G_m. At a given θ the film has an equilibrium thickness defined by the equality of the hydrostatic pressure with the disjoining pressure in the film. On the level of the perimeter of wetting that pressure is $z_0 \varrho g$ or $y_0 \sqrt{\varrho g/\sigma}\, \varrho g \approx 160$ dyn/cm^2 in the here considered case ($y_0 \approx 0.6$, $\sigma \approx 70$ and $\varrho g \approx 10^3$). At pressure of several hundreds dyn/cm^2 the equilibrium films are always considerably thinner than 10^{-5} cm especially in the cases when, as in our case, the electrostatic component of the disjoining pressure is suppressed by considerable concentration of electrolyte [see the data concerning aqueous films on silica (14)]. If we use the overestimated value for the thickness of the equilibrium film 10^{-5} cm we obtain for the weight of the film on the bare half of the sphere about $2\pi R^2 \cdot 10^{-5} \approx 6 \cdot 10^{-7}$ g which is below the accuracy of the measurement of G_m.

It is possible that the contact angle has hysteresis. At that its value will be a function of the motion velocity of the wetting perimeter along the sphere surface and the maximum of G_m will not correspond to the maximum at constant angle θ. With that the connection β_{0m} from α_m (eq. [15] and figs. 3 and 4) will not be valid. The hysteresis is easily found by the difference of the weight maxima at pull and immersion of the sphere. In our case, this difference was below the sensitivity of the balance. For the present we are not able to estimate the influence of the hysteresis and we recommend for that purpose the sphere to be chosen and (or) its surface modified in such a way that the hysteresis be below the accuracy of weighing. In any case the pull of the sphere must be carried out slowly enough so that the film on it be drained and a constant contact angle be reached. A criterion for reaching such a velocity is that diminishing the latter does not noticeably influence G_m.

It turned out possible with a sphere to describe completely the weight-method for measuring the surface tension which is impossible, at least for the present moment, with a plate or a ring. However, in spite of this and in spite of the very high reproducibility, due to the regularity of the perimeter of wetting with small spheres, the determination of σ with accuracy of a thousandth of dyn/cm is a complicated task. It would be naive to think that by the other weight-methods (plate, ring) the accuracy of the measurements is only determined by the accuracy of weighing. Therefore, with these methods the accuracy of determination of the surface tension could not be estimated at present.

We are thankful to Unilever Research Laboratory, Port Sunlight, for the feed-back electric balance and for the detailed data about the weight-methods of measuring the surface tension they placed at our disposal.

Summary

A new method for determination of the surface tension by measuring the maximum weight at the pull of a small vitreous sphere from the liquid is proposed. The exact solution of the problem is found and is shown how the wetting of the sphere must be taken into account through the central angle formed between the sphere radius passing through the perimeter of wetting and the horizontal surface. A set for measuring the maximum weight and the central angle is described. The accuracy of determination of the surface tension and of the angle of wetting is estimated to be thousandths of dyn/cm and a few minutes, respectively. Some limitations of the method are discussed as well as the possibilities to overcome them. Various approximate solutions are treated and, in particular, it has been shown that the approximation previously used in the flotation model is satisfactorily accurate in that case.

Zusammenfassung

Eine neue Methode für Bestimmung der Oberflächenspannung wird durch Messung des Maximalgewichtes bei dem Ausziehen einer kleinen benetzbaren Kugel aus der Flüssigkeit vorgeschlagen. Es wurden die genaue Lösung des Problems und die Abhängigkeit des Kugelgewichtes von dem Zentralwinkel zwischen dem Benetzungsrand und der horizontalen Oberfläche gefunden. Die Messung des Maximalgewichtes und des Zentralwinkels wird beschrieben. Die genaue Bestimmung der Oberflächenspannungen fordert die Abschätzung des Winkels mit einer Genauigkeit von einigen Minuten.

Es werden die Anwendungsmöglichkeiten der Methode diskutiert. Es wird gezeigt, daß die Fehler der Annäherungslösungen, die bei dem früheren Flotationsmodell verwendet wurden, ihn genügend befriedigen.

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