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Factors limiting the accuracy of measurements of surface tension by the sessile drop method

R. SANGIORGI, G. CARACCIOLO*, A. PASSERONE
Istituto di Chimica Fisica Applicata dei Materiali, C.N.R. Lungobisagno Istria 34, 16141 Genova, Italy

Different sources of error in determining surface tension by the sessile drop technique are discussed. The influence of uncertainties in measuring drop co-ordinates are quantitatively evaluated, and the results tested on Ag and Pb drops at different temperatures. Shifts in surface tension values, due to errors in determining the exact scale factor and to errors in reading temperature or density, are calculated, and a nomographic chart, to find the optimum drop weight, is also presented.

1. Introduction

Since 1883, when the elegant work by Bashforth and Adams [1] was published, an accurate numerical solution of the fundamental Laplace equation for uniform-tension surfaces has been available to anyone who wants to deduce surface tension values from measured curvatures of liquid interfaces.

Fluid drops resting on horizontal supports, that is, "sessile drops", have always attracted the attention of scientists, especially for measurements at high temperatures, both because such drops offer minimum contact area with container walls, and because true equilibrium conditions may be readily attained. But, in spite of their graceful and apparently simple shape, problems always arise when precise values of surface tension are required, as demonstrated by the large sum of scattered values reported in the literature, even in the case of the best-known metals.

In this paper, on the grounds of our experience in this field, we point out some main points which seem to have been disregarded or not sufficiently quantified in previous, though excellent, reviews [2–6].

The measuring of surface tension by the sessile drop technique is essentially based on the determination of the shape factor β and of the radius of curvature b at the drop apex, the two parameters being linked by the relationship:

$$\beta = \frac{b^2 \rho g}{\sigma} \tag{1}$$

where ρ is the density difference between the liquid and the surrounding medium, g the acceleration due to gravity, and σ the interfacial tension. These quantities are included in the general equation describing the free surface of the sessile drop:

$$\frac{d^2 z}{dx^2} + \left[1 + \left(\frac{dz}{dx}\right)^2\right] \frac{dz}{x dx} = (2 + \beta z) \left[1 + \left(\frac{dz}{dx}\right)^2\right]^{3/2} \tag{2}$$

which has no analytical solution. For this reason, two main procedures are nowadays employed:

(a) utilizing the tables prepared by Bashforth and Adams a century ago by the method of quadratures;

(b) utilizing computerized non-linear fitting methods, which fit the measured drop profile to a theoretical one by optimizing some parameters, like σ and β.

Typical examples of the two methods are those proposed by Dorsey [7], Kozakevitch and Urbain [8], Butler and Bloom [9], and Maze and Burnet [10].

Dorsey's method is based on the measurement of the ratio of the distance OM (Fig. 1) (when

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*Present address: Laboratorio di Chimica, Facoltà di Ingegneria, Fiera del Mare 16129 Genova, Italy.

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$\phi = 45°$), to the maximum radius of the drop. This value is then introduced in an empirical equation (derived from Bashforth and Adam's Tables), which immediately gives the required σ value.

Kozakevitch and Urbain [8] improved this technique by simultaneously measuring the $\mathrm{OM}/r_{\max}$ ratio for four different values of ϕ (45°, 60°, 120°, 135°). Four β values are then found by interpolating the above-mentioned tables, weighting these values, giving preference to those corresponding to the higher ϕ values, and finally finding the correct σ value from a special table of $p = r/b$ values against β (average).

On the other hand, computerized methods do not follow the work by Bashforth and Adams, and every time find the best fitting of the above parameters.

In the following we shall refer both to the methods of Kozakevitch and Urbain and Maze and Burnet as they represent, in our opinion, good typical examples of the two kinds of approaches.

We shall discuss three principal sources of error which affect final surface tension values. Reference will only be made to the two methods mentioned above, even if these sources of uncertainties often undermine other methods, too.

We distinguish three main classes:

(a) errors in the measurement of the drop profile;

(b) errors arising from density determination;

(c) physico-chemical effects.

2. Measurement of the drop profile

2.1. Errors in reading drop co-ordinates

With reference to the method of Kozakevitch and Urbain [8], we are able to quantify the influence of measuring errors on drop co-ordinates according to the following considerations.

The variation of σ on β values may be written, from Equation 1, as:

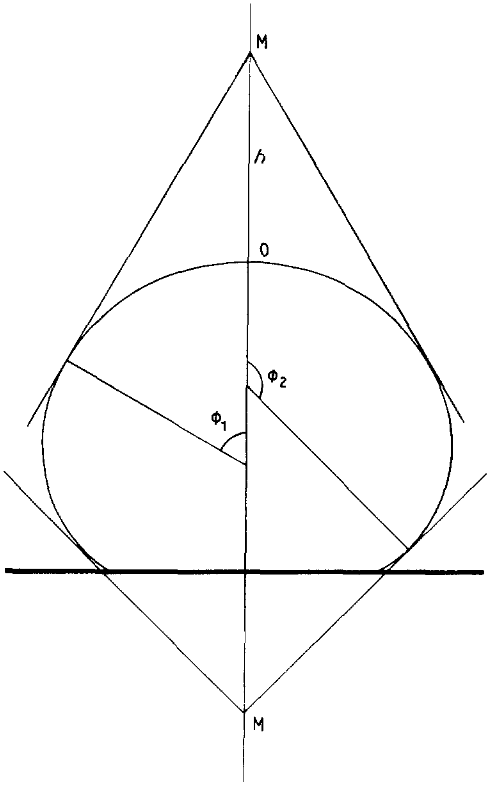

Figure 1 Sessile drop profile. Dorsey and Kozakevitch construction.

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\beta} = -b^2\rho g\frac{1}{\beta^2} - \frac{2\rho g r^2}{p\beta}\frac{\mathrm{d}p}{\mathrm{d}\beta}$$

$$= \frac{\sigma}{\beta}\left[1 + \frac{2\beta}{p}\frac{\mathrm{d}p}{\mathrm{d}\beta}\right], \qquad (3)$$

where $p = r/b$ is the ratio of the maximum radius of the drop to the radius of curvature of the apex. But, as p and $u = h/r$ (see Fig. 1) are both functions of β, then $\mathrm{d}u/\mathrm{d}\beta = f'(\beta)$ and $\mathrm{d}p/\mathrm{d}\beta = h'(\beta)$, so that:

$$\frac{\mathrm{d}\sigma}{\sigma} = \left|\frac{\mathrm{d}u}{\beta f'(\beta)}\cdot\left\{1 + \frac{2\beta}{h(\beta)}h'(\beta)\right\}\right|. \qquad (4)$$

$f(\beta)$ and $h(\beta)$ are easily found by a suitable fitting of tables similar to those published in [8]. We employ the following relationship, in order that the first derivative may be as smooth as possible:

TABLE I Coefficients of the generalized Equation 5. $0 < \beta < 8$

	ϕ	A	B	C	D	S.D.
$u = f(\beta)$	45	0.3987	5.394×10^{-2}	–	-2.1243×10^{-4}	6.4×10^{-4}
	60	0.9799	8.527×10^{-2}	–	-4.7472×10^{-4}	1.2×10^{-3}
	120	3.0781	$-0.374\,29$	6.8368×10^{-2}	-1.0882×10^{-3}	1.1×10^{-3}
	135	2.5049	$-0.472\,36$	9.5222×10^{-2}	-1.8164×10^{-3}	1.3×10^{-3}
$p = h(\beta)$	–	1.0424	$-0.159\,82$	–	7.4322×10^{-4}	1.8×10^{-3}

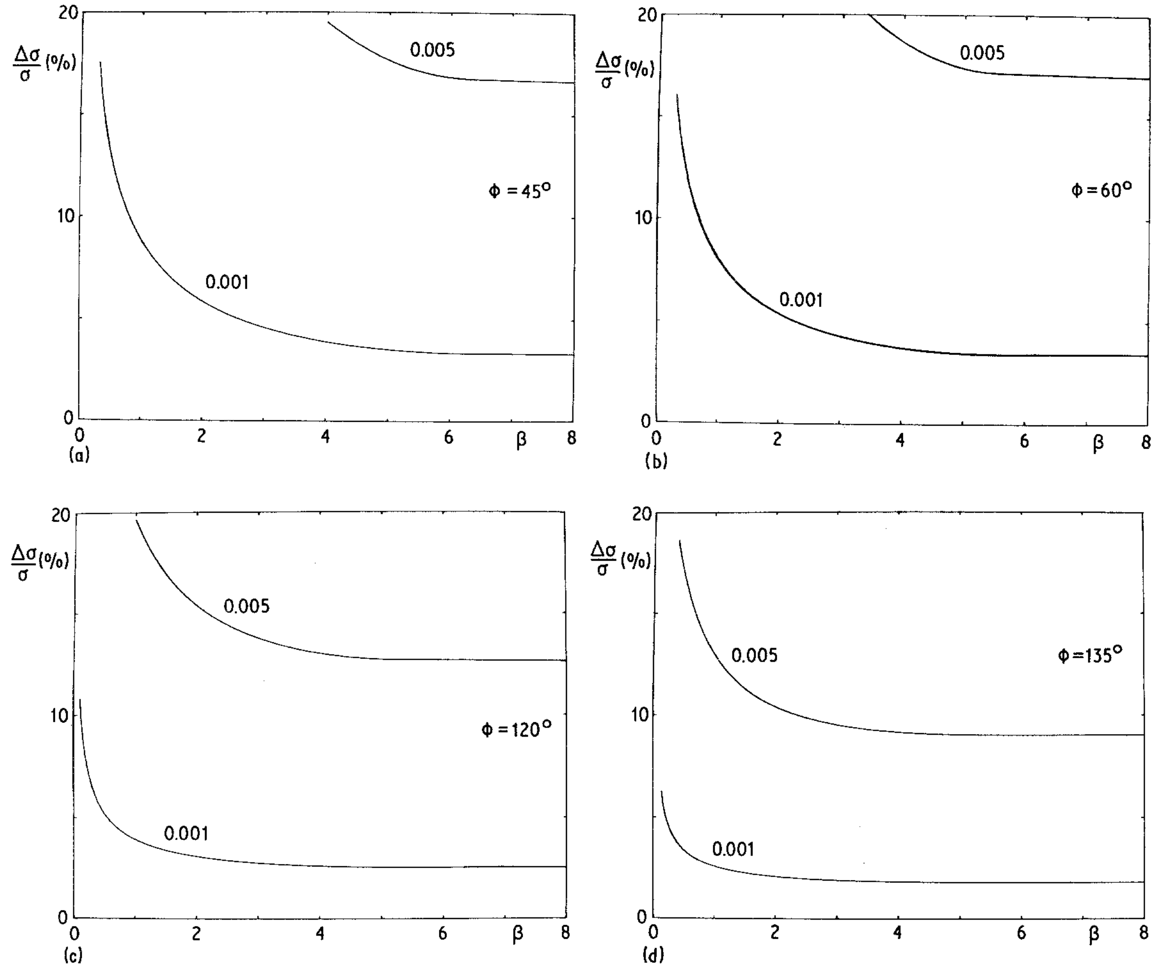

Figure 2 Relative errors in surface tension as a function of β, for measuring uncertainties of 0.1 and 0.5%.

$$u = A + B\sqrt{\beta} + C\beta + D\beta^2; \qquad (5)$$

the coefficients appearing in Equation 5 are given in Table I. $\mathrm{d}u$ can be evaluated by the relationship [8]:

$$\mathrm{d}u = \frac{\delta}{r}\left(u + 1 + \frac{1}{|\cos\phi|}\right) \qquad (6)$$

where $\phi = 45°, 60°, 120°, 135°$, and δ is the true measuring uncertainty in the X-direction.

The results of $\Delta\sigma/\sigma$ against β reported in Fig. 2 for $\delta/r = 0.1\%$ and 0.5% clearly show that, for each ϕ value, the value of σ is always affected by a large error, which turns out to be 2–5% (when $\beta > 2$) if we can read co-ordinates with an accuracy of, at least, 0.1%. The error is larger for $\phi = 45°$ and decreases for $\phi = 60°, 120°, 135°$. It is equally worth noting that, if in reading co-ordinates, a precision higher than 0.1% cannot be obtained, it would be useless to work with drops with β values less than 2, since it would result in errors of 10–50%. Nevertheless, the simultaneous application of the four sets of measurements to the same drop, strongly reduces the standard error of the sample, bringing it down to 1.5–2%, which value is commonly found through a correct application of this method.

The consideration made above also demonstrates that the effect of drop size on the accuracy of surface tension measurements found by Dismukes [19] and Bonfield [20] must be seen, in a more general way, as a dependence on the β factor. For drops of the same material at the same temperature this effect turns out to be governed by the drop size.

2.2. Errors due to uncertainties in the magnification factor

The knowledge of the magnification factor, that is, the ratio between the true and measured dimensions of the drop is a necessary condition in computing surface tension from experimental observations. Taking into account Equation 1, we see that the scale factor F affects only the radius of curvature b. The dependence of σ on F can be written as:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}F} = \frac{b^2 g\rho}{\beta} 2F$$

that is

$$\frac{\mathrm{d}\sigma}{\mathrm{d}F} = 2\frac{\sigma}{F} \tag{7}$$

The relative uncertainty in σ is then twice as great as the relative uncertainty in the scale factor. Fig. 3 shows that Equation 7 is verified in two real cases, namely Ag and Pb at 1100 and 510° C, respectively.

2.3. Presence of geometrical anisotropies

A particular example of measuring inaccuracies is given by the presence of some anisotropy, either in the optical path or in the measuring instrument. Anisotropy may also arise during the development of the photographic film. We evaluated this effect for the same drops as before, assuming the Z-scale factor to be 0.1, 0.5, and 1% larger than the X-scale factor. We can see, immediately from Fig. 4 that co-ordinates have to be measured with an accuracy higher than 0.2% of each other, in order to let the relative uncertainty in σ be under 1%. This is indeed a very important contribution to total accuracy, which requires both careful tests on spherical aberrations and consistent X–Z measurements.

As far as recording of the drop profile is concerned, the best suited method is to make measurements directly on the film. This means that an optical bench is highly recommended, and good illumination of the drop is mandatory. Smolders and Duyvis [11] pointed out that a parallel light beam is necessary in order to avoid light beams reflected by the liquid surface altering the recorded drop profile. Even if we found, in our experiments, that this condition is not so strict, if a sufficiently high length–diameter ratio is used for the laboratory furnace, it is worth noting that an error of ± 5 μm in the positioning of the drop apex, which might be due to spurious reflections, could result in an uncertainty of about ± 1% in surface tension. It is thus very advisable to use a monochromatic filter (for example, Wratten 22 on a mercury lamp in order to pass the yellow 0.577–0.579 μm band) to avoid diffraction effects, to obtain better focusing, and to exploit the photographic film in its maximum sensitivity range.

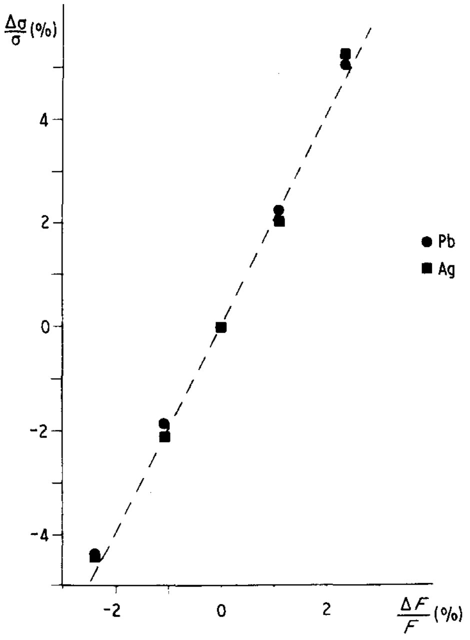

Figure 3 Relative errors in surface tension as a function of uncertainties in scale factor. Tests on Ag and Pb drops.

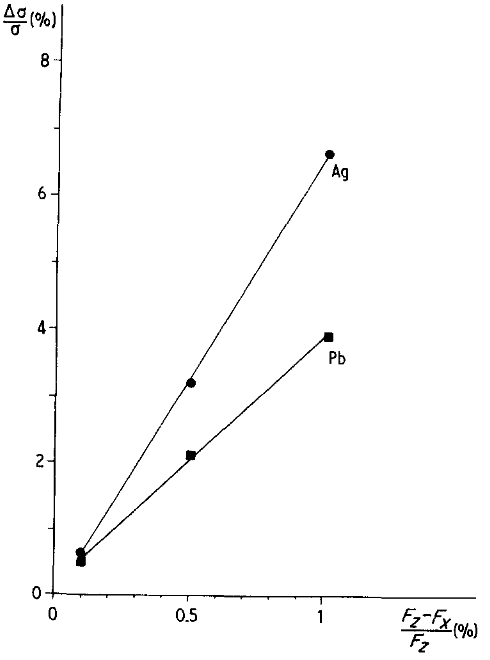

Figure 4 Relative errors in surface tension as a function of measuring anisotropy along the X- and Z-directions. Tests on Ag and Pb drops.

Drops must be perfectly levelled and with a perfect cylindrical symmetry. In order to fulfil this condition, when contact angles are not to be measured, we prefer to use supports with a small cylindrical hole or a spherical cup drilled in them.

The above considerations clearly show, in a quantitative way, that large uncertainties in σ values may stem from the following factors:

(1) choice of an inappropriate β value (lower than about 2);

(2) utilization of a "not excellent" measuring system;

(3) inaccuracies in optical arrangements and in the photographic recording system.

We think that the great dispersion of experimental data usually found even in the case of the "simplest" metals is mainly due to these effects.

3. Error in density

Density of the liquid metal is one of the "external" parameters which it is necessary to know in order to apply the sessile drop method.

In principle, the two methods described in this paper are able to give the volume of the molten drop. The knowledge of the exact weight of the drop immediately gives the required density value.

Nevertheless, we found that Kozakevitch's method does not give the volume to the necessary precision; on the contrary, in order to apply correctly the values derived from Maze and Burnet's method, it is necessary to evaluate accurately the evaporation rate of the molten phase, for example, by means of parallel experiments on a thermobalance [12]. In normal practice, good density values are taken from the literature and used to evaluate σ. However, the temperature of the drop should be known exactly. Referring again to Equation 1, we have:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}T} = \frac{\sigma}{\rho}\frac{\mathrm{d}\rho}{\mathrm{d}T}\,. \qquad (8)$$

Table II shows the magnitude of this correction for silver and germanium. From Equation 8 and from the examples shown in Table II, we see that any error in determining the true temperature of the sample is, in part, self-compensated by the effect of the negative temperature coefficient of the sample density.

4. Physico-chemical effects

The great influence of adsorption of foreign elements on surface tension values is very well-known and does not require any further discussion [13, 14]. It is only worth noting that the ability to depress surface tension, i.e. "tensioactivity", is strictly connected with the difference between the surface tensions of the two pure components. It should be pointed out that even small amounts of active elements, like oxygen, sulphur, phosphorous, etc., are sufficient to dramatically depress the surface tension of a pure metal (0.1% S lowers the σ of Fe by 30% [15], and 10^{-4}% O lowers the σ of Ag by about 15% [16]).

For this reason, not only is it necessary to make a chemical analysis before and after runs, but more sophisticated techniques, like Auger spectroscopy [17], should also be employed in order to make continuous *in situ* analysis of the surface composition of the liquid drop. Unfortunately, however, all techniques for surface analysis utilize the emission of electrons or ions, and for the same reason, UHV techniques are required. This condition severely limits the number of liquid metals that it is possible to investigate. At the same time, evaporation effects become more important, leading to a variation in surface tension values [18].

Similarly, it is equally important to know the purity of the gases employed: continuous monitoring of the oxygen content is today possible by means of solid-state probes [16].

5. Conclusions

Different sources of errors which are often encountered in determining surface tension by the sessile drop method have been investigated.

"Computerized" and "classical" methods used to obtain surface tension values from measurements on the drop shape propagate the various classes of errors in different ways. Independently of the method employed, we found that uncertainties in

TABLE II Effect of temperature in determination of σ values (from Equation 8)

Metal	Temperature (° C)	σ ($\mathrm{mN\,m^{-1}}$)	ρ ($\mathrm{g\,cm^{-3}}$)	$\frac{\mathrm{d}\rho}{\mathrm{d}T}$ ($\mathrm{g\,cm^{-3}\,K^{-1}}$)	$\frac{\mathrm{d}\sigma}{\mathrm{d}T}$ ($\mathrm{mN\,m^{-1}\,K^{-2}}$)
Ag	1100	860	9.22	-9.07×10^{-4}	8.46×10^{-2}
Ge	1100	575	5.41	-5×10^{-4}	5.3×10^{-2}

the scale factor are magnified by a factor of two in surface tension values. However, if this uncertainty is present in only one measured direction (geometrical anisotropy), final values may exhibit an uncertainty from four to six times larger (depending on the β value). On the contrary, errors in reading temperature and then in determining density affect the real value of σ to a much smaller extent.

On the other hand, an analysis of the effects of errors in measuring co-ordinates on final σ values is only possible, in a fairly simple way, when using classical methods. Our analysis demonstrated that co-ordinates have to be measured to a precision greater than 0.1% (with β values higher than 2), if an accuracy of σ of more than 2% is required.

The above considerations demonstrate that the factors limiting the precision in the determination of surface tension values are, still, accuracy and reproducibility in reading the co-ordinates of the drop profile. Every improvement in this direction, together with the control of surface segregation, will bring the sessile drop method to the same level of accuracy as typical in other low-temperature methods.

Appendix

In this paper, we have demonstrated that, in order to minimize errors, it is necessary to work with drops with values greater than two. It is then necessary to know *a priori* the weight W of the drop to be melted. From Equation 1, we see that β depends on the system we are considering: in general we need to link the mass of the drop to β through the values of ρ, σ, θ and its volume.

From the tables of Bashforth and Adams [1], we find the value of $V^* = V/b^3$, given θ and β. On the other hand,

$$W = V\rho g \tag{9}$$

From Equations 1 and 9, we obtain

$$W = V^*(\rho g)^{-\frac{1}{2}}\sigma^{\frac{3}{2}}\beta^{\frac{3}{2}} \tag{10}$$

which represents the required relationship.

Equation 10 can be represented in nomographic form as in Fig. A1.

Procedure

First, an estimation of θ is made and the value of

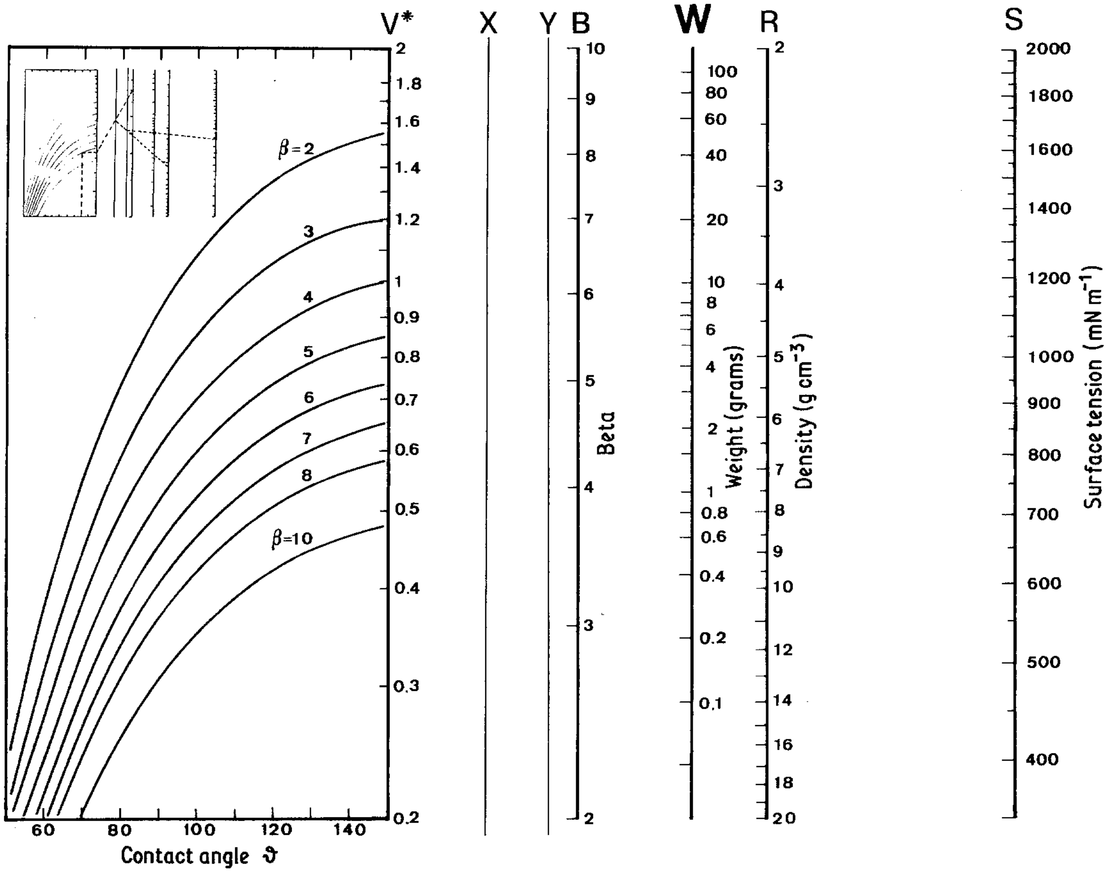

Figure A1. Nomographic chart for determining the optimum drop weight from a given set of σ, ρ and β values.

$V^* = V/b^3$, corresponding to the desired β value, is found. A line is then set up through the V^* value and the β value on the B scale: the intersection of this line with the X reference line is noted. A second line is then established from this point to the selected density value (R scale), and the intersection with the Y reference line is again noted. Then, a third line from this point to the estimated value of σ on the S scale will intersect the W scale at a value which is the required weight of the drop expressed in grams.

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