DETERMINATION OF THE DYNAMIC SURFACE TENSION WITH VARIOUS STALAGMOMETERS BY THE DROP WEIGHING METHOD

J.Kloubek[a], K.Friml[b] and F.Krejčí[c]

[a] J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, 121 38 Prague 2,
[b] Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6,
and [c] Department of Chemical Technology of Fibrous Materials,
Institute of Chemical Technology, 532 10 Pardubice

A procedure of evaluation of the dynamic surface tension suggested earlier has been verified. The dependence between the mass of the detached drop and the rate of its formation was determined by means of three stalagmometers with different sizes of the dripping area and with a different angle of the capillary edge. The results confirm that the usual correction factors of Harkins and Brown do not hold for the dynamic values measured under the conditions used even in the case of extrapolation to an infinitely long age of the surface. The evaluation of the results shows that the blunt edge of the capillary does not confine the base area of the hanging drop. For the dynamic surface tension of aqueous solutions of sodium dodecyl sulfonate a satisfactory agreement has been observed for all stalagmometers under investigation.

The surface tension is an important quantity which for pure liquids is determined with sufficient accuracy by a number of methods. Some difficulties arise in measurements of solutions of surface active compounds where so far attention has been mainly concentrated on the equilibrium surface tension, γ_e. The number of adsorbed molecules of the surface active component depends on the age of the solution surface; as a consequence, a surface having the age t exhibits a so-called dynamic surface tension, γ_t, and $\gamma_t \geqq \gamma_e$. A number of technically important processes occur under conditions where γ_t is operative, but up to now little attention has been paid to the determination of these values. In order to compare the results obtained by various methods, it seems suitable to relate γ_t measured under dynamic conditions to such effective age of the surface at which the same γ_t would be achieved by a solution with a constant surface area with exclusion of the effect of convection. For this purpose, methods of evaluation of measured values have recently been suggested for the drop weighing method[1] and the maximum bubble pressure method[2,3]. The results obtained by using both these procedures were compared for solutions of sodium dodecyl sulfate with those measured by the static Wilhemly plate method[4].

Good agreement was found between the dependence of γ_t on the effective age and on the age of the static surface[1,5].

The drop weighing method allows us to measure γ_t for surface ages starting from several seconds upwards. Its advantage consists in that it yields well-reproducible results also for solutions for which the maximum bubble pressure method is limited, *e.g.* because of foaming. Other methods are not suited for the determination of γ_t in the range of several s. For the stalagmometer examined earlier it was found[1] that in the drop-weighing method the usual correction factors of Harkins and Brown did not hold either for γ_t or for γ_e obtained by extrapolation of the dynamic values. Therefore, a procedure has been suggested the first step of which consists in an empirical determination of deviations ΔG_t from G_s extrapolated to $1/t_i = 0$ for the drop masses G_t formed under dynamic conditions at drop formation intervals t_i. These deviations determined for water hold also for aqueous solutions of surface-active compounds, for which however $G_t - \Delta G_t = G_s$ is not constant, unlike pure liquids, but depends on t, if $\gamma_t > \gamma_e$. For pure liquids, a linear dependence was found between the known $\gamma_t = \gamma_e$ (only γ onwards) and the determined values of G_s, which can be described by a relationship $G_s = k_s W_c$, where W_c is the cohesion work of the liquid, and k_s is a constant proportional to the size of the area on which the hanging drop is divided. As will be shown below, for values extrapolated from dynamic measurements to an infinitely long time this area is also proportional to the area of the lower end of the capillary. According to the empirical correction factors suggested by Harkins and Brown[6] the drop mass is proportional to the external perimeter of the capillary, and the correction factor depends on γ. On the other hand, in dynamic measurements k_s is independent of γ. This does not mean of course that the correctness of the correction factors should be denied. Their validity has been verified in papers of many authors for pure liquids and for drops forming for an adequately long time (according to the radius of the capillary, $3-15$ min) on capillaries possessing the required properties. However, as has been mentioned in an earlier paper[1], it is questionable if even under such conditions the use of the correction factors leads to correct results for solutions of surface-active compounds.

According to the procedure suggested for dynamic conditions, which for the time being has been verified with solutions of sodium dodecyl sulfate only on one stalagmo-
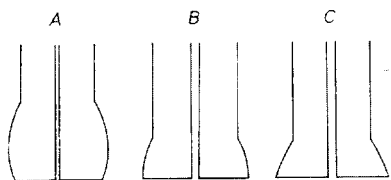

FIG. 1

Scheme of the Lower Parts of Capillaries of Stalagmometers

meter[1] and has been used for the characterization of foaming solutions and dispersions[7], it holds that $t = t_i$. A question remains whether the procedure described above is generally valid, which may be answered by obtaining reproducible results for solutions of surfactants using various stalagmometers. This is the subject of this paper, in which three different stalagmometers were used and γ_t of sodium dodecyl sulfonate solutions was evaluated.

EXPERIMENTAL

The measurements were carried out on stalagmometers denoted below by A, B, C, the characteristics of which are given in Table I. The stalagmometer B has already been used in an earlier work[1]. The shape of the orifices of the capillaries is shown in Fig. 1. The angle of the edge at the lower end of the capillary is obtuse for A, rectangular for B and sharp for C. The magnitude of the lower area of the capillary increases from A to C. The inner diameter of the capillaries is approximately characterized by the maximum flow rate of the liquid and by the respective time of drop formation. The liquid inside the stalagmometer was thermostated to $20 \pm 0.1°C$ by means of a water jacket, the room temperature was maintained at $20 \pm 1°C$. At a dripping rate higher than 10 s per one drop 10 drops were collected and weighed each time, at lower rates the number was 5 drops. The time of drop formation was measured as an average of all collected drops, but it did not differ perceptibly for the individual drops during the course of one measurement. The liquid dripped down from the stalagmometer owing to its own weight and the rate was controlled by throttling the hose mounted on the upper orifice of the stalagmometer tube. Water, $\gamma = 72.8$ dyn/cm, and n-propanol, $\gamma = 23.8$ dyn/cm, were used for the measurements. Solutions of sodium dodecyl sulfonate, m.w. 272.4, were prepared in water redistilled
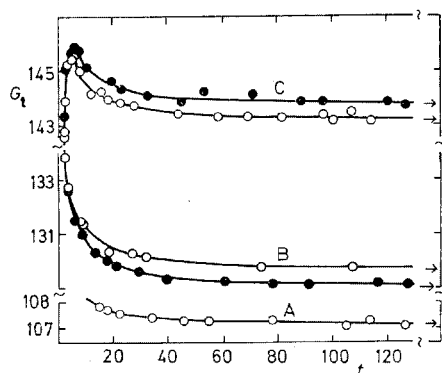
FIG. 2

Dependence of the Drop Mass G_t (mg) of Water at 20°C on Time of Their Formation t (s) for Stalagmometers A, B, and C
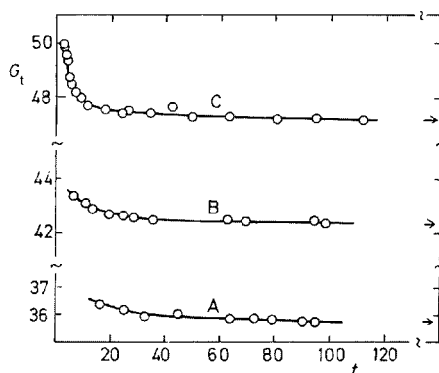   ○ First series of measurements, ● repeated series of measurements.

FIG. 3

Dependence of Drop Mass G_t (mg) of n-Propanol at 20°C on Time of Their Formation t (s) for Stalagmometers A, B, and C

from an alkali solution of $KMnO_4$ through a column with a drop trap. A comparison with the values measured for higher-boiling liquids shows[1] that the effect of the possible unsaturation of vapours in the vicinity of the drop did not influence the results any further.

RESULTS AND DISCUSSION

We found that of the variable parameters it is the lower area of the capillary and its shape which affect the drop mass; the effect of the area is obvious and has been pointed out above. The inner diameter of the capillary controls only the flow rate of the liquid, but not G_t for a given t. It is quite likely that the capillaries used did not satisfy exact requirements as presented in the paper of Harkins and Brown[6], but in the evaluation used this fact does not matter.

The results of measurements of the dependence between the drop mass G_t and the time of its formation for water and n-propanol are given in Figs 2, 3. For the stalagmometers B and C the measurements were repeated in two independent series after a major time lag. Other series of measurements are recorded in Fig. 2 (full points) and exhibit systematic deviations by c. 0·6 mg. The cause of deviations from a continuous dependence in the same series may consist in variations in room temperature. A change in the surface tension of water due to a deviation of 1°C would cause a difference in the drop mass of c. 0·3 mg. The results show that temperature did not affect the measurements to any essential degree. The vertical position of the capillary was controlled visually according to the symmetry of the hanging drop. It is possible that this control was insufficient and that the cause of systematic deviations between independent series of measurements consisted in an imperceptible change in the position of the capillary.

In Fig. 2 we can see a striking increase in G_t as a function of t for the stalagmometer at short time intervals of drop formation. After reaching the maximum, G_t decreases similarly to the other cases. It is probable that such shape of the dependence is a general one, but it was only in the given case that a sufficient rate of dropping was achieved at which the maximum appeared. Dependences in Figs 2 and 3, besides exhibiting an initial increase at C, have a shape which satisfies the equation

$$G_t = G_s + kt^{-1} . \qquad (1)$$

G_s increases with the outer diameter, d, of the lower area of the capillary, G_s/d^2 (Table I) is approximately the same for the same liquid in the stalagmometers B,C, but clearly higher for A. Assuming (contrarily to the corrections of Harkins and Brown[6]) that the hanging drop is torn apart only owing to a disturbed equilibrium between the cohesive force and the drop weight on an area proportional to the lower surface of the capillary, G_s/d^2 should be constant for the same liquid on various stalagmometers. According to this assumption, the edge of the capillary with obtuse

angle in A does not form a boundary of the drop base, but is overlapped by the margin of the drop. Compared to G_s/d^2 for the stalagmometers B and C, d for the stalagmometer A found by means of water and of propanol should be c. 0·89 cm, which approximately corresponds to the outer diameter of the capillary in the widest part having the actual diameter 0·90 cm (Fig. 1), while the diameter of the lower area is only 0·78 cm. The d values of the lower areas calculated from G_s for water by means of the correction factors of Harkins and Brown[6] — 0·77 cm (A), 0·92 cm (B), 1·02 cm (C) — are in good agreement with the measured values, but in the case of the same calculation carried out for n-propanol — 0·75 cm (A), 0·86 (B) and 0·95 (C) — the difference between the calculated and the measured value is considerable in all cases. These results show that the correction factors of Harkins and Brown, which in principle cannot hold for dynamic measurements, are not satisfactory in the case

TABLE I
Characteristics of Stalagmometers

Stalagmometer	A	B	C
Outer diameter of the dripping area, d, cm	0·78	0·98	1·02
Minimum time of drop formation, t, s[a]	15·2	2·7	2·8
Maximum flow rate (mg/s)[a]	7·1	49·4	50·9
G_s for water, mg[b]	107·1	129·6 129·0[c]	143·1 143·7[c]
G_s for n-propanol, mg[b]	35·7	42·3	47·2
k for water[d]	9·94	17·50 18·80[c]	14·56 14·82[c]
k for n-propanol[d]	8·76	3·70	7·22
G_s/d^2 for water	176·0	135·0 134·3[c]	137·5 138·1[c]
G_s/d^2 for n-propanol	58·6	44·1	45·4
S[e]	0·679	0·562[f] 0·564[c]	0·508 0·506[c,f]

[a] Water during dripping due to its own weight, *i.e.* without throttling of the upper orifice of the tube in a stalagmometer filled up to the upper edge of the widened central part of the tube; [b] Mass extrapolated from G_t for $1/t = 0$; [c] Result of the second series of measurements; [d] *cf.* Eq. (1); [e] Determined from G_s for water; $S = \gamma_W/G_s$ (W); [f] Value used in calculating γ_t of solutions of dodecyl sulfonate.

of the shapes and quality of the capillary tips used in this work even for extrapolated static drop masses, and the agreement, if any, is accidental.

From G_s for water (W) with $\gamma_W = 72{\cdot}8$ dyn/cm, the slopes S, $S = \gamma_W/G_s(W)$, were calculated, serving as a factor for calculating γ_L for liquids (L), $\gamma_L = SG_s(L)$; $G_s(L) = = G_t(L) - \Delta G_t(L)$, $\Delta G_t(L) = kt^{-1}$, and $G_t(L)$ is the measured value. For pure liquids G_s must be determined by extrapolating G_t to $1/t = 0$, because k differs for different liquids on the same stalagmometer. G_s determined for propanol on the stalagmometer A was higher by $0{\cdot}65$ mg, *i.e.* by $0{\cdot}44$ dyn/cm, which corresponds to the tabulated value $\gamma = 23{\cdot}8$ dyn/cm and to S determined from G_s for water. Similar deviations have been mentioned above for repeated measurements with water on the
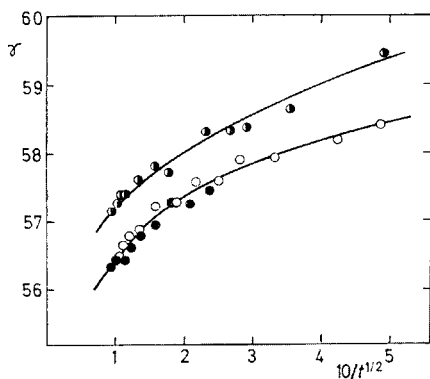

FIG. 4

Dependence of Dynamic Surface Tension γ_t (dyn/cm) on $10t^{-1/2}$ for $3{\cdot}65 \,.\, 10^{-3}$M Aqueous Solution of Sodium Dodecyl Sulfonate
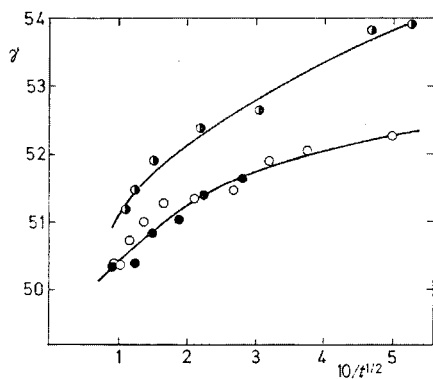
● A, ○ B, ◐ C.

FIG. 5

Dependence of γ_t on $10t^{-1/2}$ for $5{\cdot}47 \,.\, 10^{-3}$ M Aqueous Solution of Sodium Dodecyl Sulfonate
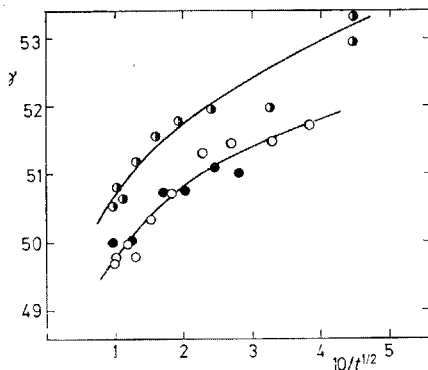
● A, ○ B, ◐ C.

FIG. 6

Dependence of γ_t on $10t^{-1/2}$ for $6{\cdot}38 \,.\, 10^{-3}$M Aqueous Solution of Sodium Dodecyl Sulfonate

● A, ○ B, ◐ C.

stalagmometers B, C, and their possible cause has been considered. The deviation of G_s for propanol from the value calculated by using S was only -0.05 mg, *i.e.* -0.03 dyn/cm for the stalagmometer B, while the same deviation for the stalagmometer C was $+0.15$ mg, *i.e.* $+0.08$ dyn/cm. This is an agreement quite sufficient for the usual requirements concerning the accuracy of determination of γ_t.

For the stalagmometer C the mass drop of water, G_t, for short times of drop formation satisfies the equation

$$G_t = a - b(t - c)^2 , \qquad (2)$$

where $a = 145.90$ (143.03), $b = 0.565$ (0.200), and $c = 5.30$ (6.40). The values in brackets hold for the second series of measurements. The constant a in Eq. (2) is the maximum drop mass depending on t, c is the time of drop formation corresponding to the maximum drop mass, $b(t - c)^2$ is the deviation from the maximum drop mass holding on condition that $t \leq c$. For $t \geq c$, Eq. (1) is valid.

A comparison of results obtained with solutions of surfactants on various stalagmometers can be taken as the criterion of the correctness of the above procedure used for the determination of γ_t depending on the age of the static surface. The results obtained with aqueous solutions of sodium dodecyl sulfonate (D) in concentrations $3.65 . 10^{-3}$, $5.47 . 10^{-3}$, and $6.38 . 10^{-3}$ mol/l for all three stalagmometers are given as a dependence of γ_t on $10t^{-1/2}$ (Figs 4–6). They show $\gamma_t = SG_s(D)$ values determined from the measured $G_t(D)$ according to $G_s(D) = G_t(D) - \Delta G_t(W)$. The $\Delta G_t(W)$ values were taken from the plot for the respective t given in Fig. 2 in accordance with Eqs (1), (2). For the stalagmometers B and C the slopes S denoted with f in Table I were used; they correspond to that series of measurements with water which was followed by the measurements of solutions. For the stalagmometers A, B the γ_t values within the range of t used are in a very good agreement and lie on a common curve in the figures. The values determined with the stalagmometer C are systematically higher by $0.7-1.6$ dyn/cm compared to the preceding values, with the deviation increasing towards lower t, *i.e.* higher G_s. However, even though there is such deviation, probably due to the same cause as in the cases described above, the agreement between the results is good compared to the experience obtained in measurements of solutions of surfactants by other methods[4,8]. Thus, the results obtained by using sodium dodecyl sulfonate solutions indicate that the procedure outlined in this paper gives, within the limits of acceptable deviations, correct results with minimum experimental requirements.

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