Strain Gauge Electromicrobalance for Surface Tension Measurement[1]

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Two types of apparatus using an unbonded strain gauge of a cantilever type for the measurement of surface tension were constructed. One is a sensitive electromicrobalance equipped with an extended arm attached to the cantilever of the strain gauge. The apparatus proved suitable as a surface balance in a completely closed system. By this apparatus, the measurement of surface tension ranging from 0 to 74 dyn/cm is possible with the accuracy of ±0.10 dyn/cm. The other type was constructed by connecting the sensing lever of strain gauge to the arm of a torsion balance with a strip of phosphor bronze. This device together with a counterbalance on the opposite side of the arm also proved to be useful as a tensiometer. Accuracy of this apparatus was a little better than that of the extended arm type balance, although a larger space is required. Both apparatus are inexpensive, easy to construct and simple to operate, and are suitable for the self-recording of time dependence of surface tension or weight change in general with sufficient accuracy. Equations proposed for the time dependence of surface tension of surfactant solution were checked by using the strain gauge tensiometer of the extended arm type.

The Wilhelmy type surface tensiometer is known to give reliable values of surface tension[2] and is considered to be the best method for the measurement of surface tension, particularly of surfactant solutions where aging is inevitable.[3]

We previously devised a self-recording tensiometer using torsion balance and differential transformer as a transducer which converts a small vertical displacement of hanging glass plate into an electrical output for recording.[4] Although the electrical output from the differential transformer was larger than that from a strain gauge of direct loading, skill is required for preparing a good working spiral spring to support the transformer core. In addition, unsteady actions of transformer and oscillator reduced the accuracy of the measurement.

In the present study, the differential transformer was replaced by a strain gauge to improve the performance of the torsion balance. Although surface tension measurements using strain gauge have already been reported,[5–7] some of them lack detailed descriptions of the apparatus while others turn out to be inapplicable for the self-recording of time dependence of surface tension. Therefore, a self-recording strain gauge tensiometer of a torsion balance type was first constructed. In this apparatus a sensing lever of the strain gauge was connected by a phosphor bronze strip to a fixed point on the arm of the torsion balance and response of the torsion balance due to the action of surface tension was converted into the electrical output which operates a recorder. This apparatus has proved more accurate and sensitive than the former one.[8]

However, for an accurate measurement of the surface tension of solutions, evaporation of solute or solvent from the solution should be prevented, since slight evaporation frequently produces a profound change in surface concentration[9] and surface tension. Therefore, the space over the surface of liquid for the measurement should be minimized. The torsion balance is not suitable for this purpose, since a large space is required. A spring balance was constructed but was unfavorable because of its size and sensitiveness towards the temperature change.[10]

A cantilever strain gauge of extended arm type was finally devised which turned out to be satisfactory for the surface tension measurement of aqueous solution, since it is compact and easy to set in a small chamber together with the solution to be measured. The apparatus proved to be insensitive to temperature and moisture.

By using this apparatus, the time dependence of surface tension of aqueous surfactant solution was measured, uninfluenced by evaporation of the solution and contamination from the surrounding atmosphere, and applicability of various equations proposed for calculating such dependence was checked.

Experimental

Construction of Surface Tensiometer. Strain Gauge: The strain gauge used was of unbonded and cantilever type (UL-120, *Shinko Communication Industry Co., Ltd., Japan*). Its maximum output is ±4 mV for permissible load of ±2 g. A maximum input of 4 volt was supplied from D. C. voltage stabilizer (NA-112, *Nippon Stabilizer Co., Ltd., Japan*). Output voltage from the strain gauge was properly attenuated, biassed with mercury cell, and was recorded by using a 1 mV full scale recorder (*Hitachi* QPD 33, *Hitachi Ltd.*,). A block diagram of the whole electrical setup is shown in Fig. 1 for tensiometer of the extended arm type.

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[1] Paper presented at the 23rd Annual Meeting of the Chemical Society of Japan, Colloid Section, held in Tokyo, 1970.

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Strain Gauge Tensiometer of Torsion Balance Type. The apparatus is shown in Fig. 2 in which S is the strain gauge, C, a counterbalance, P, a hanging plate ($20\times20\times0.02$ mm, 300 mg), and D, a magnetic dumper. A tungsten torsion wire of the torsion balance T was 0.22 mm in diameter and 60 mm in length, at the center of which a beam of 230 mm in length was fixed at a point 80 mm from its end. The sensing lever of the strain gauge was connected with the beam at a fixed point on it with a strip of phosphor bronze B ($20\times1\times0.07$ mm). Magnification of the force due to surface tension could be varied by shifting the point of connection of phosphor bronze with respect to the arm. The counterbalance was attached to the opposite side of the arm to offset the weight of the hanging plate and, if necessary, a part of the force due to the surface tension. By this means, together with the electrical attenuation of ouptut and the proper choice of the bias voltage, the range and sensitivity of the balance could be controlled according to the requirement of the experiment. In the present study phosphor bronze was fixed at a point 125 mm from the end of the arm as shown in Fig. 2. This increased the output of strain gauge six times the value of direct loading.

The performance of the apparatus is shown in Table 1. Sensitivity and accuracy are a little better than those of the former apparatus as shown in the table. The apparatus was adjusted so that the surface tension of 73 dyn/cm corresponded to about 1.8 g load of the strain gauge. The apparatus was used under two different conditions. In the first case, the output due to surface tension was so attenuated that 73 dyn/cm corresponded to the full scale of the recorder. In the second case, the output from the strain gauge was applied through the bias voltage to the recorder without electrical attenuation so that the full scale of the recorder covered a range from X_1 to X_1+25 dyn/cm, X_1 being varied between 0 and 55 dyn/cm. Temperature change of several degrees did not affect the surface tension, since the temperature dependence of output (Fig. 3) was found to be 9.05×10^{-6} mV/mg·deg and this corresponded to 0.002 dyn/cm·deg.

Strain Gauge Tensiometer of Extended Arm Type. Figure 4 shows the arrangement of a tensiometer of the extended arm type together with the liquid for measurement and the apparatus for conditioning the chamber containing them. In this apparatus, an extended arm E of thin glass rod, 330 mg in weight was attached to the cantilever of strain gauge S. The effective length of the arm was 93 mm. The tensiometer was fixed to the side column of the chamber. The weight of the Wilhelmy plate P, ($20\times15\times0.02$ mm, 250 mg) was chosen to be the sum of the force due to the surface tension of water (about 73 dyn/cm), and the weights of arm and plate are brought near the limit of a permissible load of the strain gauge. By this arrangement, the weight ranging from 0 to 300 mg could be measured with the accuracy of ±0.4 mg. This corresponds to the surface tension of 0 to 74±0.1 dyn/cm for the plate of 40 mm in horizontal perimeter as shown in Table 1.

For surface tension measurement, a clean glass plate was hung from the arm and the chamber was closed after being flushed with humidified nitrogen (Fig. 4). The liquid then was slowly introduced from the reservoir R into the vessel V until its surface just touched the lower end of the hanging plate P. The vertical force due to the surface tension acting on the plate was converted into an electrical output and recorded through the bias voltage. The recorder was so adjusted that 50 dyn/cm corresponded to a

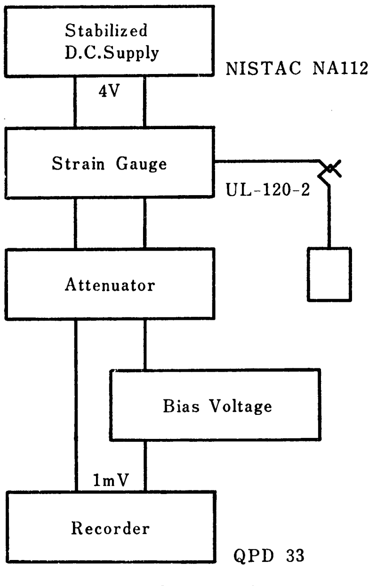

Fig. 1. Electrical setup of the strain gauge tensiometer.

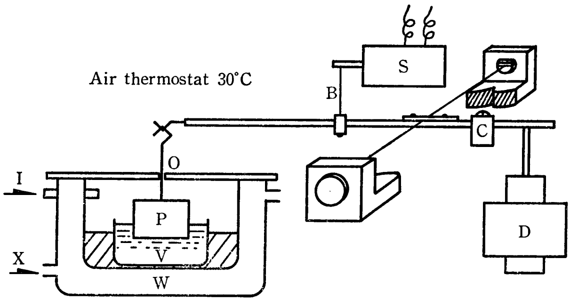

Fig. 2. Strain gauge tensiometer of torsion balance type.
B Phosphor bronze
C Counterbalance
D Magnetic dumper
I Humidified nitrogen gas inlet
O Humidified nitrogen gas outlet
P Hanging glass plate
S Strain gauge
T Torsion balance
V Solution and vessel
W Water jacket
X Thermostated water

Table 1. Performance of various types of surface tensiometer

	Strain Gauge			Differential transformer type	
	Torsion balance type		Extended arm type		
Range (dyn/cm)	0—73	X_1—X_1+25	X_2—X_2+50	0—75	X_3—X_3+40
Bias range (dyn/cm)	0	$X_1=0$—55	$X_2=0$—24	0	$X_3=0$—80
Sensitivity (mV/mg)	3.31×10^{-3}	1.00×10^{-2}	4.71×10^{-3}	3.17×10^{-3}	6.45×10^{-3}
Accuracy (dyn/cm)	0.10	0.08	0.10	0.20	0.24

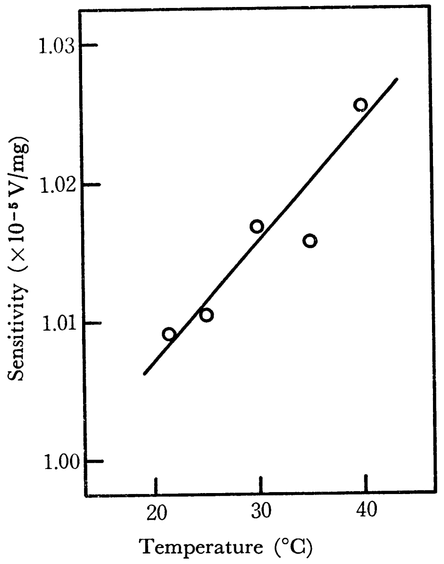

Fig. 3. Temperature dependence of sensitivity of strain gauge tensiometer.

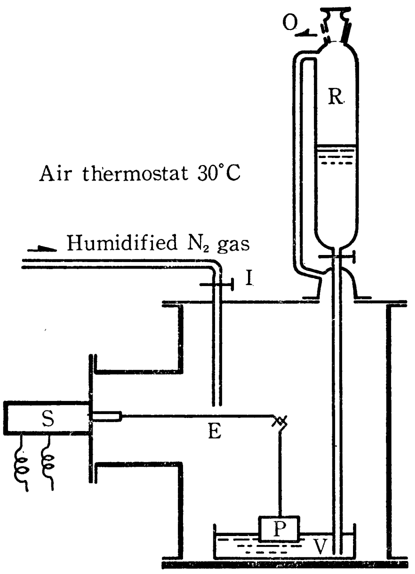

Fig. 4. Strain gauge tensiometer of extended arm type
E Extended arm
I Humidified nitrogen gas inlet
O Humidified nitrogen gas outlet
P Hanging glass plate
R Reservoir for a sample solution
S Strain gauge
V Vessel and solution

full scale, and the surface tension ranging from X_2 to X_2+50 dyn/cm could be measured, X_2 being varied between 0 and 24 dyn/cm.

Neither the hysteresis due to the load nor the effect of moisture was observed during the course of 24 hr measurement in both types of tensiometers.

Measurement of Time Dependence of Surface Tension and Equilibrium Surface Tension

Surface tension was measured for a 5.4×10^{-6} mol/l aqueous solution of hexaoxyethylene dodecyl ether (homogeneous) by using the extended arm strain gauge tensiometer, at 25°C. The results are shown in Fig. 5. Water used for preparaing the solution was distilled from acid permanganate, then alkaline permanganate solutions and finally distilled without permanganate in borosilicate flasks. Surface tension showed a relatively long aging extending over about 20 hr until it attained an equilibrium. Since measurements were carried out in a closed vessel, evaporation was completely eliminated and the system was free from comtamination from the surrounding atmosphere. Thus the observed changes are considered to be proper to the solution and the data obtained are pertinently for checking the validity of various equations proposed for the time dependence of surface tension of surfactant solution or the equations for obtaining an equilibrium surface tension. Table 2 shows the equilibrium surface tension values calculated from the following empirical equations with various ranges of observed surface tension *vs.* time values.

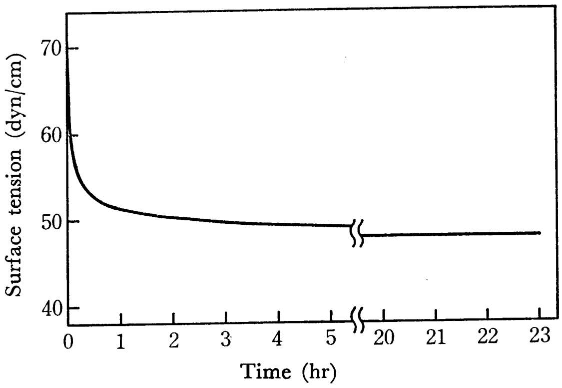

Fig. 5. Surface tension of aqueous hexaoxyethylene dodecylether (at 25°C, 5.4×10^{-6} mol/l).

$$\sigma_t = \sigma_\infty + a/t + b/t^2$$

$$\text{or, } \sigma_t + t(d\sigma_t/dt) = \sigma_\infty - b/t^2 \qquad (1)^{11)}$$

$$\sigma_t = \sigma_\infty + (\sigma_0 - \sigma_\infty)\exp(-\alpha t)$$

$$\text{or, } \sigma_t = (-1/\alpha)(d\sigma_t/dt) + \sigma_\infty \qquad (2)^{12)}$$

$$\sigma_0 - \sigma_t = (\sigma_0 - \sigma_\infty)/(c/\sqrt{t}) + 1 \quad \text{or,}$$

$$1/(\sigma_0 - \sigma_t) = 1/(\sigma_0 - \sigma_\infty) + \{c/(\sigma_0 - \sigma_\infty)\}(1/\sqrt{t}) \qquad (3)^{13)}$$

In these equations, σ_t, σ_0, and σ_∞ denote the surface tension of solution at time t, $t=0$ and $t=\infty$ respectively, and α, a, b, and c constants.

It is seen in Table 2 that, as regards the extrapolated equilibrium values of surface tension σ_∞ obtained from the σ-t values of longer time range (0.5—5 hr), Eq. (1) is found to give the best value, being the nearest to the equilibrium value obtained after 20 hr. Since σ_∞ obtained by using σ-t values of shorter and earlier time range is not reliable, the agreement of σ_∞ obtained from Eq. (3) and σ-t values of 5—25 min range is considered to be accidental. Thus, Eq. (1) is recommended here as an empirical formula, but 4 hr measurement is necessary in order to obtain a reliable value of equilibrium surface tension.

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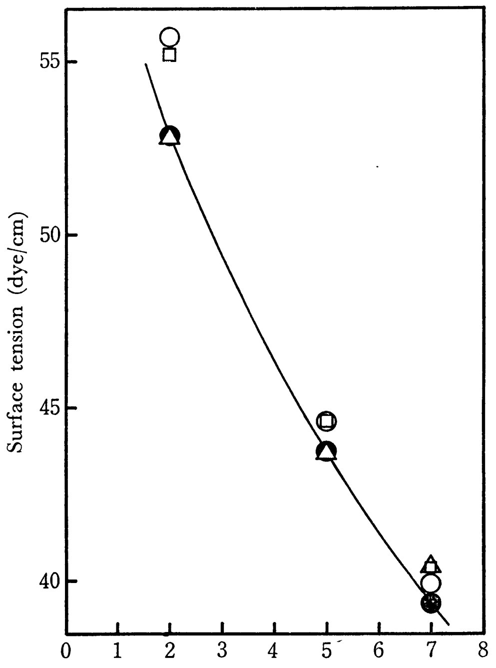

Fig. 6. Calculated and observed equilibrium surface tension. ○: Eq. (1), □: Eq. (2), △: Eq. (3), ● and —: Observed value.

Surface tension was further measured for aqueous solutions of ionic surfactant, sodium dodecyl sulfate, and the validity of the above three equations was checked for three different concentrations. The results are shown in Fig. 6 together with the equilibrium value (solid line) observed after 20 hr. The values of σ_∞ were calculated from σ-t curve of 0.5—4 hr range. We see that the difference between the observed and calculated σ_∞ decreased with increasing concentration and decreasing time dependence of surface tension in the case of Eqs. (1) and (2), while the relation is reverse in the case of Eq. (3). The general tendency is such that the observed equilibrium values of surface tensions to be equal or smaller than the values calculated from these equations.

Table 2. Calculated and observed equilibrium surface tension

	Surface tension (dyn/cm)				
	5—25 min	0.5—2 hr	2—4 hr	0.5—5 hr	After[a] 20 hr
Eq. (1)	50.8	49.3	47.9	47.6	47.8
Eq. (2)	50.8	49.5	48.5	48.8	
Eq. (3)	47.8	46.9	47.3	46.9	

a) Equilibrium surface tension measured for 5.4×10^{-6} mol/l aqueous solution of hexaoxyethylene dodecyl ether at 25°C.

It is concluded from the above observations that the applicability of these equations may differ for different solutions, and a common equation applicable for all systems cannot be obtained. This is quite natural since these equations are empirical, and it is difficult to derive a theoretical equation predicting the change of surface tension with time, because the mechanisms of surface aging may differ for different solutions which are not clear at present, although some explanations have been proposed.[14]

However, from the practical view point Eq. (3) seems convenient since a linear plot is applicable. But also in this case, a 4 hr measurement of surface tension completely free from evaporation and contamination seems desirable for calculation of a reliable value of equilibrium surface tension.

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