

MEASUREMENT OF DYNAMIC SURFACE TENSION OF SURFACTANT SOLUTIONS WITH THE DROP VOLUME METHOD USING AN AUTOMATIC DROP DETECTOR

K. Koczó and J. M. Soós

Institute for Physical Chemistry,
Technical University, Budapest

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Abstract

The dynamic surface tension of TRITON X-100 surfactant solutions were measured with the drop volume method using a stalagmometer supplied with automatic drop counter. The apparatus constructed at the Physical Chemistry Institute consists of four stalagmometer units and a four-channeled electronic drop- and time-counter.

The dynamic surface tension decreased with the dropping time because of a diffusion barrier of the surfactant molecules at low concentrations and because of the time necessary for the micelles to decompose into surfactant molecules at high concentrations.

Introduction

Surface (and interfacial) tension of solutions changes from the static value when the surface is dilated or compressed. This phenomenon has a great importance in many processes taking place with interfaces. During foam formation e.g. liquid films are drawn, dilated from surfactant solution (foam beating) [1].

The behaviour of surfactant solutions in these circumstances can be investigated and characterised by measuring the surface tension at dilating surface [2].

Theory

One of the most frequently used method of interfacial tension measurements is the determination of drop volume: the liquid is dropped from the horizontal, finely ground, exactly circular tip of a stalagmometer (a pipette, scaled on both the upper and lower part) and the number of drops formed from a given volume of liquid is counted.

The interfacial tension can be calculated with the formula of Harkins and Brown [3]:

$$\sigma = \frac{V_d \Delta \rho g}{r} f\left(\frac{r}{V_d^{1/3}}\right) \quad (1)$$

where V_d : volume of a drop
 $\Delta\rho$: density difference of the fluids
 g : acceleration due to gravity
 r : radius of the stalagmometer tip
 $f(r/V_d^{1/3})$: Harkins factor, modified by Lando and Oakley [4].

Before detaching the tip the surface of the drop is dilating with a nearly constant speed, therefore in case of solutions — especially of surfactant solutions — a stationary dynamic interfacial tension is measured, which is higher than the static one. Expansion of the interfaces can be characterized by the relative rate of dilation or the adsorption time. The latter is the time necessary to reach the state of the stationary dilating interface from a state when there is no surfactant on the interface and the surfactant diffuses from the bulk in static conditions.

For a drop formed by constant flow rate it is approximated by Joos and Rillaerts [5]:

$$t \simeq 0.43 t_d \quad (2)$$

where t : adsorption time
 t_d : drooping time

Description of the apparatus

The SJ 85 type stalagmometer supplied with an automatic drop counter can be used to measure the surface tension of liquids and the interfacial tension between immiscible liquids.

The apparatus constructed at the Physical Chemistry Institute consists of four stalagmometer devices (Fig. 1) and a four-channeled electronic drop- and time-counter (D-T meter, Fig. 2). The stalagmometer devices have the following parts: thermostated stalagmometer, photodetector, stand, electrolysis cell. (Four types of stalagmometers with different sizes can be applied according to the range of the interfacial tension and density difference of the liquids.)

The electronic unit consists of ten main parts (Fig. 3). The system operates as follows:

- the drops falling down on the effect of the pressure made by electrolysis cell a supplied by stabilized current source 1 interrupt the light beam of lamp d powered by light stabilizer 2
- the light interruption causes signs in phototransistor c , which are amplified by selective input amplifier 3
- the amplifier gives the starting signal for the single pulse generator 4 , that inhibited by dead time generator 5 . This inhibition is important for cutting

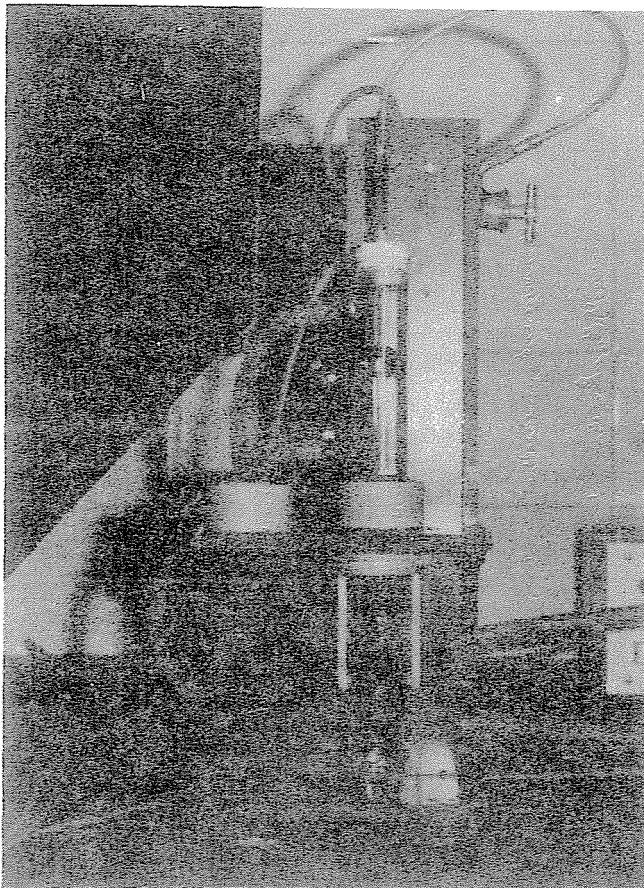


Fig. 1. Photo of a stalagmometer device

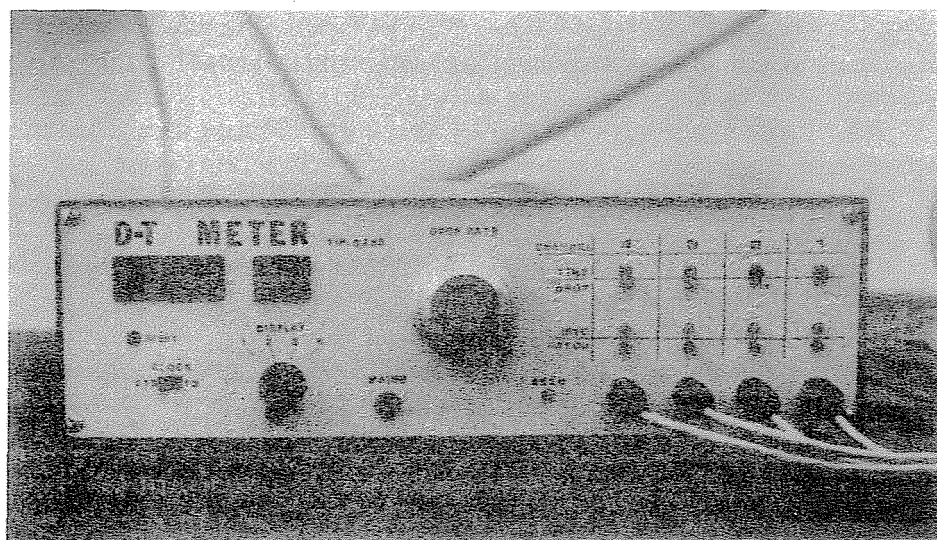


Fig. 2. Photo of the electronic unit

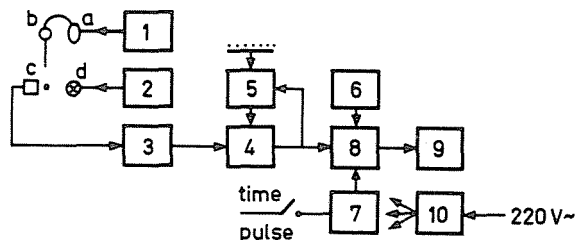


Fig. 3. 1. Gas cell stabilizer supply; 2. Lamp's light stabilizer; 3. Selective input amplifier; 4. Controlled single pulse generator; 5. Dead-time generator; 6. Clock; 7. Mode selector; 8. Multiplexer; 9. Scaler; 10. Power supply
a) Electrolysis cell; b) Stalagmometer; c) Phototransistor; d) Light

- off optical noises. The operator has to set in this dead time (somewhat shorter than the shortest dropping period)
- after the setting in of mode selector 7 the pulses are connected to scaler 9 by multiplexer 8 in “drop” mode or are permitted the pulses of clock 6 during a dropping period in “time” mode
 - the units of the apparatus are powered by multivoltage stabilized supply 10.

Measurement

The surface tension of TRITON X-100 (octylphenyl-polyglycol ether, n : 9–10) solutions were measured at 25 °C with different dropping times (from 5 s to 3 min), using stalagmometer tubes with tip radius of 2.5 mm.

Conclusions

The measured surface tension in function of the surfactant concentration and dropping time is plotted in Fig. 4.

Kinetic effects are negligible in the measured dropping time. The static surface tension measured with pendant drop method is also drawn.

The critical micelle concentration (C_M) read off from the static curve is 10^{-1} g/dm³.

It can be seen that the dynamical surface tension is decreasing with the increase of dropping time (decrease of the rate of surface dilation of the drops) in the investigated dropping rate region. A “dynamical critical micelle concentration” of about 0.2 g/dm³ can be determined from the dynamical surface tension curves.

This phenomenon can be explained that the adsorption time of the surfactant molecules diffusing from the bulk to the dilating surface and the

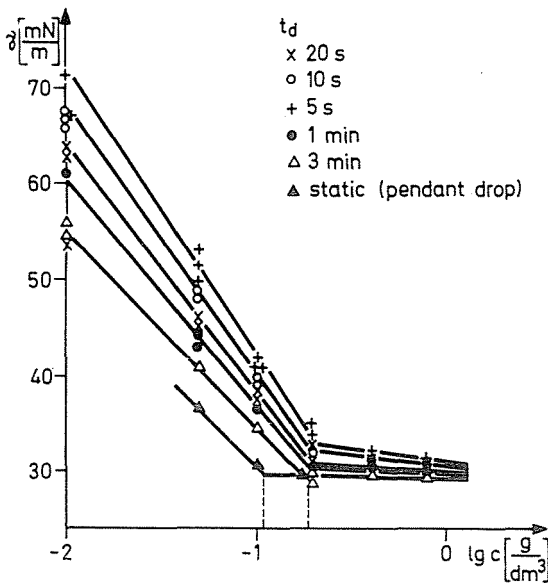


Fig. 4

dropping time are in the same interval at low surfactant concentrations [2]. At higher concentrations (above c_M) the decomposition time of the micelles into surfactant molecules is the rate-controlling step [6].

The dynamic surface tension in function of the adsorption time for a diffusion controlled process [6]:

$$\sigma_d = \sigma_e + \frac{RT\Gamma^2}{c_0} \left(\frac{\pi}{4Dt} \right)^{\frac{1}{2}} \quad (3)$$

where Γ : adsorption of the surfactant

σ_e : equilibrium surface tension

D : diffusion coefficient.

Eq. 3 is an approximation of the equation of Ward and Tordai [7].

σ_d is plotted in function of $t^{-\frac{1}{2}}$ in Fig. 5, for concentrations below the c_M . It can be seen that the function is linear in the case of 0.05 g/dm³ and 0.1 g/dm³ solutions. The line bends in 0.01 g/dm³ solution, because the dynamical surface tension is near to the surface tension of the water in the investigated t -region.

Supposing $\Gamma = 2.5 \cdot 10^{-10}$ mol/cm² [2], the diffusion coefficient of the surfactant molecules were calculated from the slope of the lines of the 0.05

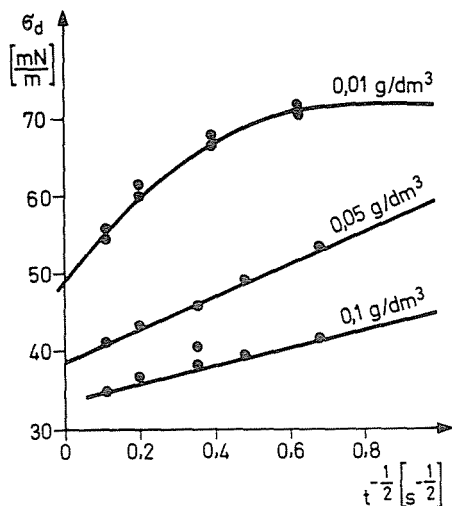


Fig. 5

g/dm³ and 0.1 g/dm³ solutions, resulting $D = 7 \cdot 10^{-7}$ cm²/s and $5 \cdot 10^{-7}$ cm²/s. These diffusion coefficients agree well with the value ($7 \cdot 10^{-7}$ cm²/s) obtained by van Hunsel and Joos [8] using six different methods.

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Kálmán KOCZÓ }
 Dr. János SOÓS } H-1521, Budapest