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SOME EXPERIMENTS ON FREE FILMS OF AQUEOUS SOLUTIONS
OF NONIONIC DETERGENTS

BY

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Summary

The thicknesses of films drawn from solutions of nonionic detergents and neutral electrolytes are measured. The apparatus is described briefly. The existence of two types of equilibrium films observed at low electrolyte concentrations is discussed.

In order to obtain values of the equilibrium thicknesses of free detergent films in air with very low values of the ionic strength we have performed measurements with films drawn from 10^{-3} M solutions of the non-ionic surfactants OP-7, OP-10 and OP-20, to which different amounts of NaCl were added. (OP-n=isoctylphenol with an average of n ethoxy groups). The film thicknesses were calculated in the usual way from the amount of light reflected by these films.

Most apparatuses, used to measure the light reflection by thin films, have the disadvantage that the beam projected on the film passes through the same lenses as the reflected beam does. In this case an amount of light reflected by lens surfaces will be added to the light reflected by the film. This amount can be considerable because a very thin film (thickness in the order of 50-100 Å) will reflect 0.05 to 0.2 % of the incident light, while an uncoated glass surface reflects about 4 %.

SCHELUDKO [ref. 1, 2] did overcome this difficulty by using the inclined covering glass plate of the cuvette containing the soapfilm as a semi-transparent mirror. In this way the incident and the reflected beams were separated.

In our apparatus these two beams were separated by giving them an inclination of 15° . The correction caused by this inclination in the formulae relating the thicknesses of the films to their reflection coefficients is small (about 2 %) and can easily be calculated.

Fig. 1 gives a schematic diagram of the apparatus.

The light source is a high-pressure mercury arc. The interference filter selects a green or violet line of the spectrum. The intensity of the reference beam can be diminished by a known factor by inserting neutral filters and turning the polaroid filters with respect to each other. The intensities

of the main reflected beam and the reference beam can be matched in the photometric prism, the reproducibility being 1 to 2 %.

Light from the strongly reflecting thick border of the film is intercepted by means of diafrags in the incident and reflected beam. The correct position and orientation of the soapfilm is verified by controlling the positions of the images of diafrags. The apparatus is calibrated by comparison with surfaces of known reflection coefficient.

The cuvette which contains the film is shown in fig. 2. The design is very similar to that used by DERJAGUIN and TITIEVSKAJA [ref, 3, 4].

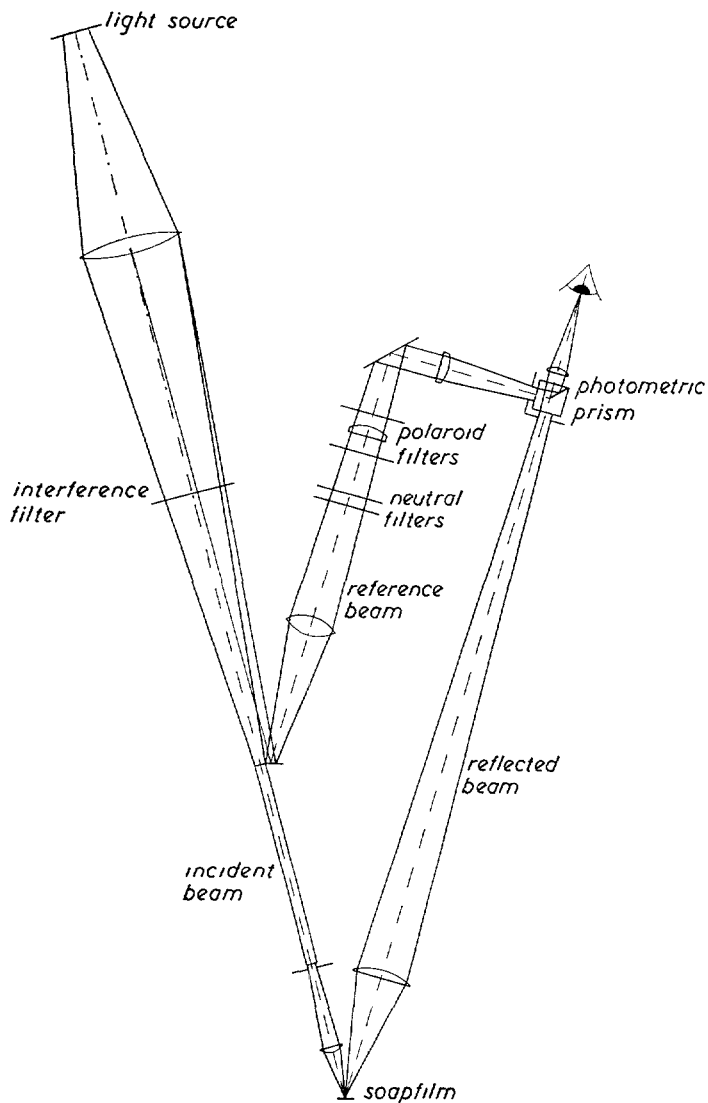


Fig. 1. Reflectometer. In this apparatus the light reflected from a film (or other smooth surfaces) can be compared with light of the reference beam. The latter can be diminished to a known extent.

The surfactants OP-n are commercial products (Servo, Delden, The Netherlands). The conductivity of their solutions is low; for instance the conductivity of a 10^{-3} M solution of OP-10 is $3 \cdot 10^{-6} \Omega^{-1} \text{ cm}^{-1}$.

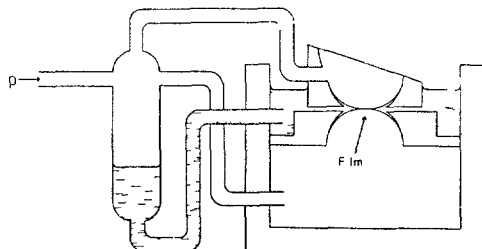


Fig 2 Cuvette containing the film to be measured. The hydrostatic pressure applied to the film corresponds to the difference in height between the level of the film and the surface of the liquid in the manometer at the left.

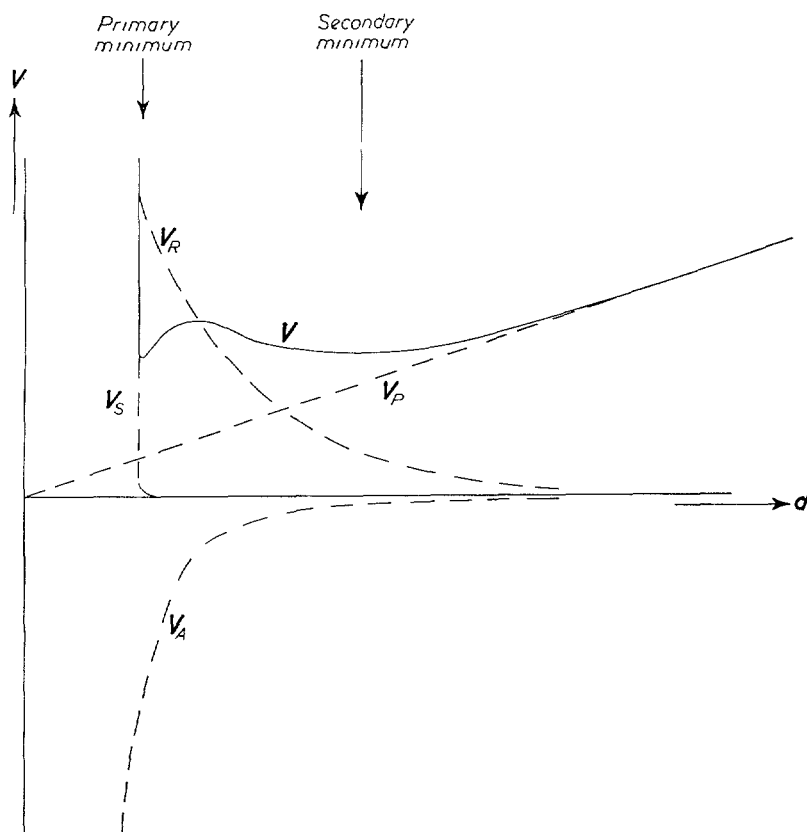


Fig 3 The total free energy V (full line) as a function of the thickness d . The dotted lines represent: V_R the free energy of repulsion between two ionic double layers, V_A the free energy of the van der Waals' attraction, V_S the free energy of repulsion originating from steric hindrance, V_P the free energy resulting from the hydrostatic pressure.

As was reported earlier [ref. 5], two different regions of equilibrium thicknesses were found at low electrolyte concentration (e.g. 10^{-4} N NaCl): one very small, about 80 Å for OP-7 and OP-10 and about 105 Å for OP-20; the other much thicker. In the latter case the thickness is equal to the equilibrium thickness calculated from the repulsion between ionic double layers, the van der Waals' attraction and the applied pressure, using a surface potential of 15 to 20 mV and a van der Waals constant $A = 7.5 \cdot 10^{-13}$ erg [ref. 6].

From the thicknesses of the very thin films, which are remarkably close to twice the lengths of the soap molecules, the conclusion must be drawn that there were no very thick hydration layers in these films.

The transition from the "thick" film to the "thin" one and vice versa can be brought about quite easily by changing the hydrostatic pressure applied to the film.

If these two thicknesses are both equilibrium thicknesses the curve of the free energy (V) versus thickness (d) must have two minima: a primary one where the steric hindrance counteracts the van der Waals' attraction, and a secondary minimum where the electric repulsion, the van der Waals attraction and the applied pressure are in equilibrium (fig. 3).

With NaCl concentrations of 10^{-4} N or less, the two thicknesses can easily be observed; with 10^{-3} N NaCl and higher salt concentrations the secondary minimum is either not realizable or only with difficulty.

The two types of films occurring at low electrolyte concentration are in equilibrium with each other. This can be shown easily in a vertical film made by pulling a rectangular frame partially out of the solution in a closed vessel at constant temperature in a saturated atmosphere (fig. 4).

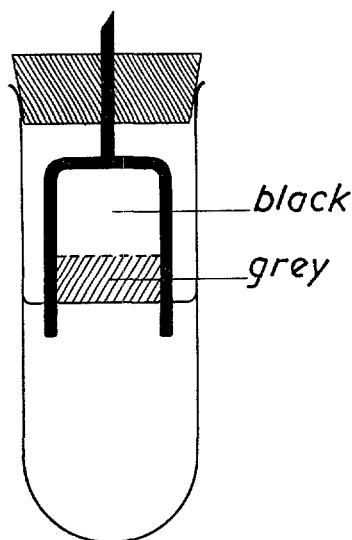


Fig. 4. Vertical film in rectangular frame with boundary between black and silvery grey parts.

The film thins down until it has a grey colour in reflected light; then a border above which the film is black (and consequently very thin) appears at the top of the film. This border moves downward to a certain height where it is observed to remain during several days. When, after equilibrium has been reached, the frame with the film is moved downward or upward, the border rises or descends again to the same equilibrium height above the level of the liquid.

After equilibrium has been reached, the hydrostatic suction by gravity causes, at each spot of the film, a pressure difference between the atmosphere and the inner part of the film. This pressure difference is equal to ρgh (ρ = density of the liquid, g = gravitational constant, h = height of the spot above the surface of the bulk liquid). So this experiment shows that there is a very well reproducible pressure at which the two thicknesses are in equilibrium with one another. For instance, for a film made from a solution of 10^{-2} M OP-10 and 10^{-4} N NaCl the equilibrium height was $3,2 \pm 0,1$ mm during five days.

More details about measurements of the equilibrium level of the boundary between black and grey parts of vertical films will be published [ref. 7].

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