

which when coupled with the Gibbs adsorption isotherm yields (neglecting activity coefficients)

$$\gamma - \gamma_0 = RTkc \sum v_i + \frac{aRT \sum v_i}{eW - /RT \sum v_i - v_-} \ln \left[l - \frac{\{eW - /RT \sum v_i - v_-\} kc}{be W - /RT} \right] \quad (2)$$

The term $eW - /RT \sum v_i$ can be shown to be very much smaller than v_- , with the result that (2) reduces to

$$\gamma - \gamma_0 = RTkc \sum v_i - \frac{aRT \sum v_i}{v_-} \ln \left[l + \frac{kv - c}{be W - /RT} \right] \quad (3)$$

where γ is the surface tension at concentration c (moles per litre), a is the number of adsorbing points per sq. cm., b is the number of water molecules per sq. cm., W_- is the potential energy of the negative ion at the surface in excess of its value in the interior of the liquid, and k is the ratio between the concentration in moles per sq. cm. and moles per litre, and depends on the thickness of the adsorbed layer, which we take as the diameter of the water molecule plus that of the adsorbed solute.

Knowing the diameters of the water molecule and of the solute ions, and estimating a and W_- from the data of Jones and Ray, it is possible to calculate the surface tension from (3) for potassium chloride solutions, for example (lower solid line of Fig. 1), and to compare with the experimental results (crosses of Fig. 1). The agreement is satisfactory.

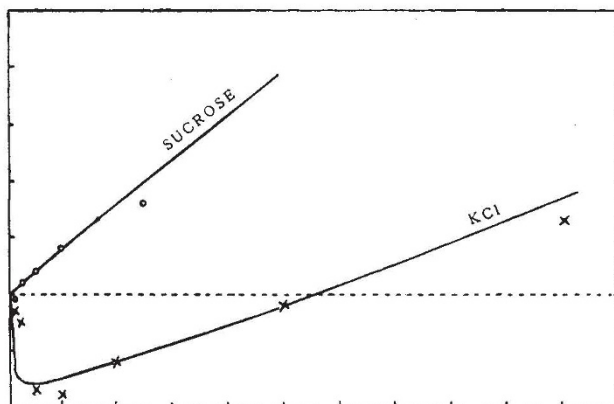


Fig. 1.

In the case of capillary inactive non-electrolytes like sucrose, a will be equal to zero and (3) becomes

$$\gamma - \gamma_0 = RTkc. \quad (4)$$

From the density of solid sucrose one can calculate an approximate value of its molecular diameter allowing an evaluation of k to be made and a computation of the surface tension from (4). The upper solid line of Fig. 1 represents the theoretical calculations, while the circles are the experimental data of Jones and Ray. Again the agreement seems to be satisfactory, and lends support to the original postulate.

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¹ Jones, Grinnell, and Ray, W. A., *J. Amer. Chem. Soc.*, **59**, 187 (1937).

² Wagner, C., *Phys. Z.*, **25**, 474 (1924).

³ Onsager, L., and Samaras, N. N. T., *J. Chem. Phys.*, **2**, 528 (1934).

Viscosity of Monomolecular Films

ALTHOUGH the viscosity relations of films are of fundamental importance for an understanding of their structure, it has not in the past been possible, with the surface viscosimeters used, to determine the viscosity of a true film, that is of a monolayer. Two viscosimeters which are sufficiently sensitive are described below, and others are in process of development.

1. Capillary slit viscosimeter for liquid surface films.

The film is allowed to flow under its own pressure, or a difference of pressure, through a long transverse slit in a barrier which confines the film. The following relation gives the viscosity (η):

$$\eta = \frac{f d^3}{Q 12l} \text{ dyne sec. cm.}^{-1},$$

where f is the surface pressure in dynes per cm., d is the diameter, and l the length of the slit, and Q is the number of sq. cm. of film which disappears through the slit per second.

VISCOUSITY OF SURFACE FILMS OF FATTY ACIDS IN SURFACE POISES

No. of C Atoms	Saturated Acids at 25°C.	Unsaturated Acid at 20°C.
14	Myristic	0.000161
15	Pentadecylic	0.000228
16	Palmitic	0.000248
17	Margaric	0.000317
18	Stearic	0.000307
19	Nonadecanoic	plastic solid
20	Arachidic	0.001790
18	Oleic	0.000162

2. Torsion ring surface viscosimeter for liquid and plastic-solid films.

A torsion pendulum, with a horizontal circular disk at the bottom, was constructed. This disk may be allowed to vibrate in the surface, but is insensitive to the film. A thin metal cylinder, 1 cm. high, was soldered to the outside of the ring in such a way that only the sharp lower edge of this cylinder could be put in contact with the surface of the water. By allowing this ring (10 cm. in diameter) to vibrate in contact with the clean surface, and then with a film outside, but not inside the ring, the viscosity of the film could be calculated from the logarithmic decrements of angle between successive swings.

This instrument gave data of great interest. For example, cetyl alcohol on 0.01 molar hydrochloric acid at 22° C. compresses at very low pressure to a liquid monolayer of 21 sq. A. area permolecule. As the pressure is increased, the viscosity of the liquid film increases, as is shown by both types of viscosimeter. The force-area relation is linear to 11 dynes and 19 sq. A., and at this kink point a change of phase occurs, in which a plastic solid film of very much higher viscosity and lower compressibility appears. The viscosity of this film increases rapidly with pressure. Pentadecylic acid, which forms an expanded film the pressure of which begins to increase above 0.1 dyne per cm. at 44 sq. A., forms a liquid film both below and above the kink, and the solid plastic form appears where no kink is visible at a molecular area of 21 sq. A.

The viscosity of monolayers is found to be highly dependent upon the tightness of packing of the molecules in the film, and, as the table indicates, it increases rapidly with the length of the molecule in condensed films which exhibit an orientation of the molecules perpendicular to the surface.

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