Viscosity of Monomolecular Films
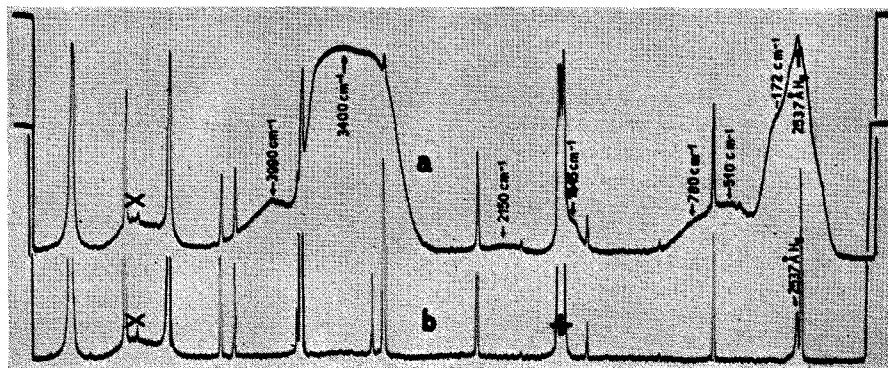
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FIG. 1. The Raman bands of water (curve a) fall off (curve b) when the resonance line 2537A of the employed low pressure mercury arc is absorbed.

Without any doubt, this statement is to be attributed, as indicated by J. H. Hibben,[3] to the great differences between the mercury lamps at low pressure, exclusively used by the former workers, and the ordinary lamps, apparently used by Rao and Koteswaran. In the first type of lamps the resonance line 2537A is remarkably sharp and particularly intense (a thousand times more than any neighboring line); in the other type of lamps the same line, instead, is greatly weakened by self-reversal, so that it does not at all assume a prominent position between the other lines.

For that reason, and because the lines accompanying the 2537A are too numerous, and some are diffused, the ordinary lamps are absolutely unallowable in Raman work in ultraviolet. With their use to study the Raman spectrum of water, one cannot do better than observe the very intense group of frequencies at 3400 cm⁻¹ excited by the various lines, and so do Rao and Koteswaran. The weak frequencies 172, 510, 780, 1645, 2150, 3990 cm⁻¹ indeed, either are not photographed or, if photographed, are masked by the numerous bands corresponding to the quoted intense group of frequencies.

Independently of these considerations, it is to be noted that in 1933, when I have observed the frequencies in question, I have carried out and published an experiment to decide definitely its assignment.[4] In my experiment, a filter of mercury vapor at about 200°C was used in order to absorb, in the exciting spectrum of the low pressure mercury arc, the resonance line 2537A. I am giving in Fig. 1 two microphotometric curves of a plate made in 1933: *a* is the complete Raman spectrum of water obtained *without* the mercury filter, *b* is obtained *with* the mercury filter (3*h*, 30*m* and 3*h* exposures, respectively). I feel that no doubt will remain that the frequencies 172, 510, 780, 1645, 2150, 3990 cm⁻¹ *really exist:* it is a fact that they fall off when the line 2537A is absent in the exciting spectrum.

The band indicated with a cross in both the curves has been considered by M. Magat[5] corresponding to a frequency 5100 cm⁻¹, as excited by the line 2537A. It is evident that it should be considered as excited by the

group of lines at 2653A (indicated with plus sign in *b*), with the resulting displacement of about 3400 cm⁻¹.

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[1] I. Ramakrishna Rao and P. Koteswaran, J. Chem. Phys. **5**, 667 (1937).
[2] There are some discrepancies, generally not essential, between the values given by different authors. I am referring the values given by me in Nuovo Cimento **10**, 101 (1933); in this paper I have also measured the low frequency 60 cm⁻¹, not afterwards observed by other authors. On this frequency and on the pointed discrepancies I will return elsewhere.
[3] J. H. Hibben, J. Chem. Phys. **5**, 994 (1937).
[4] G. Bolla, Nuovo Cimento **10**, 101 (1933), §3.
[5] M. Magat, J. de phys. **5**, 347 (1934).

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There have appeared in the numbers of *Nature* of September 11, 1937 and of the *Journal of Chemical Physics* of January, 1938, two editorial letters by Harkins and Myers, and Harkins and Kirkwood, respectively, concerning a surface viscosimeter. We wish to call attention to the previous results that we have obtained with a viscosimeter of the same type.[1]

We have shown experimentally that the surface flow per second, Q, is in fact proportional to the difference of pressure and inversely proportional to the length of the canal, but we think it necessary to insist that there is no law analogous to Poiseuille's law concerning the width of the slit. The corresponding Poiseuille equation for a two-dimensional fluid should contain a factor d^3 (d = width of slit). The results of our systematic study with canals of different widths show clearly that the problem is much more complicated. There is no doubt that we have simultaneous entrainment of the water and that the viscosity of the substrate becomes the preponderant factor as soon as canal widths of the order of one centimeter are reached, i.e. the flows per unit time become independent of the nature of the fluid as the diameter increases, finally reaching the same value. The relation with d^3 would be valid only as a limiting law for very narrow canals, since, as the diameter decreases, we find *linear* variation until

5 mm, this variation gradually changing to d^2 at 0.5 mm.

We think that even with corrective terms one can hope to attain only the order of magnitude of the two-dimensional viscosity of the film. The calculation made by Kirkwood is valid only for a deep canal, which is not the case for the viscosimeters used by us and by Harkins. The theory introduced by Bresler and Talmud[2] would give results in better qualitative accord even for large canals, although it introduces arbitrarily a frictional term proportional to the speed in the differential equation. Unfortunately, an error in the integration prevented these authors from observing the accordance cited above.

The correct integrated form should be:

$$Q = \frac{2\phi}{SA\kappa}\left[R - \left(\frac{\eta}{A\kappa}\right)^{\frac{1}{2}}\tanh\left(\frac{A\kappa}{\eta}\right)^{\frac{1}{2}}R\right],$$

where

ϕ = pressure gradient,
S = surface per gram,
A = constant,
κ = viscosity of water,
$R = d/2$,
η = viscosity of the film.

This gives for large canals the expression:

$$Q = 2\phi R/SA\kappa$$

and for infinitely small canals:

$$Q = 2\phi R^3/3S\eta.$$

Nevertheless, in spite of this theoretical difficulty, one can by using the experimental values of the flow for a given canal detect very accurately changes of state in monolayers. We have shown,[3] for example, that a liquid film of triolein exhibits at about 115A^2 a sharp change in the variation of the viscosity. In the same manner a fluid film of stearic acid on 0.001 N HCl gives changes at about 20.5 and 22A^2. Thus, from this point of view alone, the measurements of surface viscosity constitute already a very promising new method of investigation.

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March 16, 1938.

[1] Dervichian and Joly, Comptes rendus 204, 1318 (1937). See also M. Joly, J. de phys. 8, 471 (1937).
[2] Bresler and Talmud, Physik. Zeits. Sowjetunion 4, 864 (1933).
[3] Dervichian and Joly, Comptes rendus 206, 326 (1938).