The Viscosity (or Fluidity) of Liquid or Plastic Monomolecular Films

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$$\begin{vmatrix} A\lambda-a & B\lambda & C\lambda & -d & 0 \\ B\lambda & A\lambda-a & C\lambda & 0 & -d \\ C\lambda & C\lambda & D\lambda-c & 0 & 0 \\ -d & 0 & 0 & \dfrac{C}{2}\lambda-b & 0 \\ 0 & -d & 0 & 0 & \dfrac{C}{2}\lambda-b \end{vmatrix} = 0, \quad (1)$$

where a, b, c and d are force constants defined in Sutherland and Dennison's paper, and

$$A = \frac{2m(m+M)}{2m+M}, \quad B = \frac{2m^2}{2m+M}, \quad C = m, \quad D = \frac{2m+M}{2}.$$

That their treatment of these vibrations is satisfactory is shown by the fact that the five observed frequencies satisfy quite well the relation which results on eliminating the four force constants among the five equations from (1). The modes of these vibrations are shown in Fig. 1.

To decide between the two assignments $\begin{cases} \delta_{\pi s}=1342 \\ \nu_{2\pi s}=1623 \end{cases}$ and $\begin{cases} \delta_{\pi s}=1623 \\ \nu_{2\pi s}=1342, \end{cases}$ let us denote the normal coordinates by ξ_i, $i=1, 2, \cdots, 5$. The transformation equations between the coordinates x_1, x_2, x_0, q_1, q_2 and these normal coordinates are then

$$x_1 = \Sigma c_{1i}\xi_i, \quad x_2 = \Sigma c_{2i}\xi_i, \quad x_0 = \Sigma c_{3i}\xi_i, \quad q_1 = \Sigma c_{4i}\xi_i, \quad q_2 = \Sigma c_{5i}\xi_i,$$

where $c_{1i}\cdots c_{5i}$ are proportional to the minors of the elements in any one row in the secular determinant (1) in which λ is given the value of the ith root, i.e., of the ith normal vibration. For the ith vibration, we have, except for a common factor of proportionality,

$$x_1 = \begin{vmatrix} A\lambda_i-a & C\lambda_i & -d \\ C\lambda_i & D\lambda_i-c & 0 \\ -d & 0 & \dfrac{C}{2}\lambda_i-b \end{vmatrix} \xi_i,$$

$$x_2 = -\lambda_i\left(\frac{C}{2}\lambda_i-b\right) \begin{vmatrix} B & C \\ C\lambda_i & D\lambda_i-c \end{vmatrix} \xi_i,$$

$$x_0 = C\lambda_i \begin{vmatrix} B\lambda_i & A\lambda_i-a & -d \\ 1 & 1 & 0 \\ 0 & -d & \dfrac{C}{2}\lambda_i-b \end{vmatrix} \xi_i, \quad (2)$$

$$q_1 = d\left(\frac{C}{2}\lambda_i-b\right)^{-1} x_1, \quad q_2 = d\left(\frac{C}{2}\lambda_i-b\right)^{-1} x_2.$$

From these, the relative values of the coordinates x_1, x_2, x_0, q_1, q_2 for the five fundamental frequencies can be obtained. The result is given in Table I. Consideration of the vibrational form of $\delta_{\pi s}$ (Fig. 1) shows that x_1/x_0 and x_2/x_0 must be negative, while q_1/x_0, q_2/x_0 must be positive. These relations are satisfied only by the frequency 1623 cm^{-1}, while the relative displacements for the frequency 1342 cm^{-1} are compatible with $\nu_{2\pi s}$, if the amplitudes of the H atoms are larger than those of the C atoms, and if on approaching together of the two CH$_2$ groups the H atoms in each group are pushed apart a little, as shown in Fig. 1.

TABLE I. *Relative displacements in the normal vibrations of C_2H_4.*

	2988 cm^{-1}	1444 cm^{-1}	3060 cm^{-1}[3]	1623 cm^{-1}	1342 cm^{-1}
x_0	0	0	$\neq 0$	$\neq 0$	$\neq 0$
x_1/x_2	-1	-1	1	1	1
q_1/q_2	-1	-1	1	1	1
x_1/x_0 or x_2/x_0	—	—	<0	<0	>0
q_1/x_0 or q_2/x_0	—	—	<0	>0	<0
x_1/q_1	>0	<0	>0	<0	<0
assignment	$\nu_{\pi a}$	$\delta_{\pi a}$	$\nu_{\pi s}$	$\delta_{\pi s}$	$\nu_{2\pi s}$

But these are just what one would expect on purely mechanical considerations. Thus we are led to the assignment of Sutherland and Dennison, namely, $\delta_{\pi s}=1623$, $\nu_{2\pi s}=1342$ in contradiction to that of Mecke.

In view of this change, the values of the frequencies for C$_2$H$_4$, cis, trans and asymmetric C$_2$H$_2$D$_2$, C$_2$D$_4$ given in another article "On the Fundamental frequencies of CH$_2$, CHD, CD$_2$, CHCl, CDCl and Cis and Trans C$_2$H$_2$D$_2$ and C$_2$H$_2$Cl$_2$"[4] should be interchanged. This does not, however, necessarily invalidate the usual assignment to the vibration $\nu_{2\pi s}$ of frequencies in the region 1500–1600 cm^{-1} in molecules in which one or more H atom is replaced by another atom or a group of atoms. The frequency of the vibration $\nu_{2\pi s}$ depends not only on the force constant between the double bond carbon atoms, but also on the force constants and masses in the CH$_2$, CHX, or CX$_2$ group.

In Table I, the signs for the ratios x_1/q_1 are obtained from Eq. (2) with the positive sign for d, i.e., $d=+1.46\times10^5$. Consideration of Fig. 1 shows that the signs of x_1/q_1 for all the five vibrations are just as expected. Thus we are led to choose the positive value for d, in agreement with the conclusion of Sutherland and Dennison based on a different reason.[1]

TA-YOU WU

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National University of Peking, Peiping,
March 22, 1937.

[1] G. B. B. M. Sutherland and D. M. Dennison, Proc. Roy. Soc. A148, 250 (1935); R. Mecke, Zeits. f. physik. Chemie B17, 1 (1932); Hand und Jahrbuch d. chem. phys., Bd. 9/II, 395 (1934); Bonner, J. Am. Chem. Soc. 58, 34 (1936).
[2] Sutherland and Dennison, Proc. Roy. Soc. A148, 250 (1935). Reference is made to this paper for the notation and values of the force constants used in this letter.
[3] It is found that a change of the value 3019 to 3060 is necessary in order to satisfy the relation (5) in Sutherland and Dennison's paper and hence to give consistent solution for the force constants.
[4] J. Chem. Phys. 5, 392 (1937).

The Viscosity (or Fluidity) of Liquid or Plastic Monomolecular Films

Theories of the structure of monomolecular films are in an unsatisfactory state on account of a lack of knowledge of the change of properties of the films as the film pressure (f) increases. A determination of the viscosity relations of the films would be of great value, not only to the theory, but also in connection with the phenomena of penetration of liquids into solids, and of the rate of spreading of films. Unfortunately the literature contains no values for the viscosity of liquid films. In the work reported here such vis-

TABLE I. *Viscosities in surface poises (s. p.) of liquid monolayers at 25° C.*

No. C atoms	Saturated Acids	η in dyne sec./cm	Unsaturated Acid
14	Myristic	0.000161	
15	Pentadecylic	0.000228	
16	Palmitic	0.000248	
17	Margaric	0.000317	
18	Stearic	0.000307	Oleic 0.000162
19	Nonadecanoic	Plastic solid	
20	Arachidic	0.001790	

cosities have been obtained by the use of two new viscosimeters, while a third type has been designed.

1. The capillary slit surface viscosimeter

A transverse slit 5 to 15 cm long, produced by two movable jaws adjusted by a screw, occupies the middle of an ordinary metal barrier, used to compress the film on the surface of a trough filled with water. The film is put on the surface of the water between this barrier and the film balance, which may be of the usual type or a much more simple type recently developed in this laboratory. The slit is usually used at diameters (d) between 0.2 and 1.5 mm, and after being given a very light coat of paraffin, is placed so that it rests just in contact with the surface of the water. The film flows under its own pressure through the slit on the horizontal water surface. The theory developed for this case gave the equation:

$$\eta = \frac{f}{Q}\frac{d^3}{12l}.$$

Q, the quantity of the film which passes through the slit in unit time was found to vary exactly as the cube of the diameter instead of as d^4 in a capillary tube. Some viscosities obtained are given in Table I.

All of these films, with one exception gave a linear f, Q relation and the straight line passed through the origin, so all of these are true liquid films. With nonadecanoic acid the relation was nonlinear and the linear part of the curve did not extrapolate through the origin. The film is therefore a plastic solid. Cetyl alcohol films were investigated both by the capillary slit and torsion viscosimeters, and exhibited the same general behavior with both, as described later. In the less viscous regions these two latter films gave viscosities as low as 0.0019 s.p.

Preliminary work with a small difference of temperature seems to indicate an increase of viscosity with temperature. At 20°C the viscosities are 0.000162 for oleic acid and 0.000289 for stearic acid, both with 18 carbon atoms, and 0.000142 for myristic acid with 14 carbon atoms. The viscosity is found to be much more dependent upon the tightness of packing of the molecules in the film than upon the number of carbon atoms in the chain.

2. Torsion ring surface viscosimeter

The differential equation of the torsion pendulum gives on integration the angular deflection:

$$\theta = e^{-rT/I}C'\sin\left(\frac{k}{I} - \frac{r^2t}{I^2}\right)^{\frac{1}{2}},$$

where r is the damping factor due to the medium, I the moment of inertia of the oscillating system, C' is a constant and k is the wire constant for restoring torque. The amplitude is $C'e^{-rT/I}$ and the period $T = 2\pi(I^2/(kI - r^2))^{\frac{1}{2}}$ = const. and for two successive amplitudes $\theta/\theta' = e^{rT/I}$. It can be shown that

$$2.303\Delta = 2.303(\log\theta - \log\theta_1) = rT/I,$$

where Δ is the logarithmic decrement.

With a true liquid film the viscosity is independent of amplitude, and a plot of the logarithm of the amplitude against the number of swings gives a straight line whose slope is a measure of the viscosity. With a plastic solid the line is curved. Thus the torsion ring pendulum is a powerful tool for the indication of changes of structure in a film.

In order to change the sensitivity of the apparatus it is advisable to use different torsion wires. In order to make the results with two different wires comparable it is necessary to compare the ratio of the log decrements at the same film pressure.

With a clean water surface.—

$$2.303(\log\theta_1' - \log\theta_2') = \Delta' = 2\pi r'/(kI - r'^2)^{\frac{1}{2}} = r'T'/I$$

and with the film

$$\Delta'' = 2\pi(r'+r'')/[kI - (r'+r'')^2]^{\frac{1}{2}} = (r'+r'')T''/I$$

or

$$B = \frac{r'+r''}{r'}\cdot\frac{(kI - r'^2)^{\frac{1}{2}}}{(kI - (r'+r'')^2)^{\frac{1}{2}}}.$$

In order to make B larger the value of r'' was increased with respect to r' by soldering a ring with a lower razor edge to the bottom of the circular disk of the torsion pendulum. This greatly increased the sensitivity. For the two wires used kI was 2,304,000 and 50,600 and r'^2 7.37 and 1.88, in units of g²cm⁴ sec.⁻².

*Cetyl alcohol films: on 0.01 m HCl.—*The film is very tightly packed, with a molecular area at high pressure of about 19 sq. A. Below the kink point at 13 dynes at 25°C the f, a relation is expressed by a straight line which represents an extremely low compressibility. At all pressures below this kink point the films are true liquids, but the viscosity increases rapidly and almost linearly with the film pressure. Above the kink the compressibility is even less, the film is a plastic solid, and the viscosity increases even more rapidly with the pressure.
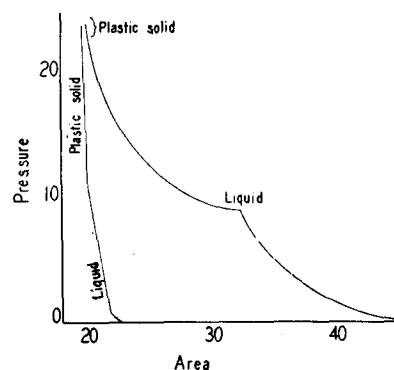

FIG. 1. Pressure area relations with regions and plastic solid films for cetyl alcohol and pentadecylic acid.

Pentadeclyic acids.—This acid forms an expanded film on 0.01 m HCl at 25 degrees. At 0.1 dyne a is 44 sq. A. As the film is compressed it remains liquid, but the viscosity increases to the kink at 9.00 dynes and 32.3 sq. A. Just above this kink the viscosity remains nearly constant as the area decreases and then the viscosity increases more and more rapidly. At about 23 dynes per cm pressure the film changes to a plastic solid.

It is obvious that the intermolecular forces between the molecules in the film have much greater effects when the film is tightly packed than when it is expanded. With the aid of further measurements it is hoped to learn the part played by the forces between the molecules of the film and the underlying water.

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