and hence the lack of any discernible vibrational structure in the band even at −50°.

Summary

1. The adsorption spectrum of triketopentane dissolved in an inert hydrocarbon solvent (isooctane) has been measured and compared with that of diacetyl and acetone under similar conditions.

2. On the basis of this comparison of absorption spectra, together with a consideration of the molecular dimensions, non-coplanar structure is assigned to the triketopentane.

BERKELEY, CALIFORNIA RECEIVED SEPTEMBER 3, 1940

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Viscosity of Monolayers: a Test of the Canal Viscosimeter

BY GEORGE C. NUTTING AND WILLIAM D. HARKINS

Experimental and theoretical studies of the rate of flow of monolayers through surface slits or canals have been made by several investigators, among whom Bresler, Talmud and Talmud were the first.[1–6]

For the limiting case of a deep and very narrow canal it has been proposed[6] that the rate of flow is related to the absolute viscosity of the monolayer by the expression

$$\eta = \frac{(f_2 - f_1)a^3}{12(l)(Q)} - \frac{a\eta_0}{\pi} \qquad (1)$$

in which f_2 and f_1 are the film pressures at the ends of the canal, in dynes per cm.; a is the width and l the length of the canal in cm.; Q is the area in sq. cm. of the film flowing through the canal in 1 sec.; and η_0 is the bulk viscosity of the subsolution at the temperature of the experiment. The first term is completely analogous to the Poiseuille formula for the flow of liquids through long capillary tubes. Applied to a film it presupposes that the canal width is small and that the ratio of length to width is large in order that flow may be laminar rather than turbulent and that end corrections may be negligible. It is also assumed that there is no slippage of the film along the sides of the canal.

The second term is a correction for the inevitable drag exerted upon a flowing film by the viscous fluid upon which it is spread. It has been derived for the case of a canal with smooth, parallel walls which extend below the surface to a distance much greater than the distance between the walls. The conditions assumed in the development of this equation imply that the film is incompressible, and possesses a practically constant viscosity while passing through the canal. This obviously makes it necessary to keep the fall of film pressure in the canal as small as possible.

In the work presented in this paper the principal object was to determine what type of canal gives the best results, so large decrements of pressure have often been used. However, to minimize the effects of the change of area with pressure the investigations have been confined almost entirely to the alcohols, which give films of very low compressibility.

The Canal Viscosimeter and Experimental Methods

The procedure involved in the determination of viscosity is to measure the amount of film passing through the canal in unit time under a given pressure difference between the ends. The viscosimeter was assembled on a paraffined brass trough of inside dimensions 75 × 25 × 2 cm. The film pressure on the entrance side of the canal was measured by means of a film balance, a detailed description of which has been given already.[7,8] The film pressure was maintained constant by moving forward a barrier (piston) at a rate which just compensated for the loss of film from the high pressure side by its passage through the slit.

In much of the work the supports of the slit served as the barrier. That is, the slit itself was moved slowly forward as the experiment proceeded. The apparatus is diagrammed in Fig. 1b. The compressed film is contained in the area II between the float, A, of the film balance and the slit-barrier, B. III is a clean surface of 0.01 N sulfuric acid, and area I behind the slit contains the film material in so small an amount that the film pressure is negligible. The jaws of the slit were supported on brass rods 1.3 cm. square which rested on the sides of the trough. The forward and backward motion of the slit-barrier was accomplished through an accurately threaded rod (not

---

[1] Bresler, Talmud and Talmud, *Physik. Z. Sowjetunion*, **4**, 864 (1933).

[2] Dervichian and Joly, *Compt. rend.*, **204**, 1318 (1937).

[3] Joly, *J. Phys.*, **8**, 471 (1937); **9**, 345 (1938).

[4] Myers and Harkins, *Nature*, **140**, 465 (1937); *J. Chem. Phys.*, **5**, 601 (1937).

[5] Washburn and Wakeham, THIS JOURNAL, **60**, 1294 (1938).

[6] Harkins and Kirkwood, *J. Chem. Phys.*, **6**, 53, 298 (1938).

[7] Harkins and Myers, *ibid.*, **4**, 716 (1936).

[8] Nutting and Harkins, THIS JOURNAL, **61**, 1180 (1939).

shown) turned manually by means of a 30 to 1 worm reduction gear. Any jerkiness in the motion of the slit-barrier makes film flux measurements non-reproducible. For this reason the supports for the slit and the top of the trough were ground flat, and particular care was taken to secure an even coat of paraffin over the brass, and to produce smooth transmission of force to the slit supports through the screw and gears.

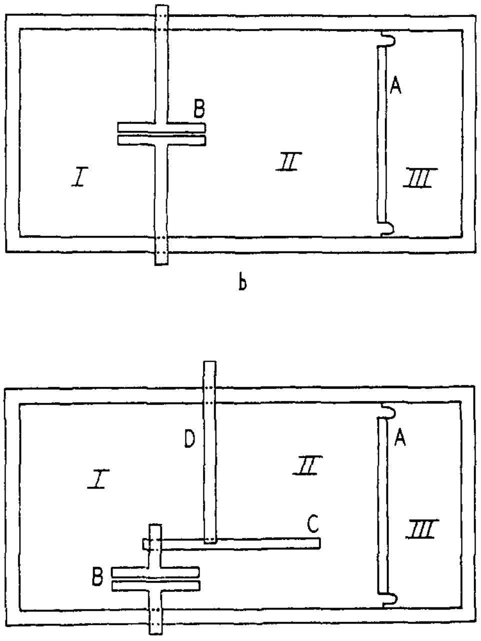

Fig. 1.—Diagrams showing the disposition of the viscosimeter canal, piston and film balance on the film trough.

In a second and more satisfactory arrangement of the apparatus (Fig. 1a) the canal was stationary. C is a brass strip 1.3 cm. wide and 30 cm. long firmly attached to the floor of the trough about 5 cm. from one side. The upper surface of C was ground coplanar with the sides of the trough and was lightly paraffined. A square rod, D, which rested on C and the far side of the trough, served as piston and was moved as before by the screw and gears. Because of the paraffin coating C was not covered by the solution in the trough, so the film pushed forward by the piston to replace that lost through the canal passed between C and the float into the 5-cm. passage ending in the canal, B.

Except in one series of measurements, which will be described presently, the pressure on the film leaving the canal was that of the surface vapor pressure of the film at the temperature of the experiment. Before flow began the rather large area, I, behind the canal was swept thoroughly, and this area increased during flow through the movement to the right of either the canal or the piston.

The long chain alcohols and acid were presented by Professor E. E. Reid of the Johns Hopkins University. The preparation and purification of the compounds has been described.[9] All of the films were spread on 0.01 *N* sulfuric acid. The profound influence of minute amounts of metal ions on fatty acid films spread on neutral and alkaline solutions made such a procedure necessary in the work with stearic acid. It might be supposed that the properties of the alcohol films are not sensibly different on water or 0.01 *N* acid. Experiments showed, however, that the viscosity of hexadecyl alcohol on water was about three times that on acid. The difference may possibly be attributable to the effect of heavy metal ions from the apparatus on small amounts of fatty acid present as an impurity in the alcohol. The water from which the acid solutions were made up was distilled from alkaline permanganate. The alcohols and acid were spread from dilute solutions in purified petroleum ether.

In a slit viscosimeter the jaws, or thin sheets of mica, which produce the slit, do not dip beneath the surface of the subsolution, and the level of the liquid in the slit is the same as that outside. In the canal viscosimeter the vertical sides extend some distance below the surface of the liquid in the canal (Fig. 2).

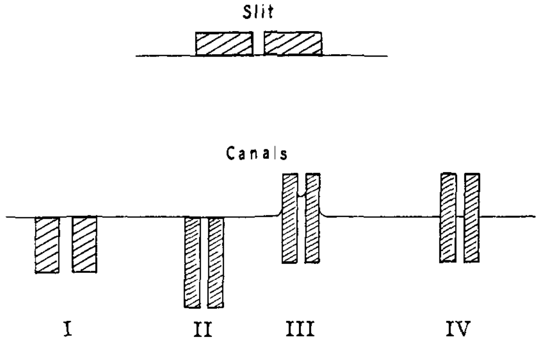

Fig. 2.—Cross-sectional representation of the slit and canal viscosimeters.

Five different slits or canals were used and a brief description of each follows.

Slit Viscosimeter.—This was a surface slit, that is, the jaws did not extend below the surface of the subsolution, so the film flowed at the bottom of the jaws. The correction to the apparent viscosity determined with such a surface slit is smaller than for a canal, for which the correction is $a\eta_0/\pi$, but its magnitude has not yet been calculated from theory.[10] The slit was of brass, 15.3 cm. long, with plane ends 1 cm. wide, and when in use was coated with paraffin.

Canal Viscosimeter Ia.—This was of paraffined brass, 10.0 cm. long, with large plane ends. The depth of the canal was 1 cm., and the film flowed along the top. The jaws were adjustable in the vertical direction so that the level of the film at the top of the canal might be made equal to the height of the free surface of liquid in the trough.

Canal II.—The jaws were made of microscope slides with their top edges ground smooth and flat and lightly paraffined. The top edges were at the level of the free surface; length 7.6 cm.

Canal III.—The jaws were made of plate glass, 7.5 × 7.5 × 0.6 cm., with plane ends lightly paraffined. The

---

[9] Reid and Meyer, This Journal, **55**, 1574 (1933).

[10] Hermans, *Physica*, **6**, 313 (1939), in a reinterpretation of the experimental work of Joly[3] on the viscosity of stearic acid monolayers concludes that the corrected equation of Harkins and Kirkwood is applicable also to a slit viscosimeter made of mica sheets resting on the liquid surface.

bottom of the slit was 1 cm. below the free surface of the subsolution. The length of the slit varied with the separation of the jaws and the film pressure because of a capillary rise in the slit.

Canal IV.—Same as Canal III with a thin coating of paraffin above the level of the free surface of the subsolution, so there was no capillary rise. The jaws below the free surface were wet thoroughly by the subsolution, unlike the paraffined Canal Ia; length 7.5 cm.

Slit and canal widths from 0.020 to 0.157 cm. were used. To ensure parallelism of the jaws as well as the desired separation, an appropriate combination of thickness gages was inserted between the jaws, which were then clamped at the top and bottom and at both ends. The gages were then removed.

Ligroin solutions of the alcohols were dropped in the middle of the area included between the film balance and the barrier, in an amount slightly less than that required to cover the area with a monolayer of the alcohol. A period of ten to twenty minutes was then allowed for complete evaporation of the solvent before compression was begun.

After moving the barrier forward until the desired film pressure was attained, the canal was cleaned by drawing a thin phosphor bronze strip through it several times. Then perhaps two to four minutes was allowed for the establishment of a steady rate of flow before measurements were begun. The measurements were of the amount of forward movement of the barrier in sixty second intervals during which the pressure on the film was kept constant. In an apparatus free from leaks, with an insoluble film below its collapse pressure, such observations afford an adequate measure of the quantity of film flowing through the canal.

The motion of the barrier was indicated on a circle divided into 720 parts and mounted on a threaded rod of 0.2 cm. pitch. The extreme movements of the barrier corresponded to about 25 and 400 degrees per minute, equivalent to a minimum and maximum flow of the film of about 4×10^{-3} and 7×10^{-2} sq. cm. per sec. For a canal of length 10 cm. and width 0.07 cm. the time taken by the average molecule to traverse the canal is then from ten to two hundred sec.

At a given film pressure the usual practice was to record area decrements during one minute intervals for ten minutes after steady flow was attained. If the decrements were unusually concordant fewer observations were made, while occasionally as many as 30 to 50 readings were required. A typical group of measurements on a stearic acid film follows. The unit is degrees per min. on the divided circle: 31, 37, 36, 28, 29, 32, 32, 32, 25, 36, with an average of 32.

After each series of measurements the canal was cleaned. Experience showed this to be a desirable procedure for otherwise gradual closure of the canal often resulted. Whether this was due to accumulation of dust or microcrystals or formation of a "built-up" film along the jaws was not determined, but it was probably not the last of these on account of the great number of layers necessary to produce an effect.

Viscosity measurements at 15 pressures were made as a rule for each canal width. A certain randomness was introduced into the sequence of pressures in order to show up spurious results arising from slow changes in the film properties, unsuspected narrowing of the canal, back pressure due to accumulation of film at the rear of the canal, or other causes. The following is a characteristic sequence of film pressures, in dynes per cm.: 2.7, 4.6, 6.4, 8.3, 10.2, 7.4, 5.5, 3.6, 1.8, 5.8, 8.9, 12.0, 13.9, 15.8. On proceeding from a higher to a lower pressure, the pressure was released by allowing film to flow through the canal rather than quickly moving the piston rearward and then compressing once more.

No attempt was made to determine the temperature coefficient of viscosity of any of the films. The temperature change in the course of an experiment was probably never as much as 1° and the range of temperature was from 19 to 25°.

Results

Stearic Acid.—The viscosity of stearic acid was obtained with Canal Ia, width 0.020 cm., at pressures from 2 to 15 dynes. With the width 0.05 cm. the corrected viscosity was negative at a pressure of 2 dynes, and at a width of 0.010 cm. flow through the slit was very erratic. With a width of 0.020 cm. the value of the first term in the viscosity equation varied from 0.66 to 1.19 $\times 10^{-4}$ surface poise, showing no trend with pressure. The average was 0.93×10^{-4}. The value of the second term was 0.61×10^{-4}, equal to a minimum correction of 51%. The average of the corrected viscosities is 0.18×10^{-4} poise at 20°. The numerical value is of small significance because of the large correction term but it is interesting that the uncorrected viscosities are much less than that (0.0003 poise) found by Harkins and Myers with a slit viscosimeter.[4] The correction for surface slits is less than for canals so it would be expected that the uncorrected viscosities from the slits would be somewhat smaller. The fact that they are actually much greater is probably because the film slips along the paraffined upper edge of this particular type of canal but does not slip with the type of slit viscosimeter used by Harkins and Myers.

The viscosities of hexa- and octadecyl alcohols determined with the slit were likewise much larger than with Canal Ia so a new canal (III) was made from plate glass and new measurements on stearic acid were begun.

Glass was chosen because when clean it is wet by both oil and water and the probability of slippage along the canal walls by the film and substrate is thus minimized. The use of a canal like III presents a number of difficulties. First is the magnitude of the capillary rise, which varies with the separation of the walls and also with the surface tension of the liquid, and this in the present case varied continuously along the canal. The capillary rise (h) between parallel plates of separation (d) is given by the equation

$$\gamma = \frac{\Delta\rho d h g}{2} \tag{2}$$

where γ is the surface tension of the liquid, g is the gravitational constant and $\Delta\rho$ is the difference in density of the liquid and its vapor.

The capillary rise at both ends of the canal was measured with a cathetometer for the three canal widths used (0.05, 0.07 and 0.10 cm.) at several film pressures. The results were consistent with the predictions of the formula and the assumption of a uniform gradient of surface tension from the value measured with the film balance at the free surface level at the beginning of the canal to the value zero at the surface level at the end of the canal.

The end faces of the glass plates were paraffined lightly in order to define better the length of the canal. If the ends are wet the liquid rises rather gradually from the free surface into the canal. The apparent viscosity of hexadecyl alcohol measured with a canal with paraffined ends was about twice as great as when the ends were wet. The assignment of the correct width to the canal is difficult, since the effective width is along the curved surface. Since the viscosity varies (approximately) as the cube of the width, a small error in this quantity produces a much larger error in the viscosity. For a small capillary slit the profile of a meniscus approximates a semicircle, so a in equation (1) is taken for this type of canal as $\pi/2$ times the separation of the glass plates as measured by a thickness gage.

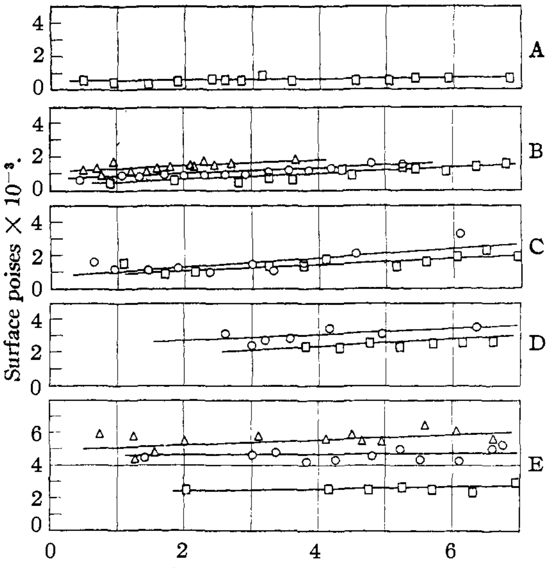

Fig. 3.—Viscosity of monolayers of the alcohols and stearic acid as determined with Canal III: □, canal width 0.078 cm.; ○, 0.110 cm.; △, 0.157 cm.; temperature 23–24°; A, stearic acid; B, pentadecyl alcohol; C, hexadecyl alcohol; D, heptadecyl alcohol; E, octadecyl alcohol.

In using Canal III it also has been assumed that Eq. 1 is as correct for a capillary which imposes several sudden changes in the direction of the flowing film as it is for a straight capillary.

Corrected viscosities of stearic acid films obtained with Canal III are represented as a function of film pressure in Fig. 3-A. The pressures given are equal to one-half the observed pressure on the film on the entrance side of the slit; they are thus mean pressures within the slit assuming a linear gradient. The value of η obtained by this procedure increases from about 4×10^{-4} to 7×10^{-4} surface poises as the pressure changes from 0.5 to 7 dynes/cm.

Hexadecyl Alcohol.—Hexadecyl alcohol was investigated with the slit and all of the canals. Graphs of results are contained in Figs. 3-C, 4-A, D and 5-A. As with stearic acid the slit gave much higher calculated viscosities than Canal Ia, while Canal III gave the highest of all. For the slit and all of the canals for which data are available the calculated viscosity increases with width, indicating either that Eq. 1 is not exactly applicable, or that the meniscus shape assumed when determining a was incorrect. For all except III the meniscus was taken to be a straight line and a the perpendicular distance between the jaws. It is difficult with very narrow slits or canals to be certain that the meniscus has the specified shape.

Canal IV was made from Canal III by covering the jaws with a thin layer of paraffin, then completely removing the paraffin below the level of the subsolution. The viscosity of hexadecyl alcohol measured with Canal IV was relatively high, above 6×10^{-3} poise at all pressures, and with 0.05 cm. canal width, constant flow was not attained at pressures below 15 dynes.

The pressure–area curves of the long chain alcohols at room temperature consist of two straight lines. The one which corresponds to the higher pressures is much the steeper, which indicates greatly increased resistance to compression. An accompanying discontinuous change in the viscosity of the films might be expected. The sudden change in compressibility of a hexadecyl alcohol film occurs at 10.2 dynes, yet the usual slow upward trend of viscosity with increased pressure is not altered above this critical pressure, as the graphs show. However, the viscosities measured by the damping of a torsion pendulum increase greatly within a rather small pressure range beginning somewhat below 9 dynes[11] but in these experiments the entire film is presumably under the same pressure.

To adapt the canal viscosimeter to measurements of changes of viscosity with pressure it is necessary to provide an auxiliary device which will maintain the film pressure at the rear of the canal at any desired value. This may be done best mechanically[3] but also with a series of piston oils. An experiment on hexadecyl alcohol with Canal III was carried out by the use of ethyl cinnamate as a piston oil. The spreading pressure at 25° of the particular specimen of ethyl cinnamate used was 14.6 dynes, well above the transition pressure of the alcohol film. The pressure at the front of the slit was varied from 18.8 to 24.7 dynes so that the mean pressure was 16.7 to 19.7 dynes. In this range the viscosity measured with a slit width of 0.157 cm. was almost constant with an average value of 2.67 × 10^{-2} poise. The fact of greatly increased film viscosity above the transition pressure is thus confirmed, but one of the severest limitations of the canal viscosimeter is also clearly brought out. Owing to the desirability amounting almost to necessity of using a pressure drop along the canal of several dynes it is not possible to follow changes of viscosity which take place at a constant pressure or within a very small pressure range.

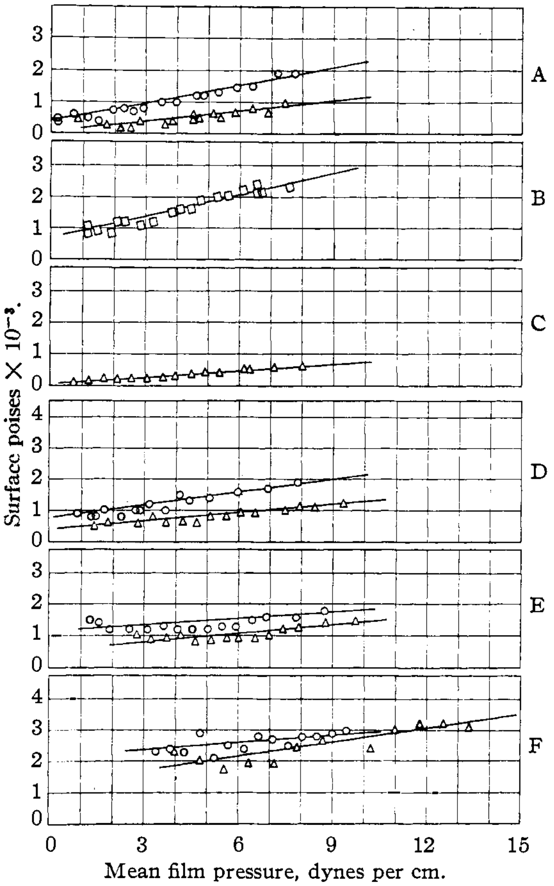

Fig. 4.—Viscosity of alcohol monolayers—A, hexadecyl alcohol, 20°: ○, slit of width 0.070 cm.; △ Canal I, 0.050 cm. B, octadecyl alcohol, 20°; □, slit of width 0.100 cm. C, D, E, F, Canal II, △, 0.050 cm., ○, 0.070 cm., 24–25°. C, pentadecyl alcohol; D, hexadecyl; E, heptadecyl; F, octadecyl.

Octadecyl Alcohol.—The viscosity found for octadecyl alcohol films likewise depends on the type of slit or canal. That determined with Canal III is higher than with II, and this in turn is

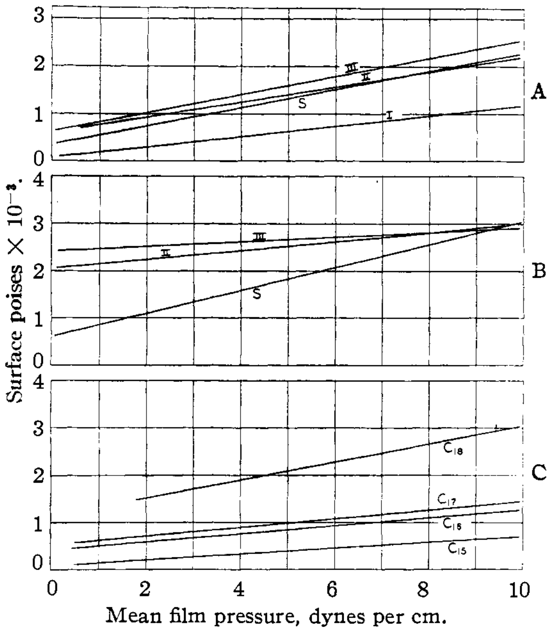

Fig. 5.—A, Viscosity of hexadecyl alcohol as measured with several viscosimeters: S, slit, 0.070 cm., 20°; I, Canal Ia, 0.050 cm., 20°; II, Canal II, 0.070 cm., 24°; III, Canal III, 0.078 cm., 24°. B, Octadecyl alcohol: S, slit, 0.100 cm., 20°; II, Canal II, 0.070 cm., 24°; III, Canal III, 0.078 cm., 23°. C, Variation of the surface viscosity of the alcohols with pressure as determined with Canal II, width 0.050 cm., 24–25°.

---

[11] Fourt and Harkins, *J. Phys. Chem.*, **42**, 897 (1938).

higher than with the slit (Fig. 5-B). Also the viscosity increases with canal width for II and III (Figs. 3-E and 4-B, F).

Pentadecyl and Heptadecyl Alcohols.—The viscosity of these alcohols was measured with Canals II and III only. The same trends with pressure and width noted already for the other alcohols were observed. The data are plotted in Figs. 3-B, 4-B, 5-C and 3-E, 4-E, 5-C.

A comparison of the determinations on the four alcohols under conditions as nearly alike as possible shows that the viscosity increases with the molecular weight of the compound. The viscosity of heptadecyl alcohol is only slightly greater than that of hexadecyl alcohol, while the two are considerably separated from both penta- and octadecyl alcohols. Corrected viscosities at a mean pressure of 3 dynes per cm. are: C_{15}, 0.00025; C_{16}, 0.00067; C_{17}, 0.00080; C_{18}, 0.00168.

Discussion

Dervichian and Joly[2] have established that for liquid films the rate of flow is proportional to the length of the slit and to the pressure gradient. They found also that the flux is proportional to the slit width for widths in excess of about 0.3 cm., but no extensive investigation was made on very narrow slits.[12] From their data for stearic acid on 0.01 *N* hydrochloric acid uncorrected viscosities as given by the first term of Eq. 1 may be computed. The results and comparable ones obtained in this Laboratory by Harkins and Myers[4] are contained in Table I.

The uncorrected value 0.9×10^{-4} poise reported for the present work is not strictly comparable with the others since the canal was of a different design.

TABLE I

VISCOSITY OF STEARIC ACID FILMS ON 0.01 *N* H^+

	Temp., °C.	Slit width, cm.	Uncor. viscosity (surface poises $\times 10^{-4}$)
Dervichian and Joly	17	0.066	4.4
	17	.117	6.1
Harkins and Myers	20	.062	2.7
	20	.080	3.1
This work	20	.020	0.9

Fourt and Harkins[11] have measured the surface viscosity of five long chain alcohols with a torsion pendulum. The method has not yet been developed to the point of giving absolute viscosities since the subsolution correction is not known. The comparative results obtained by the torsion pendulum and the canal method are of some interest. The materials used in the two investigations were from the same source. At low pressures the logarithm of the viscosity as measured by the pendulum increased almost linearly with the number of carbon atoms, from tetradecyl to octadecyl alcohol. The logarithm of the viscosity of the liquid condensed films apparently is equal to a constant plus a constant times the film pressure. Within a short pressure range in the neighborhood of the transition Liquid ⟶ Plastic Solid Film the viscosity increases with especial rapidity. At slightly higher pressures the viscosity becomes almost constant, but now the sequence is reversed and the lighter alcohols have the higher viscosity. Table II presents data taken from the published graphs of Fourt and Harkins, together with the viscosity at a mean pressure of 3 dynes per cm. determined with Canal II. It will be observed that the viscosity increase in the pressure range 3–10 dynes is tenfold in octadecyl and three thousand-fold in tetradecyl alcohol; also that the viscosities as measured by the pendulum at 3 dynes are about ten times as great as those measured with the canal.

If it is granted that the viscosities given by the canal viscosimeter are the more accurate, it must also be considered that the range of usefulness of the canal is more limited than with viscosimeters which maintain the film pressure constant. Changes of resistance to flow with pressure may be expected in a great variety of films and these changes cannot at present be adequately measured with a canal viscosimeter.

The magnitude of the subsolution correction given by the second term of Eq. 1 is of interest. It varies with the canal width and the viscosity of the subsolution, which is a function of temperature. Extreme values of the corrections applied in this work were 0.5×10^{-4} for $a = 0.02$ cm. and 5.0×10^{-4} for $a = 0.157$ cm. and 20°. Thus in most cases the correction was a significant fraction of the uncorrected viscosity.

Of all of the devices tried out Canal II gave the most satisfactory results and a canal of this type is to be recommended more highly than the others. A further investigation of the apparent failure to obey exactly the law of slit or canal

---

(12) It is of course possible that the linear relation between flux and slit width found by Joly and Dervichian for 0.3 cm. and wider slits is not replaced by the limiting cube relation until the width is considerably less than 0.1 cm. In fact in a more recent publication Joly[3] proposes that the flux varies as the square of the slit width if the width approximates 0.1 cm.

TABLE II

VISCOSITY IN SURFACE POISES OF LONG CHAIN ALCOHOLS ON SUBSOLUTION WITH 0.01 N H^+

Alcohol	Viscosity at P = 3 dynes per cm.		Viscosity at P = 20 dynes per cm.		Transition press. dynes per cm.,
	Torsion pendulum	Canal II	Torsion pendulum	Canal II	
Tetradecyl	3×10^{-4}		1.1		6.2
Pentadecyl	2×10^{-3}	2.5×10^{-4}	1.3		8.2
Hexadecyl	6×10^{-3}	6.7×10^{-4}	0.85	3×10^{-2}	10.2
Heptadecyl	9×10^{-3}	8×10^{-4}	.60		11.8
Octadecyl	2×10^{-2}	1.7×10^{-3}	.17		12.9

width should be made. Observations on particles of talc flowing through the slit with the film indicated that the surface was to a sufficient approximation plane. A closer study might, however, demonstrate a small curvature which would change the actual slit width by an amount adequate to remove the discrepancy.

Summary

The viscosities of films of stearic acid and the normal alcohols containing 15 to 18 carbon atoms have been measured at 20–25°. All films were spread on 0.01 N sulfuric acid. Several types of canal viscosimeters were employed, and apparent viscosities determined with the different instruments varied considerably. The canal regarded as most satisfactory was made from glass plates with lightly paraffined edges. The top edges of the plates were at the surface level and the sides extended considerably below. The sides were purposely hydrophilic. Canal widths ranged from 0.02 to 0.157 cm.

The viscosity calculated from the equation of Harkins and Kirkwood was found not to be exactly proportional to the cube of the canal width, but to be higher at the greater widths. The viscosity increases somewhat, and in a linear fashion, with the mean pressure on the films. The best values of the viscosity at a mean pressure of 3 dynes per cm., expressed in surface poises, are: stearic acid, 0.00009; pentadecyl alcohol, 0.00025; hexadecyl alcohol, 0.00067; heptadecyl alcohol, 0.00080; octadecyl alcohol, 0.00168.

The usefulness of the canal viscosimeter is severely limited by its incapacity for indicating changes in viscosity with small changes in film pressure. Since it does give absolute viscosities, its principal usefulness may be in standardizing other surface viscosimeters.

CHICAGO, ILLINOIS RECEIVED MAY 28, 1940

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF WISCONSIN]

The Mechanism of Chemical Reactions Accompanying the Isomeric Radioactive Transition of Br^{80} †

BY JOHN E. WILLARD

Artificially radioactive Br^{80} has two radioactive isomers. The one of these which has the higher nuclear energy changes into the other by the transition: Br^{80} (4.4 hr. half-life) $\rightarrow$ Br^{80} (18 min. half-life) + a gamma ray or a conversion electron. It has been observed[1–6] that this transition is frequently accompanied by a chemical reaction of the Br^{80} (18 min.) atoms which it produces.

Before the energy of the conversion electrons had been measured[7] this unusual reactivity was thought to be due to the recoil energy[1,2,3] acquired by a bromine atom when it loses a gamma ray or a conversion electron, but has since been attributed to the highly reactive electronic state of the bromine ion which results from the loss of a conversion electron from the K or L shell of the atom.[4,5,6,8]

The purpose of this paper is to present results which indicate that the reaction of the daughter activity of the Br^{80} transition with carbon tetrachloride is not due solely to the reactive nature of the bromine ion which has just undergone transi-

---

† Paper presented before the Division of Physical and Inorganic Chemistry at the April, 1940 meeting of the American Chemical Society.

[1] Segrè, Halford and Seaborg, *Phys. Rev.*, **55**, 321 (1939).

[2] DeVault and Libby, *ibid.*, **55**, 322 (1939).

[3] LeRoux, Lu and Sugden, *Nature*, **143**, 518 (1939).

[4] Willard, THIS JOURNAL, **62**, 256 (1940).

[5] Fairbrother, *Nature*, **145**, 307 (1940).

[6] Suess, *Z. physik. Chem.*, **B45**, 312 (1940).

[7] Valley and McCreary, *Phys. Rev.*, **56**, 863 (1939).

[8] Seaborg, Friedlander and Kennedy, THIS JOURNAL, **62**, 1309 (1940).