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Surface Viscosity of Monomolecular Films of Long-Chain Aliphatic Amides, Amines, Alcohols, and Carboxylic Acids

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ABSTRACT

The surface viscosities of monomolecular films of 14-, 16-, and 18-carbon aliphatic alcohols, amines, acids, and amides were determined from the rate of flow of the film material through a narrow and relatively deep viscometer canal. The surface viscosities were measured as functions of film pressure, substrate pH, and the rate of flow of the film. The surface viscosity data for alcohols and acids were in good agreement with those previously reported viscosity values also determined by the canal technique. The values determined with a canal viscometer are often an order of magnitude less than those obtained with other types of viscometers. There are no corresponding data available in the literature with which to compare the surface viscosities of the amide and amine monolayers. Experiments were also carried out for distinguishing between Newtonian and non-Newtonian behavior in the monolayers.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

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SURFACE VISCOSITY OF MONOMOLECULAR FILMS OF LONG-CHAIN ALIPHATIC AMIDES, AMINES, ALCOHOLS, AND CARBOXYLIC ACIDS

INTRODUCTION

The orientation and packing of long-chain n-aliphatic compounds at water/air interfaces are known to vary with the nature of the polar groups that are present, as well as with hydrocarbon chain length, film pressure, temperature, and substrate composition. The effects of these parameters on the molecular arrangement in adsorbed films have been investigated by several surface chemical techniques (1,2), including film balance studies, surface potential determinations, and to a lesser extent surface viscosity measurements. In connection with a current project at the Naval Research Laboratory it became necessary to determine the surface properties, and in particular the surface viscosities, of a variety of surface-active materials that occur naturally at the surface of the ocean. Due to the unsaturation of many of these compounds, it was expected that their surface viscosities would be quite low. A survey of the literature indicated that of the surface viscometers described, those based on the rate of flow of films through a narrow canal were the most sensitive in the range of 10^{-3} surface poise or less and were the only viscometers giving absolute viscosity values. It was also noted that there was considerable variation among the surface viscosity values reported. The present study was therefore undertaken to give a reliable method for determining surface viscosity and to help establish the true surface viscosity values of a series of long-chain aliphatic compounds. Surface viscosities of the 14-, 16-, and 18-carbon alcohols, acids, amines, and amides were measured as functions of film pressure, substrate pH, and the rate of shear of the surface film.

The various experimental methods that have been used for determining surface viscosity might arbitrarily be grouped into three classifications: (a) those based upon the rate of damping of successive oscillations of a bob or disk suspended in the interface (3-7), (b) those methods depending upon the rate of flow of surface film through a canal or slit (5,6,8-11), and (c) those techniques in which either the substrate liquid or a ring or disk suspended in the interface is rotated at a constant rate (12-15), the surface viscosity being determined from the drag the moving interface exerts upon a concentric surface. Of the three types of measurements only the second is capable of giving the absolute or true surface viscosity (16-18) of a film. The other techniques certainly give useful information, but they will also give surface viscosities that can be more than an order of magnitude higher (19) than those given by the canal method. By varying the width of the canal, this viscometer can also be used to study the effect of rate of shear of the surface film on its surface viscosity. Of the various types of slit or canal viscometers investigated by Harkins and Nutting (11), they suggested that one employing a narrow, deep canal would give the most accurate surface viscosity measurements. Therefore, a canal viscometer of this type was constructed for use in the present investigation.

EXPERIMENTAL METHOD

The Viscometer

The canal used in this viscometer was formed from two glass microscope slides 7.5 cm long, 0.1 cm thick, and 1.6 cm wide, with the edges ground flat. The slides were placed in the film balance trough so that the upper 7.5-cm-long edges were exactly level with the free water surface to prevent the formation of a meniscus. Only the upper edges of the slides were paraffined; the portions of the slides remaining in contact with the

water were left hydrophilic to prevent slippage between the substrate water and the sides of the canal. The depth of the canal was limited to 1.6 cm by the depth of the film balance tray. Each microscope slide was held in position at the interface by a chrome-plated brass plate to which it was attached with paraffin. Each brass plate was 7.5 cm long, 0.5 cm wide, and 3.5 cm high, 2.0 cm of which extended above the level of the free water surface. All portions of the brass plates in contact with the water were lightly coated with paraffin. The upper portions of the brass plates were coupled together much as the two jaws of a vise, with two micrometers, one near each end of the canal, used to control the width and alignment of the canal. The width of the canal could easily be varied from 0 to 0.5 cm with an accuracy of ±0.0005 cm. The alignment of the canal was checked at several widths with a cathetometer and was found to vary no more than ±0.0005 cm from one end of the canal to the other.

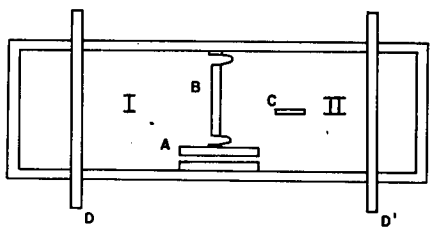

Fig. 1 - Schematic diagram of surface viscometer: A - viscometer canal, B - mica float, C - platinum plate of surface tensiometer, D and D' - movable barriers

The variable-width canal was mounted in a Cenco hydrophil balance about midway between the ends of the trough and adjacent to one side. One end of the mica float of a Cenco torsion head was attached to the inner brass plate of the canal assembly and the other end to the opposite side of the film tray, as shown schematically in Fig. 1. This arrangement is much like that used by Joly (6). In this figure, A is the canal, and B is the float of the Cenco torsion head. D and D' are movable barriers for expanding and compressing the film, and C is the platinum plate of a Wilhelmy-type tensiometer used to monitor the film pressure in compartment II of the viscometer. The surface of the platinum plate was roughened to assure wettability and was connected by a lever arm to a calibrated torsion wire. It had a sensitivity of ±0.05 dynes/cm, about the same sensitivity as the Cenco torsion head. Those surfaces of the brass hydrophil balance that come in contact with the substrate were made hydrophobic by coating with a thin layer of paraffin.

Materials

The sources and melting ranges of the long-chain alkyl derivatives used in this study are presented in Table 1. Spreading solutions of the compounds were prepared by dissolving known amounts of the material in suitable organic solvents. The alcohols, acids, and amines were dissolved in petroleum ether, the concentration of each solution being of the order of 5×10^{-4} g/ml. Due to the low solubility of the amides in hexane and petroleum ether, benzene was used as their spreading solvent. Each of the solvents, C.P. petroleum ether and C.P. benzene, was percolated through adsorption columns of activated Florisil and alumina prior to use in order to remove any polar impurities. The spreading solutions were delivered to the water surface from Misco micropipets. Each of the compounds was studied on both acid and basic substrates; the acid substrate was 0.01N H_2SO_4, and the basic substrate was pH 9.0 to 9.5 KOH. The substrate solutions were prepared from triply distilled water, the final two distillations from an all-quartz apparatus.

Experimental Procedure

In order to determine surface viscosity by the canal method, it is necessary to measure the amount of film passing through the canal in unit time, with a given pressure differential across the ends of the canal. At the beginning of each measurement the water surfaces in compartments I and II were swept clean with the movable barriers, and the torsion wires for the tensiometers were adjusted to zero film pressure. Film material

Table 1
Long-Chain Alphatic Compounds Used

Compound	Source*	Melting Range (°C)
C_{14}		
Carboxylic acid	Lachat	58
Alcohol	Lachat	37 to 38
Amine	Lachat	37
Amide	Eastman	103
C_{16}		
Carboxylic acid	Lachat	64
Alcohol	Lachat	49 to 50
Amine	Lachat	46 to 47
Amide	K and K	105 to 106
C_{18}		
Carboxylic acid	Lachat	69 to 70
Alcohol	Lachat	59
Amine	Lachat	53 to 54
Amide	Eastman	108 to 109

*The shortened names in the table refer to Lachat Chemicals Incorporated, Eastman Chemical Company, and K and K Laboratories, Incorporated.

was then added to both compartments, allowed to equilibrate for 10 min and was then compressed. The film in compartment I was compressed until the torsion head at B registered a film pressure F_1. The film in compartment II was compressed until the Wilhelmy-plate tensiometer recorded a film pressure F_2, a value somewhat less than F_1. The torsion head B then measured the difference in pressure across the ends of the canal, $\Delta F = F_1 - F_2$. When a gate made of thin polyethylene film was removed from in front of the canal, the film began to flow from compartment I to compartment II under the pressure differential ΔF. As the film material moved through the canal, barriers D and D′ were moved at a sufficient rate to maintain the proper film pressures in compartments I and II. The rate of flow of the monolayer through the canal was determined from the distance that barrier D in compartment I had traversed in a given period of time.

Harkins and Kirkwood (10) proposed that for a deep and very narrow canal the rate of flow of film through the canal is related to the absolute viscosity of the monolayer by the equation

$$\eta = \frac{(F_1 - F_2)\, a^3}{12\, \ell\, Q} - \frac{a\, \eta_0}{\pi}, \qquad (1)$$

in which F_1 and F_2 are the film pressures at each end of the canal in dynes/cm, a is the width of the canal in cm, Q is the area in cm^2 of film flowing through in 1 sec, ℓ is the length of the canal in cm, and η_0 is the bulk viscosity of the aqueous substrate. It is assumed in deriving this expression that the viscosity of the film is constant while passing through the canal. In order to satisfy this condition the film pressure drop across the canal was kept as small as possible. It was found that a pressure difference of 2 to 4 dynes/cm gave satisfactory results and was convenient to work with. At the lower film pressures, a ΔF of 2 dynes/cm was maintained across the canal.

A further condition which must be satisfied is that the ratio of canal depth to canal width must be large. To satisfy this condition, much of the data was taken with canal widths of 0.10 cm or less, in which case the canal depth was at least 16 times the width. It was also of interest, however, to determine the surface viscosity of each monomolecular film as a function of canal width. By changing the canal width one changes the rate of flow of the film through the canal and thus its rate of shear. Using this technique, it was possible to determine which of the compounds formed Newtonian and which formed non-Newtonian two-dimensional films. With Newtonian films it was found that surface viscosity was independent of rate of flow, at least with flow rates of from 0.02 to 0.25 cm^2/sec. Accurate measurements were obtained in the surface viscosity range of 1×10^{-4} to about 1×10^{-1} surface poise. At the higher values of surface viscosity it was very difficult to obtain reproducible measurements, because many of the films became non-Newtonian plastic or solid films and had high yield values. All surface viscosity measurements were carried out in a constant-temperature room, the temperature being held at 20±0.2° C and the relative humidity at 50±5%. The surface viscometer was protected from dust and airborne contamination by enclosing it in a Lucite box. The surface viscosity measurements reported for any given monomolecular film were the average of at least 10 measurements and could normally be reproduced to within ±10% at all viscosities under these experimental conditions.

Film pressure (F) versus area per molecule (A) curves were determined on both the acid and the basic aqueous substrates for each compound studied. The film balance used to measure the F versus A curves has been previously described in detail (20). It consisted of a shallow, Pyrex glass trough with the rim lightly coated with paraffin, a paraffined mica float connected to the sides of the trough with end loops of thin polyethylene ribbon, and a Cenco-duNuoy torsion head sensitive to changes in film pressure of 0.05 dynes/cm. The measurements were also carried out in a constant-temperature room at 20±0.2° C and a relative humidity of 50±5%.

RESULTS

Carboxylic Acids

The surface viscosities of n-tetradecanoic, n-hexadecanoic, and n-octadecanoic acids on 0.01N H_2SO_4 were determined as functions of film pressure and canal width. The surface viscosity values for each film were first plotted semilogarithmically against the rate of flow, as shown for n-hexadecanoic acid in Fig. 2. This plot of the logarithm of surface viscosity (log η) versus film flow rate (Q) for each film pressure for hexadecanoic acid gave a series of straight lines, showing that for film pressures up to 18 dynes/cm the surface viscosity of n-hexadecanoic acid was independent of the rate of shear. It follows, therefore, that monolayers of hexadecanoic acid on acid substrate act as two-dimensional Newtonian liquids. Similarly, monolayers of n-octadecanoic and n-tetradecanoic acids on 0.01N H_2SO_4 were also found to be two-dimensional Newtonian liquids. Plots of the logarithm of surface viscosity (log η) versus film pressure (F) were prepared for each of these acids at flow rates of 0.25 cm^2/sec. The log η versus F curves given in Fig. 3 show that the viscosity of octadecanoic acid and hexadecanoic acid increases linearly with pressure. The surface viscosity of tetradecanoic acid increased slightly going from 2 to 4 dynes/cm and then appeared to be constant at higher film pressures. This difference in behavior may be explained by the differences in the states of their monolayers, as shown in the film pressure versus area/molecule (F versus A) curves given in Fig. 4. The linear portions of the log η versus F curves for the C_{16} and C_{18} acids correspond to the liquid-condensed or linear portions of their F versus A curves. No surface viscosity values are reported for these acids at film pressures greater than 20 dynes/cm, for the monomolecular films appeared to become solid and so fragile that reproducible results were difficult to obtain. The low viscosity of the tetradecanoic acid monolayer is apparently due to the expanded state of the film.

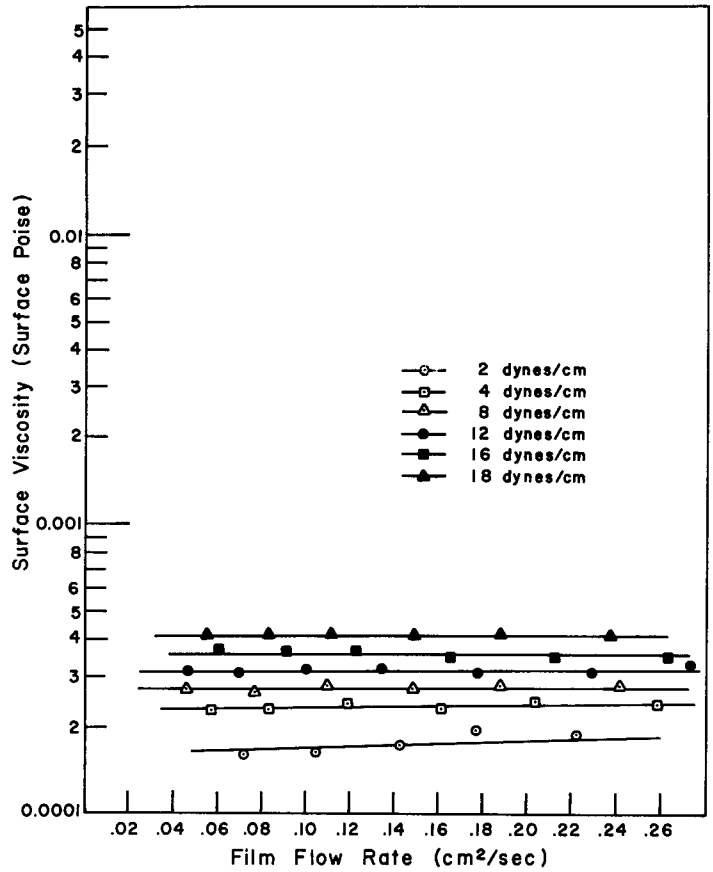

Fig. 2 - Effect of film flow rate on the surface viscosity of n-hexadecanoic acid on 0.01N H_2SO_4 substrate

Harkins and Nutting (11) determined with their canal viscometer that the best value for the surface viscosity of octadecanoic acid on an acidic substrate was 0.9×10^{-4} surface poise at 3 dynes/cm, which is 2.3×10^{-4} surface poise less than the value reported here. Joly (21,22), who also measured the surface viscosities of these fatty acids as functions of film pressure, reported surface viscosities for the C_{16} and C_{18} acids that were within $\pm1\times10^{-4}$ surface poise of the values reported here. Joly's values for tetradecanoic acid, however, do not agree with those given here. He reported the surface viscosity of the C_{14} acid decreased with film pressure, decreasing from 1.79×10^{-4} surface poise at 1 dyne/cm to 1.0×10^{-4} surface poise at 9 dynes/cm. The present data for the C_{14} acid at film pressures above 6 dynes/cm show a constant surface viscosity value of 2.4×10^{-4} surface poise and appear to be the more reasonable, for one would not expect a significant decrease in the cohesive forces between adjacent molecules as they become more closely packed.

The surface viscosities of several fatty acids have also been determined by the method of damped oscillations. Boyd and Harkins (23) gave a plot of the logarithm of surface viscosity (log η) versus film pressure (F) for octadecanoic and hexadecanoic acids. Their plots also show that viscosity increases linearly with film pressure up to about 20 dynes/cm, but their values are close to an order of magnitude greater than those determined with a canal viscometer.

An attempt was made to measure the surface viscosity of the fatty acid films on pH 9.0 to 9.5 KOH solution. On this substrate the monolayers of the fatty acids became

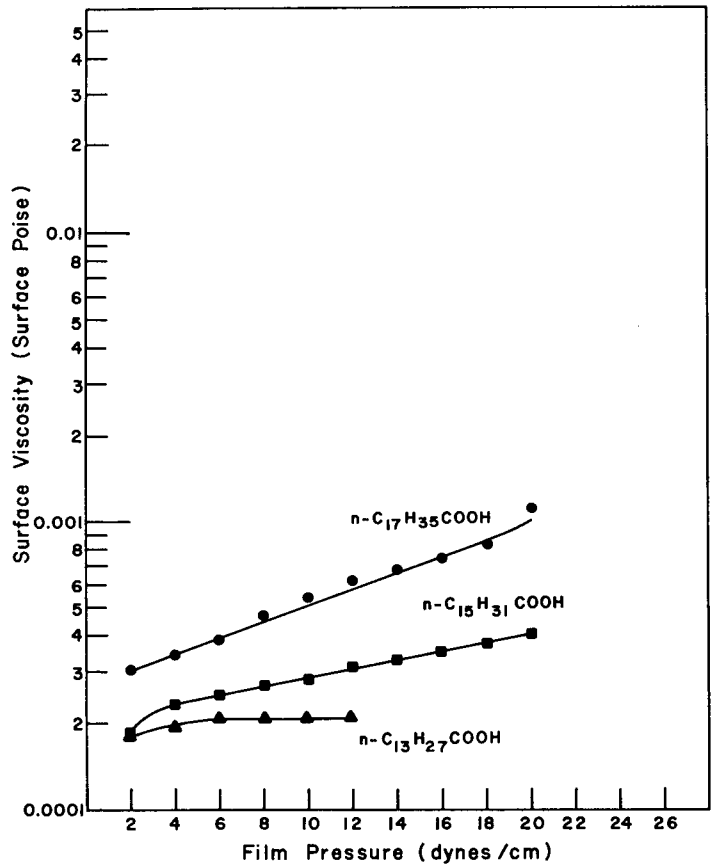

Fig. 3 - Surface viscosity versus film pressure for long-chain carboxylic acids on 0.01N H_2SO_4 substrate. (Film flow rate = 0.25 cm^2/sec.)

extremely rigid, their viscosities exceeding the capabilities of the canal viscometer. The rigidity of the fatty acid films may have been caused by the presence of trace amounts of multivalent cations in the substrate that formed insoluble soaps with the fatty acids.

Aliphatic Alcohols

Surface viscosities of n-tetradecanol, n-hexadecanol, and n-octadecanol were determined both on 0.01N H_2SO_4 and on KOH solution at pH 9.0 to 9.5. The viscosities were also measured as functions of film pressure and canal width. The viscosity values of the alcohol monolayers were also initially plotted as log η versus Q, to determine whether they, too, formed Newtonian films. These curves are given in Fig. 5(a), 5(b), and 5(c). They show that at low values of F each of the alcohol films were Newtonian; but as the average film pressure was increased above 6 dynes/cm, the viscosities of tetradecanol and hexadecanol showed a marked dependence upon the rate of shear. This agrees with the previous study of Fourt and Harkins (24), which also showed that films of these alcohols became non-Newtonian at about the same film pressures. Within the limits of experimental error, octadecanol appeared to be Newtonian at film pressures up to 20 dynes/cm, at least at the film flow rates studied.

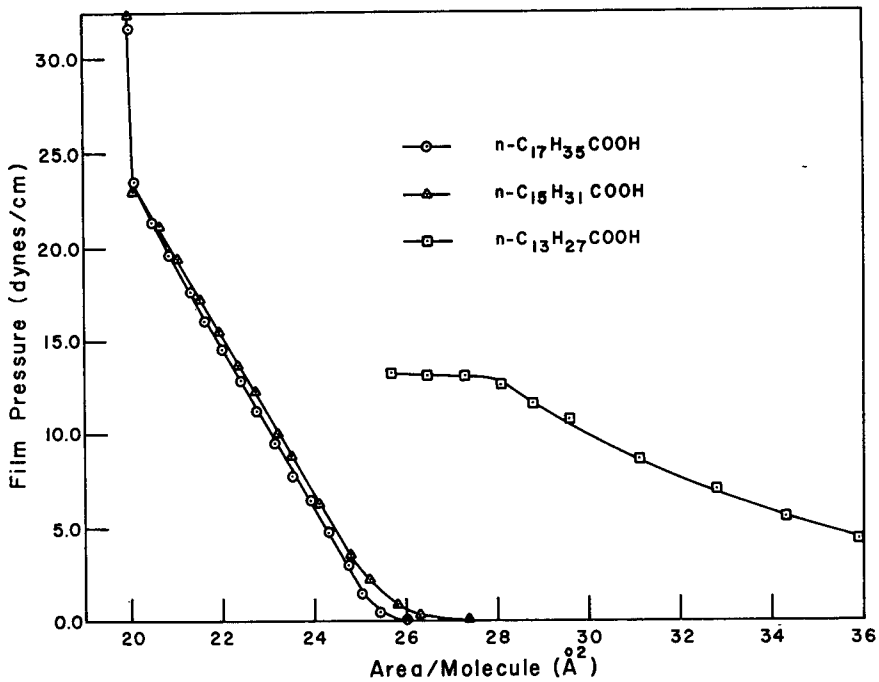

Fig. 4 - Film pressure versus area/molecule for long-chain carboxylic acids on 0.01N H_2SO_4 substrate

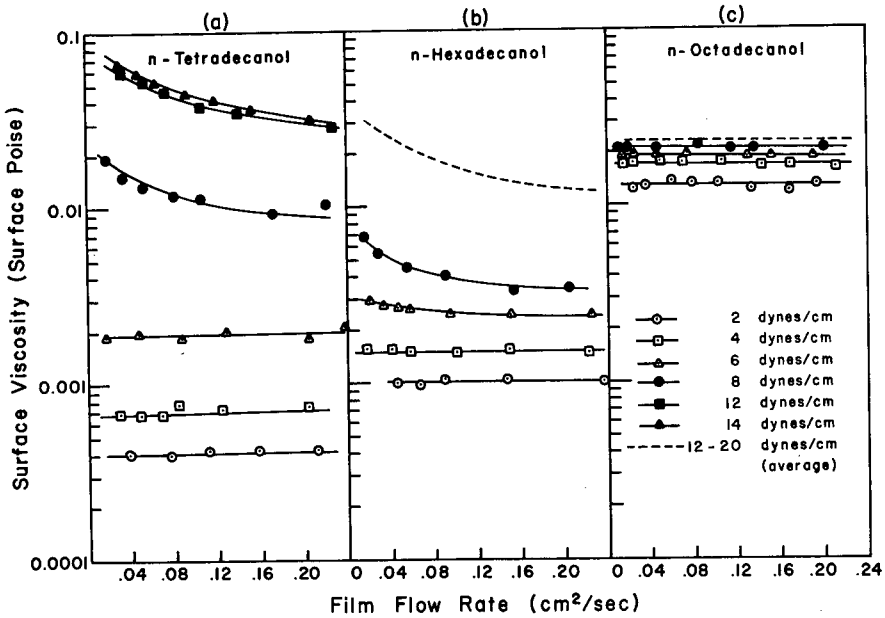

Fig. 5 - Effect of film flow rate on the surface viscosity of long-chain alcohol monolayers on 0.01N H_2SO_4 substrate: (a) n-tetradecanol, (b) n-hexadecanol, (c) n-octadecanol

Plots of surface viscosity versus film pressure were prepared for each of these alcohols for a flow rate of 0.02 cm^2/sec (Fig. 6). Fourt and Harkins (24), using the oscillating disk, reported log η versus F curves for these alcohols which are similar in shape to those shown in Fig. 6. However, their values of η at high film pressure are at least 10 times greater than those reported here. Harkins and Nutting (11) reported values of surface viscosity for C_{16} and C_{18} alcohols at low film pressures using a canal viscometer. Their best values reported at a mean film pressure of 3 dynes/cm were 7×10^{-4} surface poise and 17×10^{-4} surface poise for hexadecanol and octadecanol respectively. Their value for hexadecanol agrees well with that presented here, but their value for the C_{18} alcohol is considerably less than that reported here.

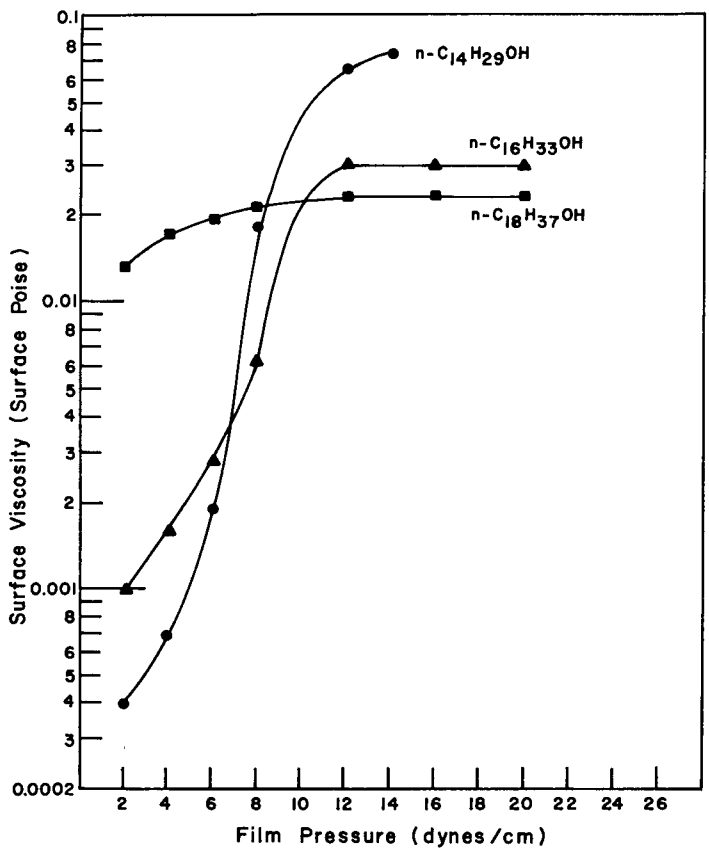

Fig. 6 - Surface viscosity versus film pressure for long-chain alcohols on 0.01N H_2SO_4 substrate. (Film flow rate = 0.02 cm^2/sec.)

Other investigators (21,24,25) have determined surface viscosity values for these fatty alcohols on acid substrate, but there is little agreement between their reported results. The difficulty may be due in part to differences in the viscometers used, and it may also be possible that small amounts of surface contamination were responsible for some of the variation in reported data. In the present study it was found that samples of tetradecanol and octadecanol purchased from different suppliers gave somewhat different viscosity values, particularly at low average film pressures. As an example, tetradecanol from Eastman Chemical Company gave a value of 1.5×10^{-4} surface poise at an

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average film pressure of 2 dynes/cm as compared to a value of 4×10^{-4} surface poise reported here for a sample of tetradecanol obtained from Lachat Chemicals Incorporated.

The F versus A curves for these alcohols on 0.01N H_2SO_4 (see Fig. 7) show that each of the alcohol monolayers are true condensed films only above film pressures of 6 to 7 dynes/cm for the C_{14} alcohol and above 10 to 12 dynes/cm for the higher homologs. The displacement for the F versus A curve for the C_{14} alcohol to a lower area per molecule than the C_{16} and C_{18} alcohols may be attributed to the slow collapse (or solubility) of the C_{14} alcohol film as it is compressed. It is only when the films of tetradecanol and hexadecanol approach the condensed state that they show non-Newtonian behavior.

The surface viscosities of the alcohols on pH 9.0 to 9.5 KOH were in good agreement with the values obtained on acid substrate, the greatest difference between the two sets of data being less than 20%. The differences in viscosity of alcohols spread on acid and basic substrates may be due to minute traces of acid impurities present in the alcohols. The shapes of the log η versus F curves were identical with each substrate, and the monolayers began to show non-Newtonian behavior at the same average film pressure. The F versus A curves determined on pH 9.0 to 9.5 KOH were indistinguishable from those given in Fig. 7 for the alcohols on acid substrate.

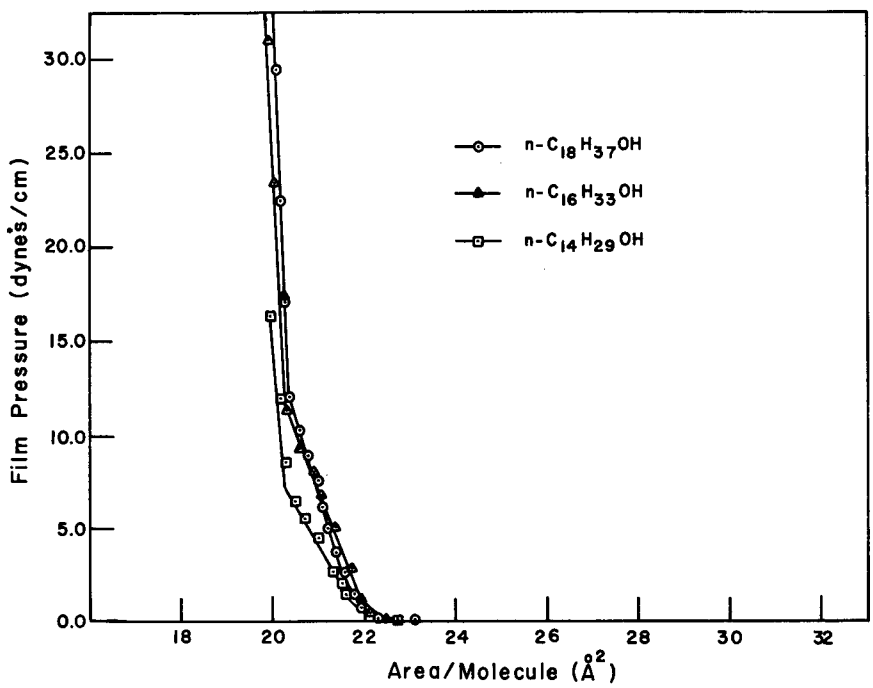

Fig. 7 - Film pressure versus area/molecule for long-chain alcohols on 0.01N H_2SO_4 substrate

Aliphatic Amides

The surface viscosities of monolayers of octadecanamide and hexadecanamide were studied on the acid as well as the basic substrate. Reproducible measurements could not be made with tetradecanamide, since it showed appreciable solubility in these aqueous substrates and therefore did not form stable monomolecular films. The surface viscosities of the C_{16} and C_{18} amides on 0.01N H_2SO_4 (Fig. 8(a) and 8(b)) were plotted as functions

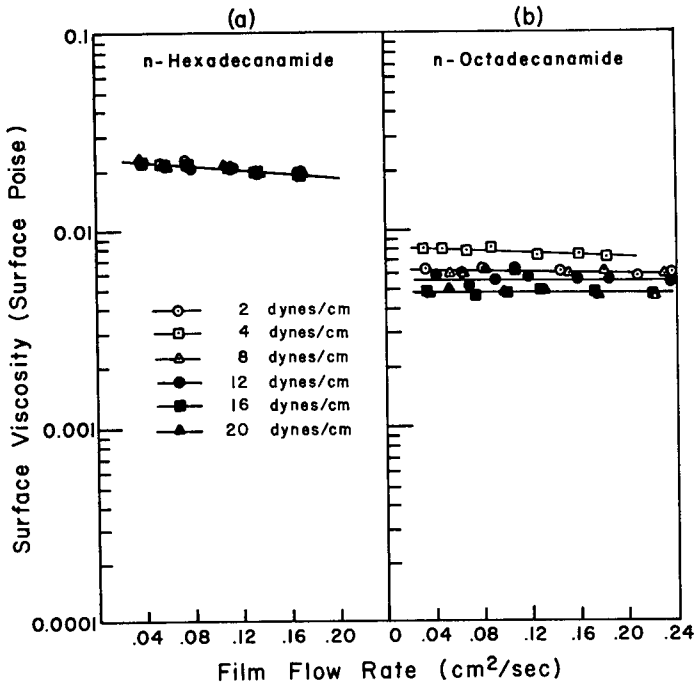

Fig. 8 - Effect of film flow rate on the surface viscosity of long-chain amide monolayers on 0.01N H_2SO_4 substrate: (a) n-hexadecanamide, (b) octadecanamide

of film flow rate at various film pressures. The surface viscosity of hexadecanamide appeared to be independent of film pressure in the range studied, i.e., from 2 to 20 dynes/cm. It did show non-Newtonian behavior, though not to the same extent as the corresponding alcohol. Its surface viscosity only increased from 0.019 to 0.023 surface poise as the flow rate decreased from 0.20 to 0.02 cm^2/sec. Only at an average film pressure of 4 dynes/cm did octadecanamide show a slight dependence upon film flow rate. Otherwise the C_{18} amide seemed to behave as a Newtonian film.

The surface viscosity behavior of monolayers of hexadecanamide at all film pressures is somewhat analogous to that of hexadecanol films at film pressures above 12 dynes/cm. At a film flow rate of 0.05 cm^2/sec, the surface viscosity of each compound is the same, 0.022 surface poise. The surface viscosity of the C_{16} alcohol, however, shows a greater dependence upon the rate of flow of the film through this canal or the rate of shear. The F versus A curves of the C_{16} compounds in Fig. 7 show that above 12 dynes/cm hexadecanol monolayers have the same molecular packing and compressibility as hexadecanamide (Fig. 9).

The F versus A curve in Fig. 9 for octadecanamide is identical with the F versus A curve of octadecanol above a film pressure of 12 dynes/cm. Unlike the C_{16} derivatives, however, the surface viscosities of the C_{18} compounds do not show much similarity. Monolayers of the C_{18} alcohol and amide do appear to be Newtonian films for the most part; however, the octadecanamide films were considerably less viscous than the alcohol films. Also the viscosity of the C_{18} amide appears to be maximum at a film pressure of 4 dynes/cm and then to decrease with increasing film pressure, up to a film pressure of 16 dynes/cm. At 4 dynes/cm, the surface viscosity of octadecanamide is about one half that of the C_{18} alcohol, 0.0080 surface poise for the amide as compared with 0.017 surface poise for the alcohol. The lower values of η for the C_{18} amide may result from the presence of trace impurities in the compound, or the different polar groups may make distinctly different contributions to surface viscosity.

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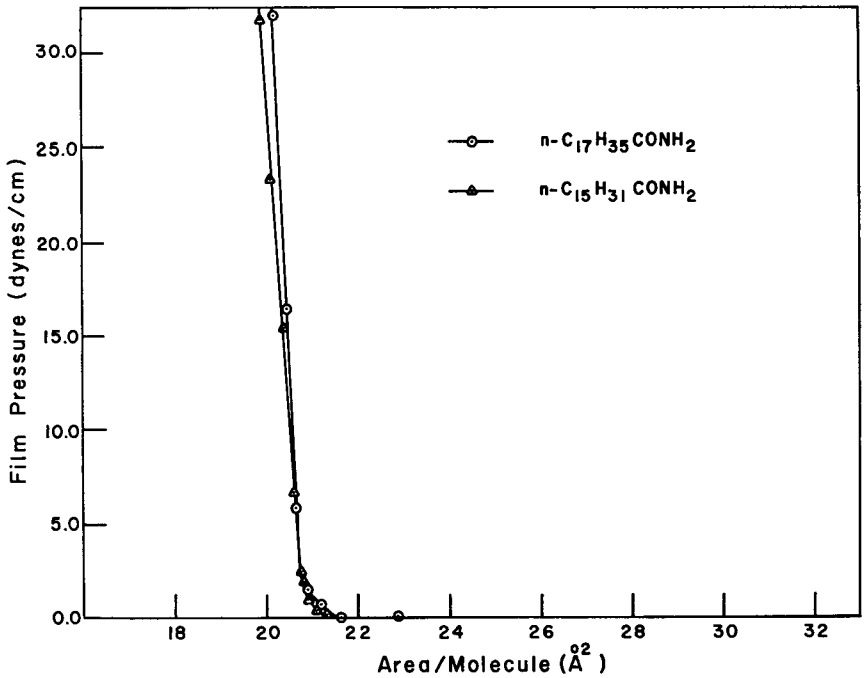

Fig. 9 - Film pressure versus area/molecule for long-chain amides on 0.01N H_2SO_4 substrate

The surface viscosity of both hexadecanamide and octadecanamide were found to be independent of substrate pH. Their surface viscosities on pH 9.0 to 9.5 KOH agreed, within the limits of experimental error, with the measurements given in Fig. 9 with 0.01N H_2SO_4 as substrate. The F versus A curves for these compounds were also the same for both acid and basic substrates.

Aliphatic Amines

The surface viscosities of the amine monolayers were observed to be sensitive to the pH of the substrate. They gave very-low-viscosity Newtonian films on the acid substrate, while on basic substrates their viscosities were greater than 0.1 surface poise, exceeding the usable range of the present viscometer. The viscosities of octadecylamine and hexadecylamine on 0.01N H_2SO_4 are given in Fig. 10. On the acid substrate the amines formed the RNH_3^+ ion, the resulting electrostatic repulsions between the ionized molecules giving very expanded monomolecular films as shown in Fig. 11. The relatively large distances between the amine molecules on 0.01N H_2SO_4 is responsible for the low surface viscosities. The amines appeared to be somewhat soluble in the acid substrate, perhaps as a result of the ionization. The C_{14} amine was so soluble that reliable measurements of its surface viscosity could not be made. It is also of interest that the surface viscosity values on 0.01N H_2SO_4 are independent of film pressure. In the film pressure range studied, the amine monolayers did not approach close packing.

The monomolecular films of the C_{16} and C_{18} amines were much more condensed on the pH 9.0 to 9.5 KOH solution than they were on the acidic substrate. The viscosity of the closely packed hexadecylamine monolayer was considerably above 0.1 surface poise, even at an average film pressure of 2 dynes/cm. Initial experiments suggested that these highly viscous films were non-Newtonian, but sufficient reliable data could not be gathered to determine the extent of their deviation from ideal behavior.

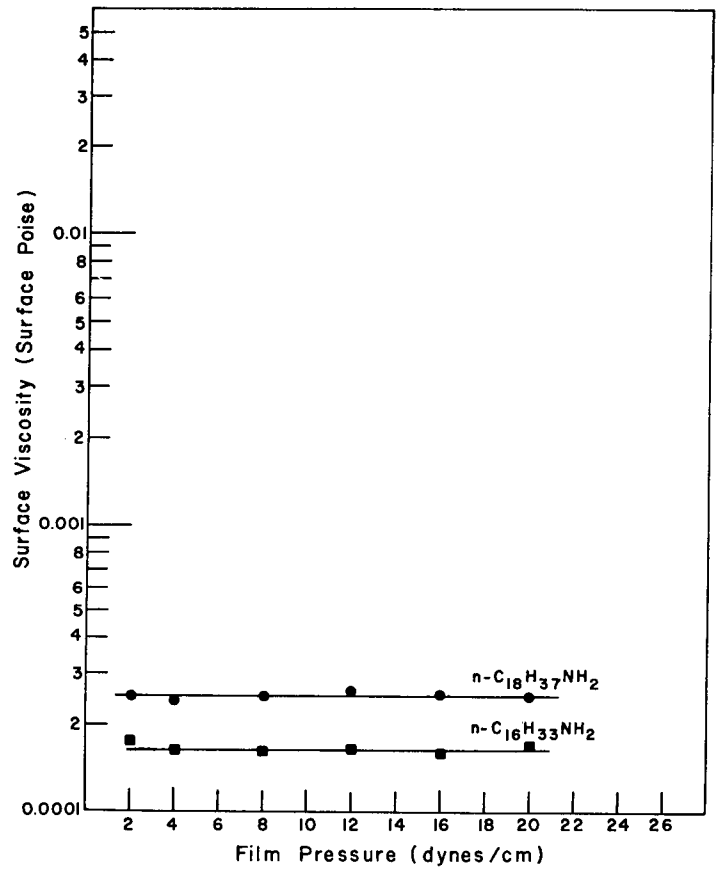

Fig. 10 - Surface viscosity versus film pressure for long-chain amines on 0.01 N H_2SO_4 substrate (film flow rates of 0.02 to 0.25 cm^2/sec; viscosity was independent of flow rate)

CONCLUSIONS

The canal viscometer, utilizing a narrow, deep canal, was found to be capable of detecting non-Newtonian behavior in a monomolecular film. The very viscous non-Newtonian films required relatively wide canals, which with viscosities greater than about 0.1 surface poise could lead to situations where the ratio of canal depth to width is no longer large enough to satisfy the requirements of the Harkins and Kirkwood (10) equation. Using this equation and restricting the determinations to a narrow, deep canal, the measured values should be very close to the absolute surface viscosities.

The data presented in this report show that the surface viscosities of monomolecular films will vary with the nature of the polar group that is present in the adsorbed molecules and with the degree of interaction between the polar group and the aqueous substrate. The viscosity values are dependent upon the orientation and closeness of packing of the molecules in the monomolecular film and thus are related to the length of the hydrocarbon chain, the film pressure, and substrate pH. The surface viscosities of each type of monomolecular film — alcohol, acid, amine, and amide — showed different responses to changes in these parameters.

In each case where the monomolecular film was Newtonian, the surface viscosity increased with increasing hydrocarbon chain length. With the 16- and 18-carbon fatty

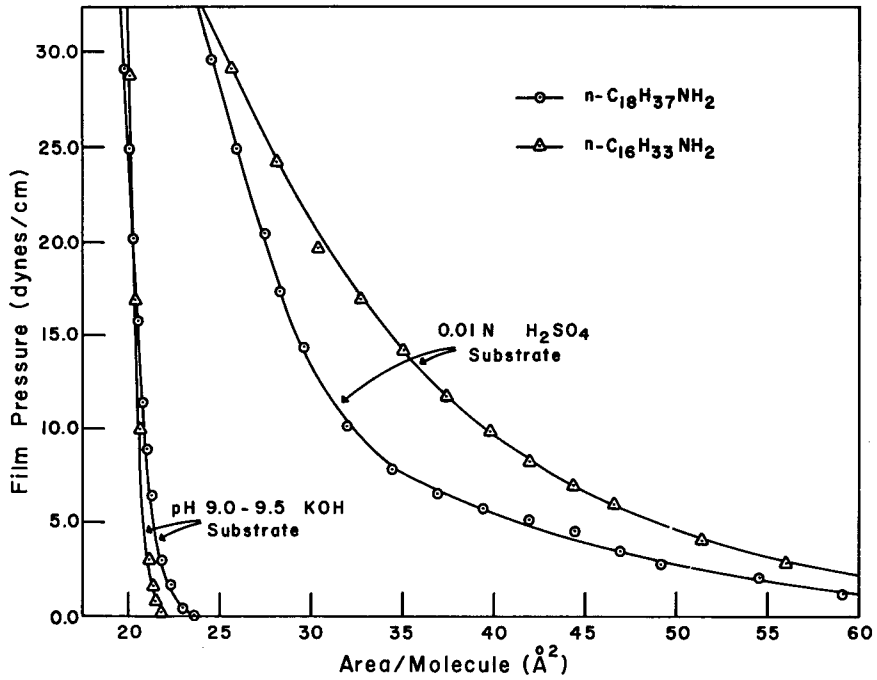

Fig. 11 - Film pressure versus area/molecule for long-chain amines on 0.01N H_2SO_4 and pH 9.0 to 9.5 KOH substrates

acids on 0.01N H_2SO_4 and the alcohols at low film pressures, the logarithm of the viscosity appeared to increase linearly with film pressure. For the very expanded Newtonian films of tetradecanoic acid and the C_{16} and C_{18} amines on 0.01N H_2SO_4, the surface viscosity values were independent of film pressure, within the limits of sensitivity of the experimental procedure. For non-Newtonian films the surface viscosity behavior was not so regular. Non-Newtonian monolayers of the amides and the alcohols at higher film pressures not only had higher surface viscosities than the Newtonian films, but the values for the lower-molecular-weight homologs were higher than those of longer chain compounds. An explanation for this behavior is not immediately obvious, although the behavior of tetradecanol may give a clue. The tetradecanol monolayer tends to collapse slowly at film pressures greater than about 6 dynes/cm. At the higher film pressure the collapsing tetradecanol molecules may form multilayers of the material at the interface, thus giving rise to nonideal behavior of the surface viscosity. The monolayers of the fatty acids and amines on pH 9.0 to 9.5 KOH, which apparently are non-Newtonian, had surface viscosities so large they exceeded the capabilities of the present surface viscometer.

The surface viscosities of two classes of compounds, the amines and the acids, exhibited a marked dependence upon substrate pH. The amines formed ionized monolayers on the 0.01N H_2SO_4 substrate, the mutual repulsion between the ionized polar groups giving rise to the expanded monolayers of low viscosity. On the basic substrate the un-ionized amines gave very high surface viscosities, indicating a high degree of cohesion between the closely packed molecules. On 0.01N H_2SO_4 the monolayers of the carboxylic acids gave very low surface viscosities. On the basic substrate however the acids apparently formed insoluble soaps with trace amounts of multivalent cations present in the water, and gave highly condensed, solid monolayers of very high surface viscosity. The alcohol and amide monolayers were relatively insensitive to changes in substrate pH.

The surface viscosities presented in this report for monolayers of fatty acids and alcohols are in good agreement with much of the previously reported data, particularly those values obtained with a canal viscometer.

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The surface viscosities of monomolecular films of 14-, 16-, and 18-carbon aliphatic alcohols, amines, acids, and amides were determined from the rate of flow of the film material through a narrow and relatively deep viscometer canal. The surface viscosities were measured as functions of film pressure, substrate pH, and the rate of flow of the film. The surface viscosity data for alcohols and acids were in good agreement with those previously reported viscosity values also determined by the canal technique. The values determined with a canal viscometer are often an order of magnitude less than those obtained with other types of viscometers. There are no corresponding data available in the literature with which to compare the surface viscosities of the amide and amine monolayers. Experiments were also carried out for distinguishing between Newtonian and non-Newtonian behavior in the monolayers.

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