# A Superliquid in Two Dimensions and a FirstOrder Change in a Condensed Monolayer II. Abnormal Viscosity Relations of Alcohol Monolayers in Condensed Liquid Phases

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# A Superliquid in Two Dimensions and a First-Order Change in a Condensed Monolayer

## II. Abnormal Viscosity Relations of Alcohol Monolayers in Condensed Liquid Phases

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The new $LS$ phase found in alcohol monolayers has the compressibility of a solid and, at temperatures near that of the first-order $L_2 \rightleftharpoons LS$ transition, the low viscosity of a very highly fluid liquid. The viscosity is almost independent of pressure, but varies in an abnormal way with temperature. For example, octadecanol exhibits a minimum viscosity at about 8.8°C. As is normal, the viscosity increases with decrease of temperature over the small range from 8.8° to 7.5°C where a transition to the $S$ phase occurs. However, above 8.8°C an increase of temperature of 16° increases the viscosity of the $LS$ phase by a factor of 25, and changes it from Newtonian to non-Newtonian. At a pressure of 18 dynes cm⁻¹ the logarithm of the viscosity above 12°C varies nearly either as $T$, or as $1/T$. At other pressures (Fig. 5) the relations are different. At 1 dyne cm⁻¹ the viscosity of the condensed liquid ($L_2$) phase decreases in a normal way with temperature, but at 12 dynes cm⁻¹ the relation is reversed and is abnormal, since the viscosity increases very rapidly as the temperature rises, to correspond with that of the $LS$ phase. This makes the pressure relations extremely abnormal, since the $LS$ phase at 25°C and the $S$ phase at 5°C do not differ greatly in their behavior from normal liquids, which follow the relation $\log \eta = \log \eta_0 + k\pi$. However, at the intermediate temperatures in the range of 8.85 to 10° the viscosity of this phase decreases only slowly with pressure at low pressure, but more and more rapidly as the pressure increases, until the extremely rapid decrease is stopped by a transition to the

$LS$ phase. The viscosity relations indicate that the transition $S \rightleftharpoons LS$ occurs very close to a molecular area of 19.98A². While the area for the transition is almost constant, its temperature increases slowly with pressure. At 16 dynes cm⁻¹ an *increase* of 0.07A in mean molecular distance *increased* the viscosity by a factor of 55. It should be noted that this effect is in the abnormal direction. The $S$ phase is the only one of the three condensed phases which exhibits normal viscosity relations. In both the $S$ and the $LS$ phases the molecules may be assumed to be oriented perpendicular to the surface. In three-dimensional crystals the hydrocarbon chains occupy an area of 18.5A², in the $S$ alcohol films from 19.5 to 20.0A², in the $LS$ films from 20 to 20.75, and in the $L_2$ films from 19.8 to 22.7. The highest temperature employed was 35°C. An increase above this temperature would increase the upper limits of area for the $LS$ and $L_2$ monolayers. It is obvious that the possibility exists for hydrogen bonding between the —OH groups of the alcohols themselves, or between these groups and the water molecules. What is needed for the explanation of the abnormal relations of the $L_2$ and $LS$ phases of the alcohols is to determine what type of binding will increase in energy as the molecular distance is increased, either by increase of temperature or decrease of pressure. The *normal* behavior of the solid surface phase of the alcohols is similar to that of the acids, which has been discussed in earlier papers.

## 1. INTRODUCTION: GENERAL VISCOSITY RELATIONS OF CONDENSED MONOLAYERS

THE viscosity relations of monolayers of the $n$ long paraffin chain alcohols are anomalous and remarkable. For example, the viscosity of a monolayer of octadecanol at a pressure of slightly more than 12 dynes cm⁻¹ is about $5 \times 10^{-3}$ surface poise if the temperature is 8.85°C, but if the temperature is either raised or lowered the viscosity increases with great rapidity. However, earlier work[1] at 25°C revealed no abnormality in the effect of pressure on the viscosity of any of the alcohols investigated,

which included the five $n$ alcohols with from 14 to 18 carbon atoms in the chain. At sufficiently low temperatures also (as 5°C with octadecanol) the pressure effect is again normal, but highly abnormal at intermediate temperatures.

According to Eyring's theory, as applied to monolayers by Moore and Eyring[2] the effect of pressure upon the viscosity of a liquid monolayer should be expressed by the relation (1) that the logarithm of the viscosity is a linear function of the pressure, or

$$\log \eta = \log \eta_0 + k\pi, \tag{1}$$

which is the equation found empirically in the

[1] L. Fourt and W. D Harkins, J. Phys. Chem. **42**, 897 (1938).

[2] W. J. Moore and H. Eyring, J. Chem. Phys. **6**, 391 (1938).

laboratory, as represented graphically in Fig. 1, which represents the behavior of the normal long chain paraffin acids at 25°C.[3]

The relation is linear at 25°C up to about 16.5 dyne cm$^{-1}$ with the 18 and 19 C atom acids, and up to 24 dyne cm$^{-1}$ if there are 20 C atoms in the molecule.

The curves obtained by Fourt and Harkins at 25°C with the long chain alcohols are exhibited in Fig. 2. The alcohol films undergo a transition from the liquid condensed ($L_2$) phase to the high pressure phase at a much lower pressure than those of the corresponding acids, so the linear portion of the curve as expressed by (1) is much shorter than with the acids.

The following additional relations emerge from these diagrams:

2. At low film pressure the liquid condensed ($L_2$) film of octadecanol has a viscosity about 14 times higher than that of the corresponding acid.

3. The viscosity is increased by a factor of about 2 for the alcohols and of about 3 for the acids for each additional carbon atom in the



FIG. 2. Similar to Fig. 1, except that it represents the normal long paraffin chain alcohols, with methyl myristate added for comparison. The alcohol monolayers have much higher viscosities than the corresponding acids. The transition from liquid condensed to high pressure phase occurs at a much lower pressure than in the case of the acids, so the linear relation between pressure and logarithm of viscosity in the liquid condensed phase is more obscured than with the acids.
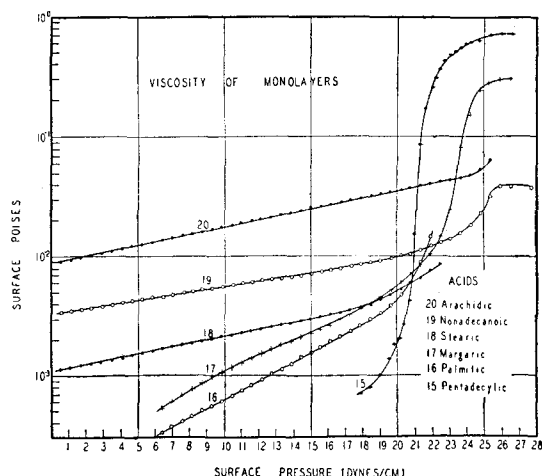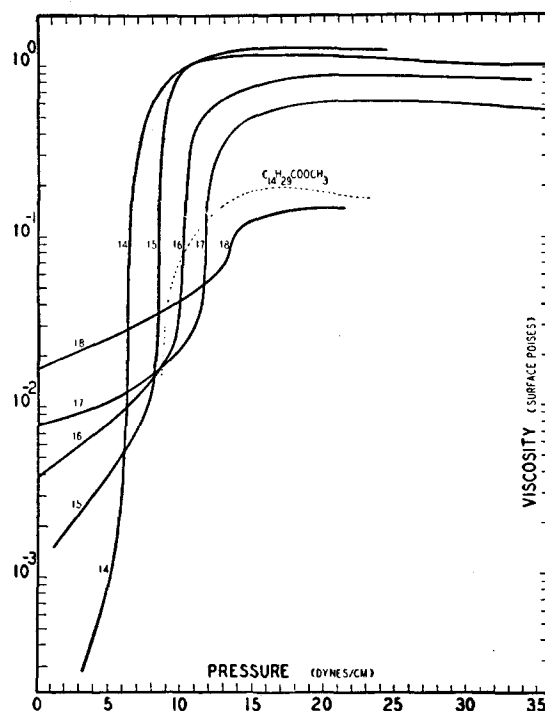


FIG. 1. Exhibits the linear relation between film pressure and the logarithm of the viscosity in the liquid condensed phase or low pressure phase. The viscosity of this phase increases rapidly, while that of the high pressure phase decreases rapidly, with increase in the number of carbon atoms in the hydrocarbon chain. The second-order transition between these phases is marked by an extremely rapid increase in viscosity. The second-order transition affects the viscosity both several dynes below and several above the transition, while the compressibility exhibits no effect except exactly at the pressure of the transition itself.

[3] W. D. Harkins and G. E. Boyd, J. Chem. Phys. **7**, 203 (1939); E. Boyd and W. D. Harkins, J. Am. Chem. Soc. **61**, 1188 (1939).

chain. Thus the viscosities become more nearly equal as the chains lengthen.

4. The liquid ($L_2$) films exhibit a Newtonian viscosity.

5. The high pressure condensed film exhibits a non-Newtonian viscosity which decreases slightly as the pressure increases. A non-Newtonian viscosity is defined as one which varies with the rate of shear.

6. The second-order transition between the low and high pressure phases ($L_2$ and $S$) of a long chain acid is represented on a pressure-area ($\pi - \sigma$) diagram by a kink produced by the meeting of two straight lines of different slope. This is true also for alcohols in the case of the transition $L_2 \rightleftharpoons S$, and nearly true for that of $L_2 \rightleftharpoons LS$ if the temperature is sufficiently far above that of the first-order transition. The relation seems always to be linear on the high pressure side. Thus the pressure-area diagram
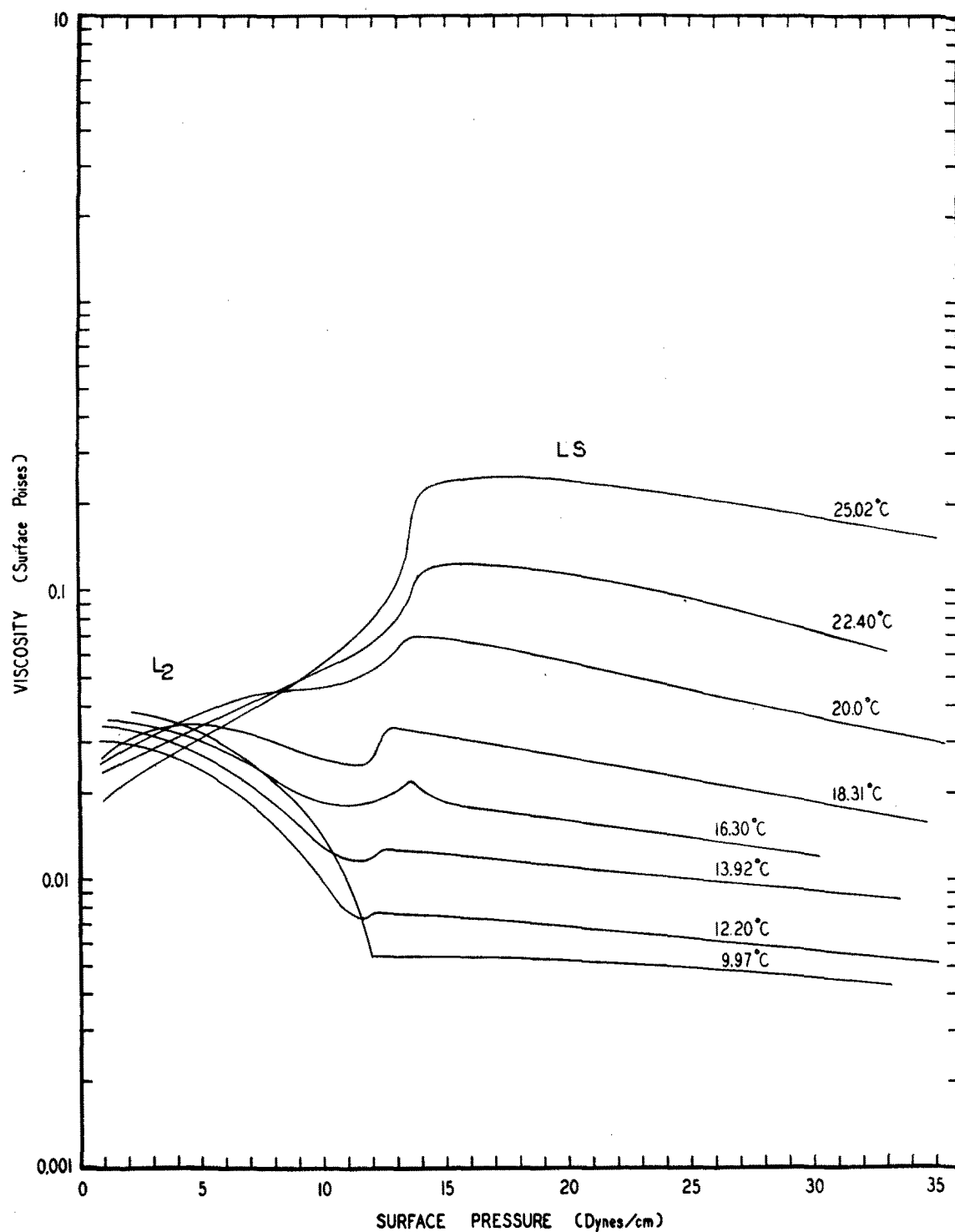
FIG. 3. Viscosity relations of the liquid condensed and $LS$ phases of monolayers of octadecanol. Exhibits the normal effect of temperature on viscosity at a pressure of one dyne, and the abnormal effect at the larger pressures. The effects of pressure itself are extremely abnormal.
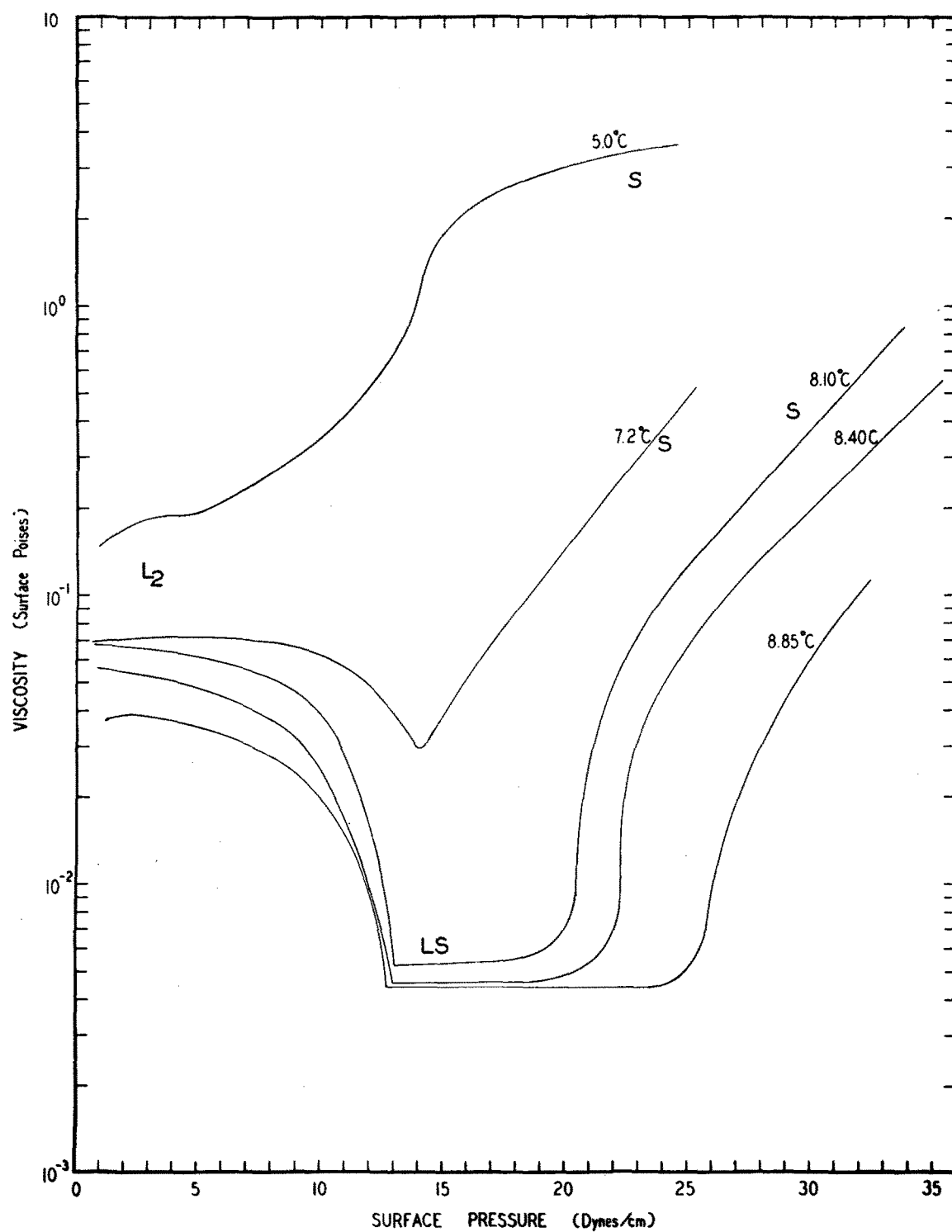
FIG. 4. Viscosity relations of the liquid condensed, and the LS and S phases of monolayers of octadecanol.

usually gives no hint that a change of phase is to occur until the pressure and area of the second-order transition are attained. In contrast with this, Fig. 1 shows very plainly that the linear relation between pressure and logarithm of viscosity begins to disappear at pressures several dynes below that of the transition, and that the approximately constant viscosity of the high pressure phase does not appear until the pressure is several dynes above that of the transition.

7. While the Newtonian viscosity of the liquid condensed ($L_2$) monolayer increases rapidly, the non-Newtonian viscosity of the high pressure phase decreases almost as rapidly, as the chain length is increased.

## 2. ABNORMAL VARIATION OF THE VISCOSITY OF LIQUID CONDENSED PHASE OF AN ALCOHOL WITH TEMPERATURE AND WITH PRESSURE (FIGS. 3 AND 4, AND TABLE I)

### Effect of Temperature

At very low film pressures the viscosity of the liquid condensed ($L_2$) monolayer of a normal long chain paraffin alcohol decreases with increasing temperature, as is normal. Thus the value is about seven times lower at 25°C than at 5°C. However, in Fig. 3 the curves for this phase are seen to cross each other at higher pressures, with the result that at the highest pressures at which this phase exists the viscosity in surface poises decreases from a little over 0.1 at 25°C to about 0.0045 at 8.85°C, or to about a twenty-fifth of its value in a *decrease* of temperature of 16°C. This is extremely remarkable, since in general the viscosity of a phase *rises* rapidly as the temperature is decreased.

As the temperature is decreased still further (Fig. 4), the viscosity of the liquid condensed ($L_2$) phase, at the highest pressures at which it exists, increases from about 0.045 at 8.85°C to about one surface poise, or the increase is by a factor of about 200 for a temperature increment of 4°C.

### Effect of Pressure

At both 5°C and 25°C the effect of pressure upon the viscosity of the $L_2$ film of octadecanol may be described as normal. As the tempera-

TABLE I. Surface viscosity of octadecanol[a] (in surface poises).

| $t°$ C | Pressure (dynes/cm) | | | |
| | 1 | 10 | 18 | 25 |
| --- | --- | --- | --- | --- |
| 5.1° | 0.150 | 0.352 | 2.65 | — |
| 7.2 | .0700 | .0620 | 0.0890 | 0.490 |
| 8.1 | .0673 | .0392 | .00555 | .126 |
| 8.4 | .0560 | .0250 | .00450 | .0655 |
| 8.8 | .0370 | .0196 | .00440 | .00515 |
| 10.0 | .0390 | .0136 | .00530 | .00493 |
| 12.2 | .0302 | .00955 | .00710 | .00620 |
| 13.9 | .0340 | .0127 | .0115 | .0102 |
| 16.3 | .0357 | .0187 | .0170 | .0140 |
| 18.3 | .0270 | .0260 | .0292 | .0207 |
| 20.0 | .0260 | .0457 | .0612 | .0452 |
| 22.4 | .0238 | .0532 | .1020 | .0935 |
| 25.0° | 0.0192 | 0.0570 | 0.249 | 0.206 |

[a] Note that at a film pressure of one dyne per cm the viscosity decreases with increasing temperature, as is normal, from 0.150 poise at 5.1° to 0.0192 at 25°C. At 10 dynes per cm the viscosity decreases (normal) from 0.352 at 5.1° to 0.0096 poise at 12.2°C, but increases (abnormal) from this temperature up to 0.0570 at 25°C. In all of the above changes the monolayer is in the liquid condensed ($L_2$) state. At 18 dyne cm$^{-1}$ the viscosity in the $S$ state decreases with extreme rapidity with increase of temperature, from 2.65 poises at 5.1° to 0.0890 poise at 7.2° and still lower. Then a transition to the $LS$ state occurs, after which the viscosity falls much more slowly to a minimum of not far from 0.0044 poise at about 8.8°C. Then the direction of the change changes and the viscosity of the $LS$ phase increases rapidly with increase of temperature (abnormal) until it becomes 0.249 at 25°C.

ture rises from the lower or falls from the higher value, the effect becomes increasingly abnormal as 9°C is approached. At 9.97°C the viscosity decreases with increasing rapidity, from about 0.04 at low pressure to 0.005 surface poise at a pressure of 12 dynes cm$^{-1}$. At 8.10°C the decrease is from 0.07 to slightly below 0.006 surface poise by an increase of pressure to 13 dynes cm$^{-1}$. This behavior is extremely abnormal since the viscosity is reduced to an eighth or tenth of its value by an increase of pressure which should give threefold or fourfold increase.

## 3. A SUPERLIQUID PHASE WITH EXTREMELY ABNORMAL VISCOSITY RELATIONS

Figures 3 and 4 indicate the existence of a new phase which exhibits extremely remarkable viscosity relations as follows:

1. Although the viscosity is Newtonian, it is essentially independent of pressure. In this constancy of viscosity with increase of pressure, it resembles solid monolayers, which, however, have a non-Newtonian viscosity.

2. Although the phase exists in the same range of high pressures as the $S$ (usually designated as solid) phase, its viscosity at temperatures of 8

to 12°C is much lower than that which is exhibited at low pressures by the liquid ($L_2$) phase from which it is formed by increase of pressure.

3. The viscosity of this phase is lowest at those temperatures at which it is formed by a *first-order* transition from the liquid condensed ($L_2$) phase, by increase of pressure.

4. As the temperature is increased in the range of the second-order transition $L_2 \rightarrow LS$, the viscosity rises very rapidly and takes on more and more the characteristics commonly exhibited by the $S$ phase, although there seems to be no indication of any change of phase. At 25° the viscosity of the $LS$ phase has become non-Newtonian, high (*ca.* 0.25 surface poise), and decreases slightly with increase of pressure. Since the viscosity is non-Newtonian, the value cited refers to the rate of shear employed in this work. A Couette type of apparatus has been designed and will be used later to determine the relation between viscosity and rate of shear.

### 4. THE TRANSITION $L_2 \rightleftharpoons LS$ AND $LS \rightleftharpoons S$ AS REVEALED BY ABRUPT CHANGES IN VISCOSITY

At temperature between 8 and 10° (Figs. 3 and 4 and Table II) the slope ($\partial \log \eta / \partial \pi$) takes on an extremely large negative value as the pressure approaches about 13 dynes cm$^{-1}$, but at this pressure changes abruptly to zero. The pressures and temperatures of these abrupt changes correspond to phase transitions from the condensed liquid to a high pressure phase as revealed by the pressure-area ($\pi - \sigma$) diagram of Fig. 2, Paper I. At 8.10, 8.40, 8.85, and 9.97°C the viscosity remains constant for increases of pressure of 4, 5.5, 11, and more than 22 dynes cm$^{-1}$, respectively.

At all of these temperatures except the highest the viscosity begins to increase rapidly at the end of these intervals, and at 8.10° and 8.40°C the slope of the curve takes on an almost infinite *positive* value, after which it decreases, but remains high.

The most obvious explanation of this extremely high slope is that it corresponds to a phase transition, which would seem to be from the $LS$ to the $S$ phase. This assumption is the basis for the inclusion, in Fig. 3 of Paper I, of a boundary between these two phases, which, as obtained from the viscosity relations, is found to be linear, with a slope which indicates a rise in the transition pressure of 6.4 dynes cm$^{-1}$ per degree C.

The evidence for the existence of the transition from the $LS$ to the $S$ phase is not that of the viscosity alone, since the effect of the transition is apparent in the entropy and energy relations. These exhibit discontinuities at this transition, and also at that between the $L_2$ and $S$ phases. At a molecular area of 19.98A$^2$ the $L_2 \rightleftharpoons S$ transition occurs at a pressure of 17.61 dynes cm$^{-1}$, and the $LS \rightleftharpoons S$ transition at 23.73 dynes cm$^{-1}$. These pressures agree with those obtained from the viscosity relations.

### 5. ABNORMAL VISCOSITY RELATIONS OF MONOLAYERS OF EICOSANOL (FIG. 5)

The pressure-area relations indicate that the temperature of the first-order transition rises about 5°C per carbon atom added to the hydrocarbon chain of an alcohol. Thus with 20 C atoms (eicosanol) the general viscosity diagram ($\eta - \pi - T$) at 20° should resemble that of the 18 C alcohol (octadecanol) at 10°C, and this is found to be true, as shown plainly by Fig. 5. The lowest viscosity with 18 C atoms was found at 8.85°C, and had a value of 0.0045 surface poise for the $LS$ phase. At 20.0°C with 20 C atoms the viscosity is 0.01 surface poise, but the temperature of the minimum viscosity is

TABLE II. Effect of pressure on $d \log_{10} \eta / d\pi$.

| $\pi$ | 5.1° | 7.2° | 8.85° | 10.0° | 25.0° |
|---|---|---|---|---|---|
| 1 | 0.0732 | 0.00647 | 0.0529 | −0.00448 | −0.0684 |
| 3 | .0245 | .00487 | −.0162 | − .0187 | .0470 |
| 5 | .0292 | −.00268 | −.0228 | − .04282 | .0470 |
| 7 | .0494 | −.00652 | −.0355 | − .07560 | .0551 |
| 9 | .0634 | −.0216 | −.0741 | − .08145 | .0570 |
| 11 | .0840 | −.0534 | −.1412 | − .0945 | .0701 |
| 13 | .125 | −.0998 | .00037 | − .000315 | .0180 |
| 15 | .109 | .129 | .00037 | − .000408 | .0126 |
| 17 | .046 | .114 | .00037 | − .00235 | .00418 |
| 19 | .0232 | .106 | .00037 | − .00386 | − .00779 |
| 21 | 0.0187 | .106 | .00037 | − .00477 | − .0107 |
| 23 | — | .106 | .00037 | − .00586 | − .0123 |
| 25 | — | 0.106 | .1355 | − .00724 | − .0130 |
| 27 | — | — | .2304 | − .00805 | − .0140 |
| 29 | — | — | .1426 | − .00797 | − .0140 |
| 31 | — | — | 0.1132 | −0.00870 | −0.0156 |

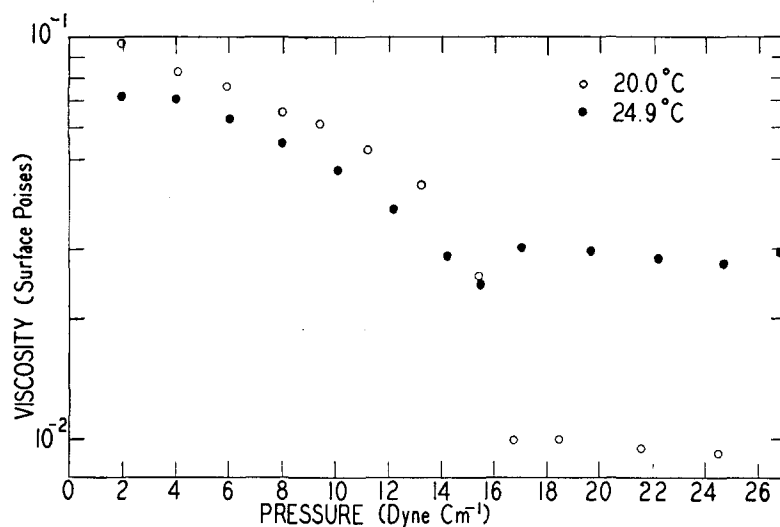Temperature (°C)

$\eta$ = surface viscosity in surface poises.

FIG. 5. Viscosity of the low $(L_2)$ and high $(LS)$ pressure phases of the normal long paraffin chain 20 carbon atom alcohol. Note that the curves cross each other. The relations are similar to those of the 18 carbon alcohol at a lower temperature.

probably slightly lower than this. At a temperature 5° higher (24.9°C) the viscosity of this phase is 0.03 surface poise. The $L_2$ phase exhibits the same relation of exhibiting a high viscosity at low pressure, which decreases rapidly with increase of pressure, as was found with the shorter chain alcohol. Also, there is to be seen in the curve at 24.9°C the same lowering of the viscosity below that of the $LS$ phase just before the $L_2$ phase is transformed into it by increase of pressure. Whether or not this represents a failure to obtain equilibrium quickly enough has not been determined.

Since the $\pi - \sigma$ diagram indicates that the pressure of the transition $L_2 \rightleftharpoons LS$ is increased by increase in the number of carbon atoms, it is to be expected that this will be revealed in the viscosity relations also. This is shown in Fig. 5 to be true, since the viscosity changes its slope from highly negative to zero at 16.7 dynes cm$^{-1}$, while with octadecanol this occurs at 12.6 dynes cm$^{-1}$.

Thus the phase transitions, the energy relations, the compressibility, and the viscosity are very much the same for monolayers of the 18, 19, and 20 C atom alcohols in their relation to the pressure, area, temperature region in which the first-order phase transition occurs.

## 6. DISCUSSION

The molecular area at which the transition $LS \rightleftharpoons S$ occurs in octadecanol seems to be almost independent of pressure and temperature, and what little work has already been done with the 20 C alcohol seems to indicate that the area for its similar transition is almost the same. Also, the range in area of the first-order transition seems to be affected only slightly by an increase in the number of carbon atoms, while both the pressure and the temperature are increased materially. These facts seem to suggest that the mechanism involved is extremely sensitive to the distance between the molecules in the monolayer. Furthermore, since similar abnormalities in pure three-dimensional liquids involve only minor changes of viscosity, the enormous effects found here would seem to be associated with the presence of the aqueous subphase. This can effect the relations in two ways:

1. By orientation of the molecules, the hydroxyl groups (also the hydrocarbon chains) of the alcohols are brought into proximity.

2. The hydroxyl groups are brought into contact with molecules of water.

By (1) there could be some type of bonding between the hydroxyl groups of the alcohols, or by (2) between these groups and the water.

To explain the results, it is necessary to assume a type of bonding which is extremely sensitive to changes of intermolecular distance. In either (1) or (2) hydrogen bonding is likely to be involved, but it seems advisable to await the accumulation of further data before attempting to discover if the formation and dissolution of these bonds can be made to accord with all of the bizarre relations presented here. The transition $S \rightleftharpoons LS$ takes place at a molecular area not far from $19.98A^2$ at any pressure at which both phases are stable. This corresponds to a temperature close to $8.6°C$. The curve in Fig. 4 which is the nearest to this temperature is that at $7.2°C$. At this temperature the viscosity of the $L_2$ phase is almost constant with increase of pressure up to 9 dynes $cm^{-1}$ and then decreases more and more rapidly until at 14 dynes $cm^{-1}$ the monolayer changes directly into the $S$ phase. At the transition point the viscosity is slightly less than 0.03 surface poise, but that of the $S$ phase rises rapidly with pressure, until at 25.5 dynes $cm^{-1}$ it is 0.5 surface poise.

At $8.85°C$ and 16 dynes $cm^{-1}$ the molecular area is $20.0A^2$ and the viscosity, which is that of the $LS$ phase, is 0.0044 surface poise. If at this pressure the molecular area of this phase is increased to $20.75A^2$ by increase of temperature, the viscosity increases by a factor of 55 to 0.2400. *Thus the binding is increased greatly by an increase of molecular area and temperature, both of which should normally decrease it very greatly.*

The extremely high fluidity of the $LS$ film is exhibited only when the molecules are tightly packed and when the temperature is relatively low. Increase of molecular distance is accompanied by an extremely rapid rise of viscosity. Thus at a pressure of 16 dynes $cm^{-1}$ the viscosity is increased 55 times by *increase* of $0.07A$ in mean molecular distance.

While the viscosity of the condensed liquid ($L_2$) phase of the alcohols decreases at low pressures with the temperature, which is normal, this is reversed at high pressures. At higher and lower temperatures, increase of pressure gives the normal increase of viscosity with pressure, but at intermediate temperatures the viscosity decreases more and more rapidly as the pressure increases, until finally a phase transformation occurs.

The behavior of liquid sulfur, in a three-dimensional system, presents some features which are analogous. The viscosity decreases from 0.1094 to 0.0709 poise[4] with increase of temperature from $123°$ to $149.5°C$. At $160°C$ the value of $(\partial \eta / \partial T)_p$ becomes extremely high, and at $200°$ the viscosity itself attains the extremely high value of 21,500 poises, after which it decreases with rise of temperature. Farr and McLeod attribute this rapid increase of viscosity with temperature to a rapid increase in the percentage of $S_8$ in liquid S in this temperature range as found by Smith and Holmes, and by Carson.[5] Rhombic or monoclinic sulfur is considered by Warren and Buswell[6] to consist of puckered 8-atom rings, with an $S-S$ distance of $2.12A$, but closest distance of approach of atoms in adjoining rings of $3.3A$. They explain the increase of viscosity with increase of temperature to breaking of the rings. Ewell and Eyring[7] find the slope $(\partial \log \eta)/\partial(1/T)$ to be much larger above $250°$ than at $160°C$ and calculate the unit of flow at the higher temperature to be about $S_{36}$. The viscosity increase above $160°C$ for sulfur is much larger than that of the $LS$ film above $8.85°C$. Unfortunately, the effect of pressure upon the viscosity of liquid sulfur has not been investigated.

If the logarithm of the surface viscosity of the liquid condensed film of octadecanol at a pressure of 1 dyne $cm^{-1}$ is plotted against the reciprocal of the absolute temperature, a curve is obtained with two linear portions: one below $10°C$ and the other above $18°C$. These indicate heats of activation for viscous flow of 38,400 and 12,100 cal. mole, respectively. For stearic acid monolayers, Moore and Eyring obtained values from 12,100 to 16,150 cal. $mole^{-1}$ and concluded, since these values are two to three times larger than for stearic acid in bulk, that the unit of flow is not a single molecule of stearic acid.

If the logarithm of the viscosity of the $LS$ phase is plotted against various functions of the

[4] C. C. Farr and D. B. McLeod, Proc. Roy. Soc. **97**, 80 (1920).

[5] A. Smith and Holmes, Zeits. f. physik. Chemie **54**, 257 (1905); C. M. Carson, J. Am. Chem. Soc. **29**, 499 (1909).

[6] B. E. Warren and J. T. Buswell, J. Chem. Phys. **3**, 6 (1935).

[7] R. H. Ewell and H. Eyring, J. Chem. Phys. **5**, 726 (1937).

temperature is is found that linearity is obtained at temperatures above 12°C at pressures of 18 dynes cm$^{-1}$ if the function chosen is the temperature (Fig. 6), and is almost as linear *versus* the reciprocal of the temperature.

The $S$ phase of the alcohols is the only one of their three condensed phases which exhibits normal viscosity relations. In both the $S$ and the $LS$ phases the molecules may be assumed to be oriented perpendicular to the surface. In three-dimensional crystals the hydrocarbon chains occupy an area of 18.5A$^2$, in the $S$ alcohol films from 19.5 to 20.0A$^2$, in the $LS$ films from 20 to 20.75, and in the $L_2$ films from 19.8 to 22.7. The highest temperature employed was 35°C. An increase above this temperature would increase the upper limits of area for the $LS$ and $L_2$ monolayers. It is obvious, as has been mentioned earlier, that the possibility exists for hydrogen binding between the $-OH$ groups of the alcohols themselves, or between these groups and the water molecules. What is needed for the explanation of the abnormal relations of the $L_2$ and $LS$ phases of the alcohols is to determine what type of binding will increase in energy as the molecular distance is increased, either by increase of temperature or decrease of pressure. The distance between the two heavier nuclei at the ends of a hydrogen bond is in the range from 2.5 to 2.8A.

The non-Newtonian viscosity of a monolayer of methyl pentadecylate in what is usually designated as the $S$ phase, is about 0.2 surface poise, and is somewhat lower than that of the acid or alcohol with 15 or 16 C atoms in the normal chain. Since the ester should not exhibit
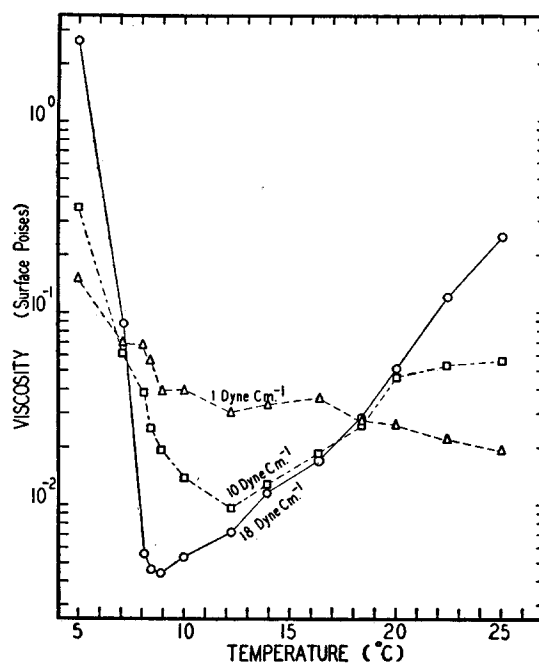


FIG. 6. Relation between the logarithm of the viscosity and the temperature of a monolayer of octadecanol at pressures of 1, 10, and 18 dynes cm$^{-1}$.

hydrogen bonding between molecules in the monolayer itself, it is unfortunate that the viscosities in the liquid condensed state have not been determined.