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The Study of the Boundary Viscosity of Organic Liquids by the Blow-off Method

B.V.Deryagin and V.V.Karasev (deceased)

A method is described for the investigation of the boundary viscosity of liquids based on the fact that, when a layer of liquid flows on a flat wall under the influence of a stream of gas flowing above it, the film assumes a wedge-shaped form (the blow-off method). It is shown that the profile of the resulting wedge resembles that of the velocity profile, which makes it possible to determine from this profile the viscosity as a function of the distance to the support. Another method for the layer-by-layer determination of the viscosity is based on the measurement of the thickness of the film as a function of the duration of the blow-off process at a specific distance from the wetting boundary. In order to determine the film profile, optical and especially ellipsometric methods have been used.
In order to extend the range of objects of study, a method has been developed for the investigation of the boundary viscosity of volatile liquids and its theory has been specified. It has been applied to hexadecane and it has been observed that the viscosity decreases at short distances from the wall.
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I. INTRODUCTION

The theory of the stability of colloids[1] is based on the idea of the wedging pressure of thin liquid layers and its components. In devising a theory of lyophobic disperse systems, only two components of the wedging pressure were initially taken into account—the ionic-electrostatic and molecular components.[1] Subsequently, the concept of the structural component of the wedging pressure, for brevity referred to as the structural forces, was introduced to account for the stability of lyophilic disperse systems. The idea of the existence of this component was first put forward by one of the authors of this review on the basis of experiments with wetting and absorption layers on hydrophilic surfaces.[2-5] These forces arise as a result of the overlap of the boundary layers, whose structure has been made anisotropic in contrast to the isotropic structure of the same phase in bulk. On this basis, attempts have been made to create a quantitative theory of structural forces.[6,7]

In order to strengthen the very basis of this approach, it is important to establish by independent, direct methods the existence and to elucidate the character of the structural features of the boundary layers on lyophilic supports. The difficulty of this problem is due to the small thickness and the possible inhomogeneity of boundary layers with an unusual structure. Dielectric structural methods therefore usually yield only an average characteristic. An exception is the method based on the determination of the weakening of the plane-polarised light transmitted through a thin layer of liquid as a function of the thickness of the latter, which has been proposed and developed by Popovskii, Altoiz, and other workers.[8-18] However, this method is applicable only to a specific class of liquids, for example, to substituted benzenes or benzoic acids, which exhibit a specific strong absorption in a definite part of the spectrum.

This review describes the outcome of experiments on the "layer-by-layer" measurement of viscosity by the method involving the blowing off of wetting films of various organic liquids. These measurements made it possible to establish the changes in viscosity occurring as the solid support is approached, as a function of the distance from it. The change in the structure of the liquids in layers near the support under the influence of the latter has been demonstrated thereby, since viscosity is a property sensitive to structural characteristics.

The determination of the viscosity of thin liquid layers is of direct interest for the study of the mass-transfer processes in narrow capillaries, slits, and disperse systems, in particular for the treatment of the boundary lubrication and filtration phenomena and membrane processes.

The flow of liquid through narrow capillaries was used in early investigations, for example in those of Traube and Siar-Hong-Wang[19] and Deryagin and Krylov,[20] who observed anomalous phenomena in the flow of water in porous bodies with a pore diameter of 0.15 μm. It was also found that, as a result of the coating of the pore walls by oleic acid monolayers, the flow rate increased by a factor of 7 (see also the studies of Somov and Churaev[21] and Peschel and Adlfinger[22]).

Deryagin and Samygin developed a centrifugation method.[23,24] It is based on the observation of the movement of a cylindrical air bubble in a sealed tube filled with the test liquid. The movement of the bubble in the direction of the centrifuge axis takes place as a result of the flow of liquid, forming a film between the air bubble and the walls of the tube, in the opposite direction. The viscosity η was calculated from the formula

$$\eta = \frac{2}{3}\frac{h^3}{rv} j \quad ,$$

where r is the radius of the tube, v the velocity of the bubble, j the centripetal acceleration, and h the thickness of the film.

In order to determine the film thickness h, the ends of the tube were narrowed. We shall denote by V_1 and V_2 the volumes of the liquid in these capillary ends by S the area of the film. By vigorous centrifugation with simultaneous heating, the liquid and the wetting film were driven to one end of the tube in which they occupied a volume V_0. The film thickness was determined from the formula

$$h=\frac{V_0-V_1-V_2}{S} .$$

An increase in viscosity at a distance of 0.1 μm from the wall was observed for certain liquids by this method. In one case it was possible to estimate the increase in viscosity at a distance of 0.02 μm. Hence it is clear that the centrifugation method is more sensitive than all previous procedures. However, in this method too the flow of liquid takes place under the influence of volume forces, which precludes the determination of the viscosity as a function of the distance from the wall.

II. THE BLOW-OFF METHOD

The layer-by-layer method for the measurement of the boundary viscosity—the blow-off method—proposed by one of the authors of the present review,[25,27] is a unique procedure which makes it possible to determine the distribution of the viscosity along the thickness of the boundary layer by the most direct and clearest procedure. Its essential feature is as follows. Imagine a channel bounded by two parallel planes which are separated from one another by a small distance $H = 0.2-1.0$ mm; a layer of the test liquid is deposited on one of the walls (Fig.1). When air or nitrogen is blown through, a flow arises in the film. The drop in air pressure arising between the ends of the channel is measured with a differential manometer.

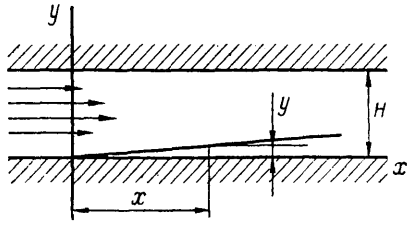


Figure 1. Schematic illustration of the blow-off method.

Tangential and normal forces act on the film. It has been shown that, when a number of conditions are satisfied, the gradient of normal forces may be neglected; in other words, the inequality

$$\delta=\frac{Q_2}{Q_1}\ll 1 ,$$

where Q_1 is the flux under the influence of tangential forces and Q_2 the flux under the influence of the gradient of normal forces, is valid.

If the law of conservation of momentum is applied to the mass of air moving in a slit, we have

$$H\Delta p-2\bar{F}\Delta l=\Delta\int_0^H \rho v^2\,dy ,$$

where $\bar{F}$ is the average tangential frictional force, Δl the length of the slit, ρ the density of air, v the velocity of air molecules, H the slit width, and Δp the pressure difference between the two ends of the slit. Taking into account the continuity equation and applying the parabolic law of the distribution of velocity in a slit, we obtain after appropriate transformations

$$H\Delta p=2\bar{F}\Delta l+\frac{8}{15}H\rho v\,\Delta v . \qquad (1)$$

Using the relations

$$F=\left(\frac{\partial v}{\partial y}\right)_{y=0}=4\eta\frac{v}{H} ,$$

$$\mathrm{Re}=H\rho v_{max}/\eta ,$$

where η is the viscosity, Re the Reynolds number, and v_{max} the maximum velocity at the centre of the slit, we finally obtain after substitution in Eqn.(1)

$$\frac{\Delta p}{\Delta l}\cong\frac{dp}{dl}=\frac{2\bar{F}}{H}+\frac{2}{15}\mathrm{Re}\frac{\Delta F}{\Delta l} . \qquad (2)$$

On substituting the resulting expression in the formula for the flux ratio, we have

$$\frac{Q_2}{Q_1}=\frac{4}{3}\frac{h}{H}+\frac{4}{15}\mathrm{Re}\frac{h}{\Delta l}\frac{\Delta F}{\bar{F}} . \qquad (3)$$

In order that δ should be small, the ratios h/H, $h/\Delta l$, and $\Delta F/\bar{F}$ should be small. As regards the first condition, it is permissible that $h/H \leqslant 0.01$. The inadmissability of the variation of $\bar{F}$ along the air stream requires that the inequality $\Delta F/\bar{F} < 0.05$ should hold, which was always the case in our measurements. Applying the continuity equation and the Boyle–Marriotte law, we replace $\Delta F/\bar{F}$ by $\Delta p/p$ and obtain the condition $\Delta p/p < 0.05$, which can be readily achieved at $p = 760$ mmHg; $h/\Delta l$ was always less than 10^{-4} in our experiments.

It it is assumed that $\mathrm{Re} < 10^3$, which corresponds to the condition for a laminar blowing off stream, then we obtain $\delta < 1.4\times 10^{-2}$ from Eqn.(1). Assuming simultaneously that $\Delta F/F < 0.05$ and $H/\Delta l < 0.005$, we find from Eqn.(2) that the following relation is valid with a relative error of approximately 2%:

$$\bar{F}=\frac{H}{2}\frac{\Delta p}{\Delta l} .$$

For sufficiently small values of δ, the flow of the film solely under the influence of tangential forces is ensured. By virtue of this condition, the velocity of the molecules is a function solely of the distance from the wall y and is independent of the distance x from the wetting boundary—a situation resembling the collapse of a pack of cards. In particular, the points located on the outer surface of the wetting film also have the same velocity $u(y)$. The velocity of the latter can be found from the change in the film profile obtained as a result of the blow-off process. If the initial profile is described by the expression $x = x_0(y)$ and the final profile, after a time τ has elapsed, is described by the expression $x = x(y)$, then $x = x_0 + u(y)\tau$. One can then write $u(y) = [x(y) - x_0]/\tau$. The viscosity can be inferred from the profile:

$$\eta(y)=\frac{F}{du/dy} .$$

When η is constant, the quantity du/dy must also be constant, which corresponds to the equation $x(y) = \text{const}\cdot y$, i.e. the film assumes the form of a wedge with a flat surface. The increase in η for low volumes of y leads to the "blunting" and its decrease to the "sharpening" of the wedge.

III. APPARATUS FOR THE STUDY OF THE BOUNDARY VISCOSITY BY THE BLOW-OFF METHOD

The apparatus for the study of the boundary viscosity by the blow-off method,[28,29] illustrated in Fig.2, consists of a metallic block *1* with a groove, open on top, having a semicircular cross-section, to which two smaller blocks *2* with tubes *7* and channels for the admission and release of gas are attached. Flexible tubing, connecting the

apparatus to the source of gas (nitrogen cylinder, air blower, etc.), is attached to one of the tubes *7*. In block *1*, there is a groove in which a steel insert *3* is placed. A steel or glass plate *4* with an optically polished lower surface is put on top of the apparatus. A gap is formed between the plate *4* and the insert *3* through which air or nitrogen is blown. By selecting the size of the inserts, it was found that the most suitable gap is 0.2 mm. In order to determine the pressure drop in the block *1*, two channels *5* were drilled and connected to the tubes *6*, to which a differential manometer was also connected. The film of the test liquid is deposited on part of the upper plate *4* or on part of the insert *3*. The wetting boundary must be located at right angles to the direction of the stream of gas (Fig.2, line *aa*). A steel plate from the "Kalibr" factory with additional optical polishing was used as the support.

The surface was cleaned with ether. In those cases where special cleanliness was required, the cleaning was carried out with the aid of a gas discharge in argon.[30] The film was deposited by the draining method developed by one of the authors of the present review.[31-33] Several drops of the test liquid were placed on the surface of the plate and the wetting boundary was smoothed out with a thin glass rod. In this deposition method, the film has an inhomogeneous thickness in the initial instant. However, special experiments showed that, in conformity with the theory, this is in no way reflected in the pattern obtained in the blow-off process even after a short time. An apparatus for the study of the boundary viscosity with a variable gap has also been used.[34]

In those cases where special cleanliness is required (for example, in the study of solutions of organic compounds at a low concentration in liquid paraffin) a glass device capable of being disassembled was used,[29] its components being washed with chromic acid mixture, which was followed by treatment in the gas discharge.

Turbine oil and solutions of "metallic soaps" in turbine oil, which are used to improve the lubricating properties of liquids, were investigated for the first time by the blow-off method.[25,26]

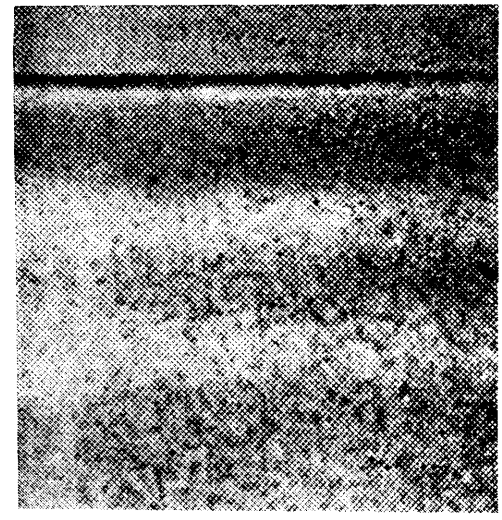


Figure 3. Interference pattern obtained in an experiment involving the blowing off of a 2% solution of aluminium naphthenate in turbine oil; blow-off time 8 min.

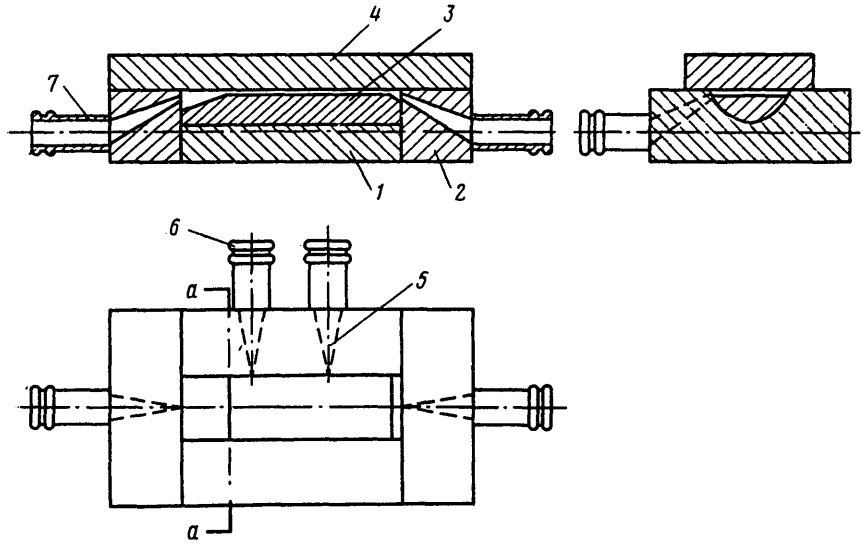


Figure 2. Apparatus for the investigation of the boundary viscosity by the blow-off method.

IV. THE STUDY OF THE BOUNDARY VISCOSITY OF LIQUIDS BY OPTICAL METHODS

1. Determination of the Thickness of Layers by the Interference Methods

Fig.3 presents the interference pattern obtained for a 2.5% solution of aluminium naphthenate in turbine oil The photograph shows the narrow first band, which indicates an increase in the viscosity of the liquid near the wall. The interpretation of this interference pattern leads to the velocity profile illustrated in Fig.4. A similar velocity profile is also observed when aluminium naphthenate is added to other oils.

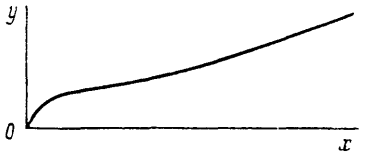


Figure 4. Velocity profile of a 1−2% solution of aluminium naphthenate.

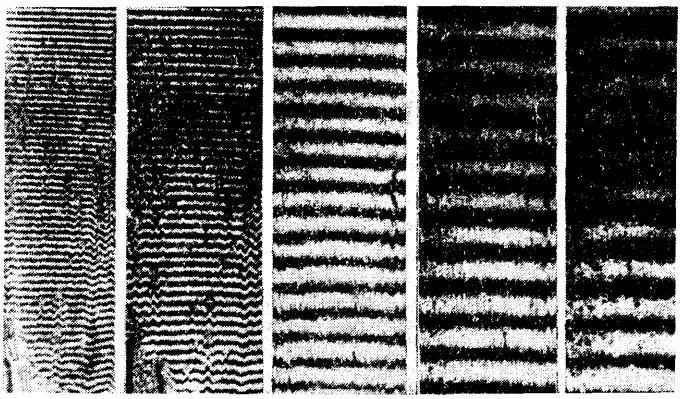


Figure 5. Inteference pattern obtained during the blowing off of turbine oil.

A series of studies have been carried out [35,36] on the properties of various high-molecular-weight organic liquids and solutions of certain polymers in turbine oil and liquid paraffin. For convenience, the authors recorded the blow-off process by filming it. The thickness of the wedge-shaped film was determined from the formula $h = (2n + 1)\lambda/4$, where n is the number of the interference band and λ the wavelength of the monochromatic light. Turbine oil was tested initially. It is seen from the film frames shown in Fig.5 that the distances between the bands are identical. Consequently the viscosity is independent of the distance from the supports, which agrees with the results of earlier studies.[25,26] The pattern is quite striking. The movement of the bands apart as a function of time is observed with a gradual retardation. The thin bands located approximately at right angles to the interference bands represent a parasitic phenomenon due to the interference in the blow-off channel by virtue of the very highly monochromatic nature of the light source.

Fig.6 presents film frames which illustrate the flow of hexamethoxydecane, having an increased viscosity at the boundary with the metal. In this case a small increase in viscosity within the limits of two to three bands is observed. Fig.7 illustrates the flow of a layer of tetraethoxyhexane; in this case the viscosity decreases within the limits of the first two bands. In order to investigate the behaviour of polymers at different temperatures, the apparatus was thermostatted.[37]

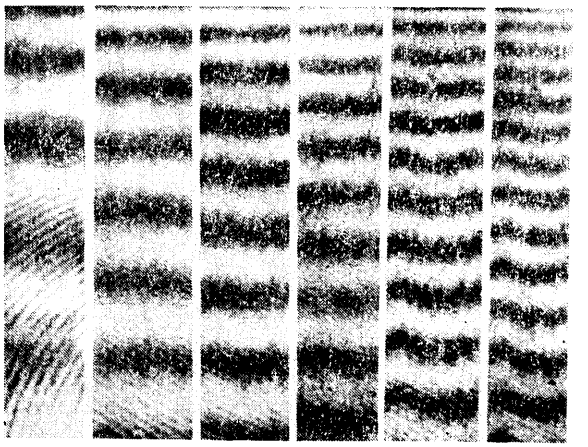


Figure 6. Interference pattern in the course of the blowing off of hexaethoxydecane.

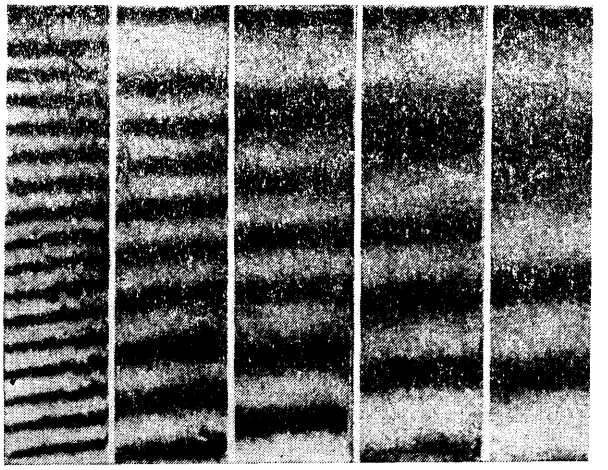


Figure 7. Interference pattern in the course of the blowing off of tetraethoxyhexane.

In the study of polymers of butyl vinyl ether (vinipol) and their solutions in turbine oil and certain other liquids, a change in viscosity was observed as a function of the distance from the solid wall within the limits of $\pm(5-6)$ μm. It was noted that, after the attainment of a definite film thickness, the interference bands disappear and a "ripple" appears on the surface of the film.[35-37] This instability extends over a distance up to 10 μm (Figs.8 and 9). The maximum instability is observed at certain added concentrations of vinipol in turbine oil, which are lower the higher the molecular weight of the vinipol.



Figure 8. Interference after blowing off a 0.5% solution of vinipol with a molecular weight M = 3850 in turbine oil (Δp = 15 mmHg, τ = 5 min); the break up of the film can be seen (instability zone).

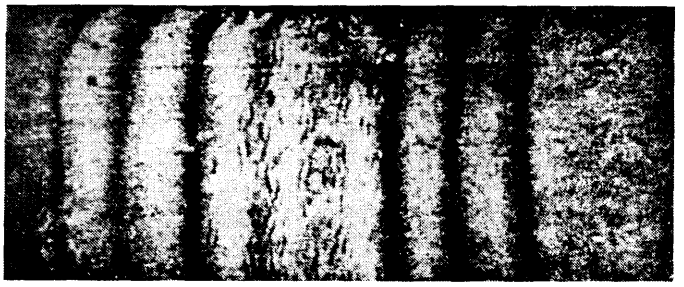


Figure 9. Interference pattern after blowing off a 0.04% solution of vinipol with M = 2100 in turbine oil (Δp = 25 mmHg, τ = 22 min).

In certain cases instability is observed also for "pure" polymers with a narrow molecular weight distribution (MWD). With increase in the molecular weight of vinipol, the thickness of the film, outside the limits of which the region of instability of the interference pattern begins, increases. The instability is manifested to a greater extent if the blowing off is preceded by prolonged contact between the film of the polymer solution and the metal. With increase in temperature, the instability of films of vinipol solutions grows very little, in contrast to the pure vinipol. It follows from thermodynamic considerations that the instability of the wetting film indicates that, in the corresponding range of thicknesses, the derivative of the wedging pressure with respect to the film thickness is positive. Since films whose thickness amounts to several micrometers are unstable, it follows that for such thicknesses the wedging pressure and its derivative have values sufficiently high for the breakdown of liquid films even when their viscosity is high. Evidently the structural component of the wedging pressure is manifested here.[38]

In order to investigate films with a smaller thickness, more accurate optical methods were employed. The photometric method was used first.[39,40] For this purpose, the outlet slit of the monochromator was projected onto the wedge shaped film obtained in the blow-off process. The film thickness was calculated from the intensity of the reflected light. A linear velocity profile was obtained by this method for carefully purified liquid paraffin, which indicates the absence of a specific boundary viscosity.

Polarimetric methods were used to increase the sensitivity still further.[28]

2. Measurement of the Film Thickness by Polarimetric Methods

The scheme illustrated in Fig.10 was used when polarimetric methods were applied to the measurement of the film thickness. When plane-polarised light is reflected from the plate with the film deposited on it, the components of the electric vector of the light wave, lying in the incidence plane and in the plane perpendicular to it, have different reflection coefficients, whose ratio depends on the film thickness. Knowing the ratio of the reflection coefficients, it is possible to determine the film thickness.

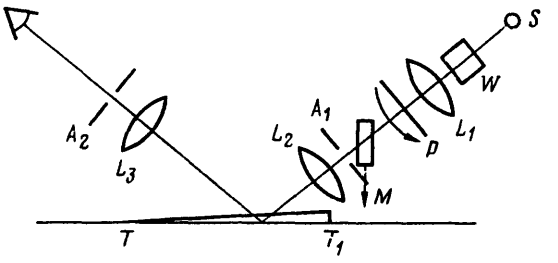


Figure 10. Schematic illustration of the apparatus for the determination of the film profile by the polarimetric method.

An apparatus with a stack of plates (Fig.10) was used to determine the ratio of the reflection coefficients. Here S is the source of monochromatic light (PRK-2 quartz lamp), W a liquid light filter (solution of neodymium nitrate with an admixture of chrysoidine and eosine), L_1 the condenser lens, P a rotating polariser (polaroid), M a stack of 9 x 12 glass plates (12 plates), A_1 an adjustable slit, L_2 a lens focussing the image of the slit onto the object, $T-T_1$ the object of study—a transparent film on a metal or dielectric, A_2 the aperture (slit) diaphragm, and L_3 an image diffusing lens.

The principle of the operation of the apparatus is as follows. If a beam of plane-polarised light is directed onto the surface of the metal with the film deposited on it, then the horizontal and vertical components of the electric vector of the light wave are in general reflected unequally, as a result of which the light flux is modulated on rotation of the polariser. The maximum intensity of the reflected light is attained when the plane of the vibrations in the rotating

polariser coincides with the direction of the most intense component of the above vector and the minimum intensity occurs correspondingly after coincidence with the least intense component (i.e. on rotation by 90°). The degree of polarisation of light transmitted through the stack of plates is known to depend on the angle between the normal to the stack and the beam incident on it. With increase in this angle as a consequence of the rotation of the stack about the axis perpendicular to the direction of the beam and parallel to the direction of the vibrations with the least amplitude, the degree of polarisation increases. Thus, we can always "attenuate" the more intense component of the electric field vector by rotating the stack, making it comparable to the least intense component. In this case modulation ceases, which is observed from the absence of periodic variations in the brightness of the reflected light. The corresponding angle of rotation of the stack depends on the ratio of the reflection coefficients of the horizontal and vertical components of the electric field vector of the light wave.

In order to increase further the accuracy of the reading and to expand the range of the measurable thicknesses towards lower values, a scheme resembling that of the Drude scheme with a photoelectric indicator was used; the scheme was applied in different versions, the locations of the light source and the indicator being interchanged.[41–46] At the present time the film thickness is calculated on a computer by means of appropriate programs.

Polished metallic surfaces are known to possess a microhardness, i.e. there are grooves approximately 40–80 Å deep and 80–160 Å wide in the direction along the plane.† At the end of the experiment, they are filled with the test liquid. However, the optical constants of the plate, measured before and after the experiment, proved to be very similar, which suggests that the liquid in the groove does not exert any special influence on the optical constants of the support. Although a random mosaic structure, consisting of islands and hollows with "diffuse" edges, filled with liquid, is observed on the surface of the metallic plate, the effective refractive index of this system remains close to the refractive index obtained for the specimen of the pure metal with a thin oxide film. Consequently, the film thicknesses are read from a certain arbitrary boundary passing near the tops of the peaks of the surface relief.

3. The Study of Certain Organic Substances by the Blow-off Method Using Polarimetric Procedures

The objects of the study of the boundary viscosity by polarimetric methods were turbine oil and liquid paraffins of different brands: paraffin purified by the acid–alkaline method, paraffin treated over a platinum catalyst by the Elovich method, D-1 oil, and pharmaceutical liquid paraffin purified chromatographically. Rigorously linear velocity profiles were obtained in all cases. After this, a 2.5% solution of vinipol ($M \simeq 4000$) in turbine oil was tested.[48] A decrease in viscosity near the wall over distances up to 1000 Å was observed in this case (Fig.11). In the study of the 0.5% solution of synthetic sodium-butadiene rubber in turbine oil,[48] some increase in viscosity in a layer 100–200 Å thick was observed (Fig.12).

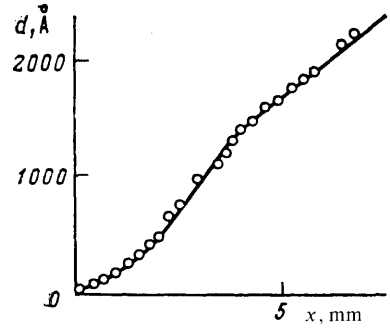


Figure 11. Film profile for a 2.5% solution of vinipol with $M \simeq 4000$ in turbine oil, obtained on the apparatus with a stack of plates.

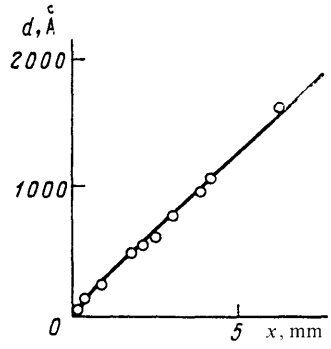


Figure 12. Film profile for a 0.5% solution of sodium-butadiene rubber in turbine oil, obtained on the apparatus with a coherence eliminating device.

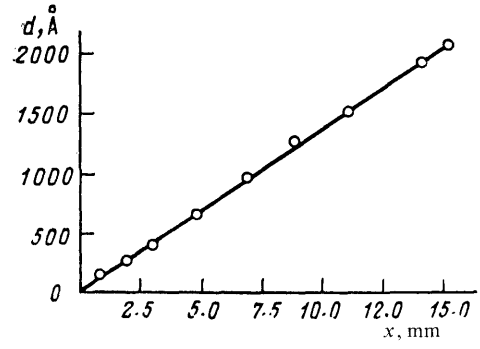


Figure 13. Film profile for purified liquid paraffin.

Further measurements were performed on ellipsometers. In the first place, the velocity profile was obtained for liquid paraffin specially purified on a platinum catalyst. The linear velocity profile was retained down to the thickness of 10 Å (Fig.13). Finally, a large number of organosilicon compounds were investigated.[49,56]

†According to electron microscope data obtained by A.E.Chalykh and Z.E.Sheshenina.

The study of the viscosity of boundary layers of polymers is of special interest from the standpoint of the elucidation of the influence of their molecular characteristics—the molecular weight, the rigidity of the molecular chain, the chemical composiiton, and the level of intermolecular interaction—on the properties of the boundary layers of polymers. We may note that organosilicon polymers and oligomers are very interesting objects for the study of the boundary viscosity. Firstly, polyorganosiloxanes retain their liquid state over a very wide range of molecular weights. Secondly, the replacement of methyl groups in polydimethylsiloxanes by other groups makes it possible to vary within fairly wide limits both the flexibility of the polymer chains of the molecule and the character and level of the intermolecular interaction in polyorganosiloxanes.[57,58]

We investigated polydimethylsiloxane liquids (PMS) with molecular weights ranging from 1000 to 40 000 and viscosities from 0.05 to 20 St[52] (at 20 °C) and a series of substituted oligo-organosiloxanes containing ethyl, phenyl, chlorophenyl, γ-trifluoropropyl, and other groups.[54] The influence of the molecular weight and of the molecular weight distribution of the polymer on its behaviour in boundary layers as well as of temperature and factors such as photo- and thermo-oxidation has been studied in relation to polydimethylsiloxanes. Their boundary viscosity was investigated on glass and metallic surfaces.

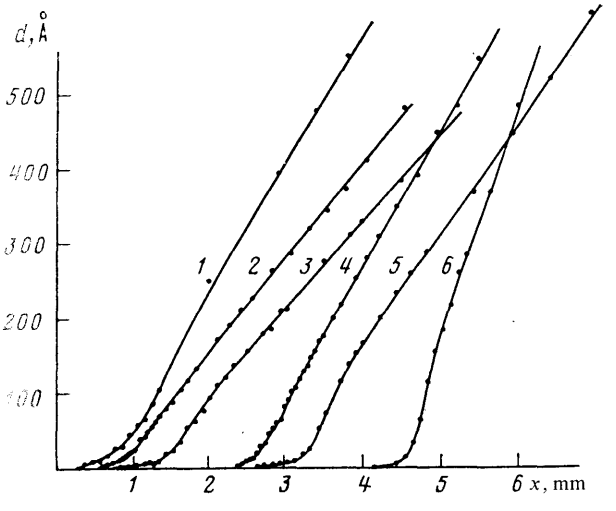


Figure 14. Film profiles for PMS having different molecular weights with a narrow MWD = 1.2–1.5 on steel: 1) PMS-5; 2) PMS-10; 3) PMS-25; 4) PMS-70; 5) PMS-400; 6) PMS-2000.

The velocity profiles for the flow of PMS films having different molecular weights and with a narrow MWD on steel are presented in Fig.14. Their common feature is the presence of three sections in the curve with different slopes and hence with different viscosities of the corresponding liquid layers. A sharp decrease in the viscosity of the liquid is observed for a layer thickness of 20–30 Å, the viscosity is 30–40% higher in the range of thicknesses from 20–30 to 150–200 Å than in the bulk phase, while the viscosity of a layer 150–200 Å thick does not differ from that in the bulk phase determined with the aid of a capillary viscometer. For example, these quantities are respectively 4.92 and 4.70 cP and 69.68 and 68.25 cP respectively for the PMS-5 and PMS-70 polydimethylsiloxanes.

Bearing in mind the extreme flexibility of the main molecular chain and the weak intermolecular interaction, the molecular structure of the PMS in the bulk phase can be represented as an assembly of species whose conformational spectrum is extremely broad—from coiled to uncoiled molecules with the former predominating. The flow velocity profile observed for PMS films can be accounted for by the variation of the conformational equilibrium of the PMS molecules in the force field of the surface of the solid phase.

The anomalously low viscosity of PMS in layers adjoining the surface of the solid phase is apparently due to the uncoiling of the molecular coils and the subsequent orientation of the uncoiled chains parallel to the plane of the support. Such orientation should be promoted by the high polarisability of the $Si^{\tau+}-O^{\tau-}$ bond, each atom of which can become a centre of attraction to the surface of the solid phase and can promote the horizontal orientation of the PMS molecules on absorption. A monomolecular PMS layer with a horizontal orientation of the molecules is known to have a thickness of 5–6 Å. Taking this into account, one can postulate that the "lower" boundary layer is made up of several horizontallly oriented layers of PMS molecules. The anomalously low viscosity can be explained in this instance by the ready slip of these layers relative to one another over planes bounded by methyl groups. The fact that the thickness of the boundary layer is independent of the molecular weight of the PMS confirms the hypothesis of the horizontal orientation of the uncoiled molecular chains. In liquid layers more remote from the support, the influence of this force field on the solid phase is weakened and the polymolecular boundary layer breaks down. The orientation of the molecules, which still have an uncoiled conformation, then becomes random; this should increase the viscosity, which has in fact been observed for liquid layers with a thickness from 20–30 to 150–200 Å. Above this level, the viscosity falls, evidently as a consequence of the coiling of the molecules, and subsequently remains constant and equal to the viscosity of the liquid in the bulk phase. In this range of thicknesses, the surface of the solid phase apparently does not influence the molecular structure of the liquid. According to the results of Fox et al.,[59,60] in the course of time the "lower" layers in the boundary phase should be gradually enriched in the high-molecular-weight component. This should lead to an increase in the viscosity of the PMS in layers fairly close to the support.

Thus the viscosity of layers in the boundary phase is determined by the occurrence of two competing processes: ordered horizontal orientation of the linear molecules, which decreases the viscosity, and the increase in the concentration of the high-molecular component which increases it. In the series of PMS, the viscosity of the "lower" boundary phase of the PMS proved to be reduced in all the cases examined compared with the bulk phase. This means that the process involving the orientation of the molecules predominates and surface fractionation is hardly manifested owing to the narrow MWD of the PMS investigated.

The phenomenon of the fractionation of polymers with respect to molecular weights in the force field of the solid phase has been confirmed in a study of the boundary viscosity of binary mixtures of PMS having different molecular weights with the polydimethylsiloxane liquid PMS-10. The flow velocity profiles of films of these mixtures (Fig.15) differ significantly from the profiles of the films examined previously. They are characterised by the presence of steps in

the range of thicknesses 10–30 Å. The overall form and height of the steps are readily reproducible in replicate experiments and are independent of the molecular weight of the dissolved PMS. It is essential to note that the stepwise profile is obtained when the blowing off is carried out after the film of the test liquid has been maintained for 30 min on the suport. The stepwise profile of the film is not a consequence of its instability, since its form is retained after the blown off film has been kept for 1.5 h with certain intermediate measurements. Steps on the flow velocity profiles of films of binary PMS mixtures (Fig.15) show that in the region adjoining the support there are layers of liquids with an enhanced viscosity which are formed as a result of the enrichment of the boundary layer in the high-molecular-weight components of the mixture,[59,60] i.e. as a result of the surface fractionation of the polymer.

The increase in the viscosity of the boundary layer may indicate the occurrence in the polymer of processes associated with the change (expansion) of the MWD by external influences such as thermo- and photo-oxidation. It is known[61–63] that these processes lead to the cross-linking of the PMS macromolecules resulting in the formation of a gel. The accumulation of the oxidation products at an early stage of the process should alter the MWD and correspondingly the shape of the flow velocity profile of the film. As can be seen from Fig.16, the profiles of the PMS-200 films after thermo-oxidation differ from the initial films by the presence of steps or slip planes in the range of thicknesses up to 20 Å. The height of the steps remains stable throughout the series of experiments regardless of the degree of oxidation. With increse in the degree of oxidation, layers with enhanced viscosity become more distinct in the film profile. On the other hand, judging from the slope of the curves, the bulk viscosity does not change significantly.

In the photo-oxidation of PMS-200, a pattern analogous to that described above is observed (Fig.17): steps and slip planes appear on the film profiles of the liquid subjected to photo-oxidation for 12 and 48 h (curve *3*), such steps and planes being absent from the initial specimen. The bulk viscosity then increases appreciably with increase in the oxidation time and, in contrast to the previous case, is more sensitive to irradiation than the viscosity of the boundary layer.

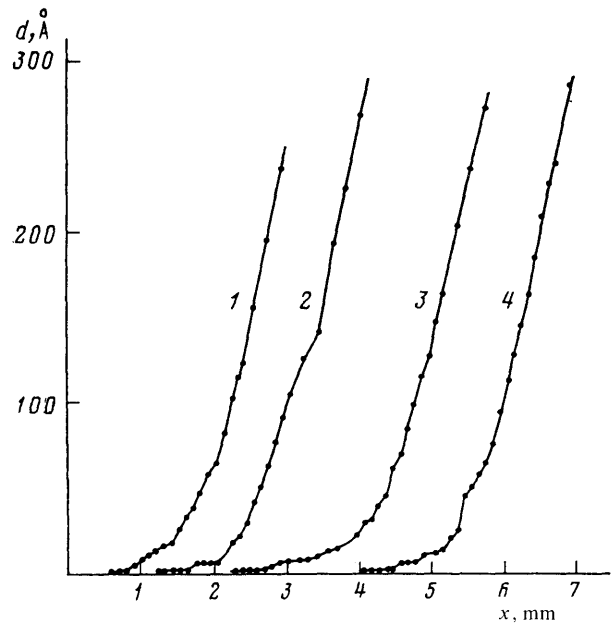


Figure 16. Profiles of PMS-200 films subjected to thermo-oxidation: 1) initial PMS-200; 2) PMS-200 oxidised for 15 h; 3) PMS-200 oxidised for 30 h; 4) PMS-200 oxidised for 45 h.

In both cases (in the thermo- and photo-oxidation of films), together with the stable elements of the profile (steps and slip planes), random bends appear on the velocity profiles which apparently reflect the random structural fluctuations in the polymer manifested in the blow-off process and caused by the presence of polar oxidation products. The formation of an adsorbed layer approximately 6 Å thick, firmly bound to the support, may be noted as a distinctive feature in the case of photo-oxidation.[55,57,58] Presumably this layer is made up of molecules of the test liquid chemisorbed on

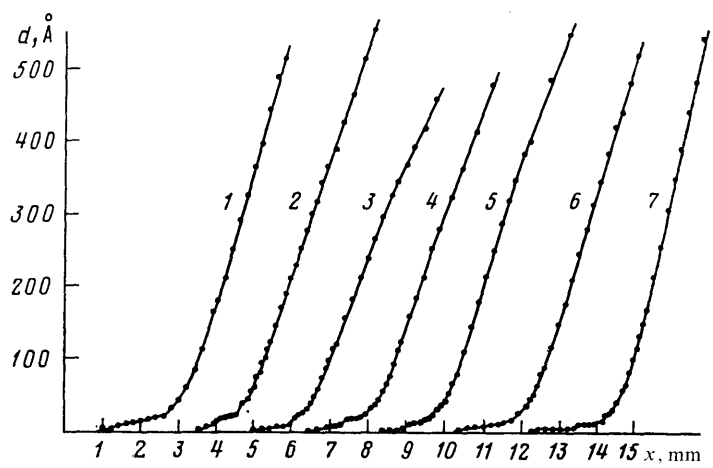


Figure 15. Film profiles for binary PMS mixtures: 1) PMS-10; 2) PMS-10 + PMS-70; 3) PMS-10 + PMS-400; 4) PMS-10 + PMS-2000; 5) PMS-10 + PMS-20 000; 6) PMS-10 + PMS-50 000; 7) PMS-10 + PMS-1 000 000.

the surface of the support by virtue of the presence in them of peroxy-radicals (CH_2OO or other reactive groups), formed as a result of oxidation processes initiated by UV radiation. This layer can be removed from the support only by repolishing its surface.

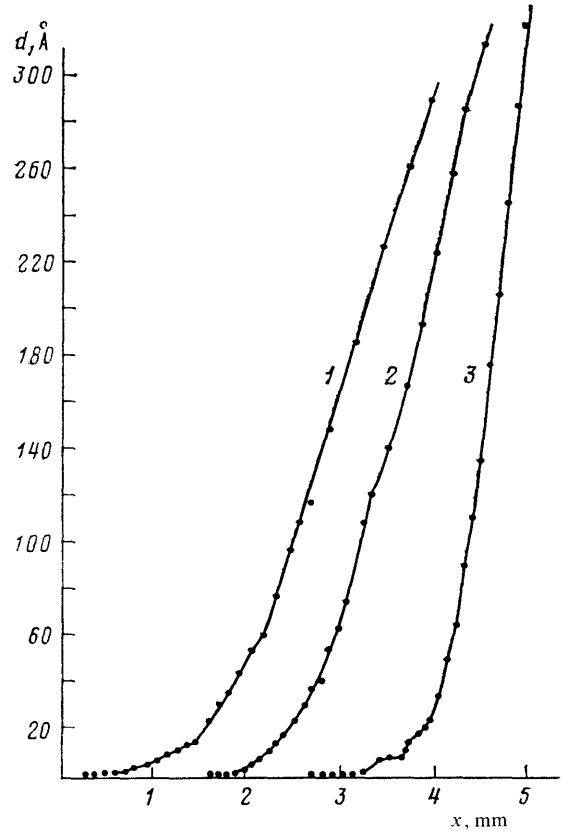


Figure 17. Profiles of PMS-200 films subjected to photodegradation: 1) initial PMS-200; 2) PMS-200 oxidised for 12 h; 3) PMS-200 oxidised for 48 h.

The substitution of methyl groups at the silicon atoms by groups of other chemical nature alters both the level and character of the intermolecular interaction and the degree of flexibility of the molecular chain.[57,58] It was shown earlier[50] that the introduction of polar β-cyanoethyl subsituents into the PMS molecule is accompanied by an appreciable increase in the level of intermolecular interaction as a result of the formation of a fluctuating network of bonds between the polar groups of neighbouring molecules. The flexibility of the molecular chains does not change significantly, which indicates an influence on the behaviour of such polymers in the vicinity of the surface of the solid. Indeed, in the presence of methyl-β-cyanoethylsiloxane units (Fig.18), an increase in the thickness of the boundary layer with an enhanced viscosity on average up to 60 Å is observed. Above 60 Å, the viscosity corresponds to the bulk phase value. It was found that the character of the flow velocity profiles of the film depends on the number of β-cyanoethyl groups. A smooth decrease in viscosity in the boundary layer is characteristic of liquids containing 6 and 100 mole% of methyl-β-cyanoethylsiloxane units (Fig.18, curves *1* and *6*). In the presence of 12.5 and 50 mole % of polar substituents (curves *2*–*5*), the appearance of slip planes at distances of 20 and 40 Å from the support is observed.

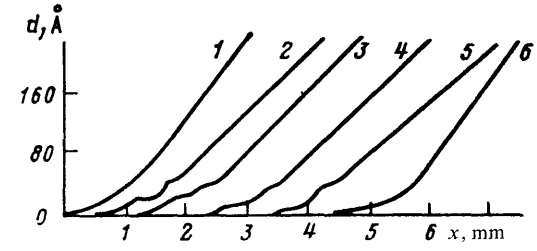


Figure 18. Profiles of films of dimethyl-β-cyanoethylsiloxanes with different contents of β-cyanoethylsiloxy-units: 1) PMS-6.25; 2) and 3) PMS-12.5; 4) and 5) PMS-50; 6) PMS-100.

In contrast to PMS, in dimethyl-β-cyanoethylsiloxanes the polar β-cyanoethyl groups are the centres of attraction to the surface of the support. One can therefore assume that in the given case the molecules are fixed on the surface of the solid phase via these groups. Depending on the number of polar groups, the conformation of the adsorbed molecule can be either extended parallel to the plane of the support or the molecule can have the form of a loop. When their content is low, these groups do not entail a significant change in the conformation of the adsorbed molecule compared with PMS. An analogous pattern has been observed also for a 100% content of methyl-β-cyanoethylsiloxane units (Fig.18, curve *6*). In these two cases, the molecules are adsorbed in a planar fashion, forming several layers, which are bounded by methyl groups and slip relative to one another. The film profiles of dimethyl-β-cyanoethylsiloxanes are therefore identical with the PMS film profiles both for slight and complete substitution of the dimethylsiloxane units.

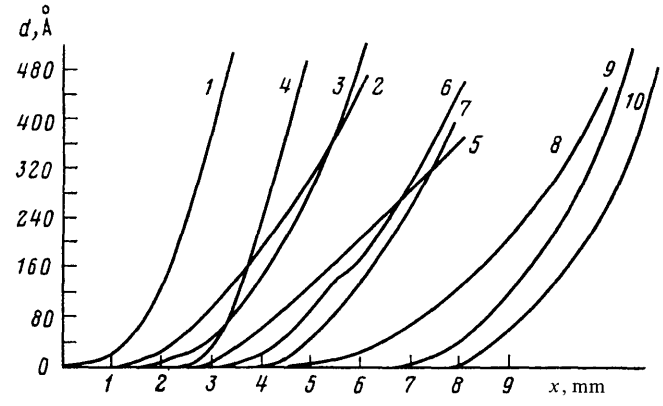


Figure 19. Profiles of films of oligo-organosiloxanes containing units of different types: 1) ethylsiloxy; 2) methylchlorophenylsiloxy; 3)–5) trifluoropropylsiloxy; 6)–9) thienylsiloxy; 10) chlorothienylsiloxy.

When the contents of the methyl-β-cyanoethylsiloxane units are 12 and 50 mole%, the molecules are adsorbed in such a way that the sections of the chains between the polar groups, linked to the surface, form loops which extend into the bulk of the liquid. The presence of slip planes at distances of 20 and 40 Å can apparently be explained by the formation of such structures.

The velocity profiles of films of oligo-organosiloxanes containing methylchlorophenylmethyl-, γ-trifluoropropyl-, thienyl-, and chlorothienyl-siloxane units (Fig.19) are outwardly identical with the film profits of dimethyl-β-cyanoethylsiloxanes, but the region of reduced viscosity extends in these substances to a greater depth (as far as 370 Å).[57,58]

The study of the surface and volume properties of a number of oligoorganosiloxanes[50,57,58] showed that the introduction of polar or bulky substituents reduces the intramolecular mobility. By virtue of this, the complete set of conformational transformations characteristic of polydimethylsiloxanes cannot be realised in the oligomers considered. The absence of an intermediate layer with enhanced viscosity, of the kind observed in PMS, is explained by this factor.

The distribution of polar groups along the molecular chain of oligo-organosiloxanes favours their horizontal orientation and adsorption on the surface. As in the case of the PMS, this reduces the viscosity in the boundary layer. On the other hand, the higher level of intermolecular interaction in oligo-organosiloxanes promotes the transmission of the influence of the force field of the solid phase into the bulk of the liquid to an appreciably greater distance than in the case of PMS. The region of reduced viscosity therefore reaches 350–370 Å in certain cases. The formation of slip planes in layers 20–30 Å thick in the oligomers considered (Fig.19, curves *2*, *3*, *6*, and *9*) can be attributed to their surface fractionation, intensified in the given instance by the presence of polar substituents at the silicon atoms and by the increased adsorption capacity of the molecules of these oligomers.[55,58]

Polydiethylsiloxane liquids in which the level of intermolecular interaction is enhanced compared with PMS occupy an intermediate position between oligo-organosiloxanes with polar groups and PMS as regards behaviour in boundary layers (Fig.19, curve *1*).[58]

It follows from the entire foregoing considerations that our flow velocity profiles of films indicate structural changes in the boundary layers. The observed anomalies in the profiles cannot be attributed to either the action of the capillary forces arising as a result of the microroughness of the support, or to the spontaneous migration of the wetting boundary, or to the surface tension gradients, because experiments with different liquids were not performed on the same support. Despite this, depending on the presence of polar groups, the degree of rigidity of the chain, and other factors, the flow velocity profiles of the films have their specific features, including the presence and absence of curvature in the range of thicknesses from zero to 50 Å. If the microroughness of the support had been the source of the anomalies in the profiles, then the latter would have appeared in all cases. Furthermore, the rate of spreading of the liquid under the influence of the microroughness is extremely low and the degree of spreading is 0.04 cm after 1300 s for the PMS with a viscosity of 0.07 St [64]# on a vertical plate, whilst according to our data a spreading of 0.06 cm was obtained for a PMS with a viscosity of 0.1 St on a horizontal plate after 5100 s. On the other hand, the blow-off experiments were performed over a short period and with viscous liquids. For example, the blowing off of PMS with a viscosity of 0.7 St was performed immediately after depositing the liquid on the support over 420–800 s.[65] The curving of the flow velocity profile of the liquid film was then observed at a distance of 0.3–0.4 cm from the wetting boundary. Judging from the data presented, this fact cannot be explained by the influence of the roughness of the support. Furthermore, the movement of the wetting boundary during the blow-off process was not observed in the experiments.

#Having observed conditions under which the blow-off method involves appreciable errors, Bascom and Singleterry[64] decided to abandon this method. Despite the subsequent explanation,[68] many investigators followed their example having decided to ignore a wide variety of results which we obtained. This is an example of how it is often difficult for a significantly new and novel development to achieve recognition.

V. THE STUDY OF THE BOUNDARY VISCOSITY OF ORGANIC LIQUIDS IN THE BLOW-OFF PROCESS

All the versions of the blow-off method described hitherto are suitable solely for liquids producing films which are stable in time. The blow-off method has been modified for the investigation of unstable films. For this purpose, a procedure has been developed for the observation of films in the course of the blow-off process.[29] The essential feature of the method is that the measurement of the film thickness is always performed at the same site and the dependence of the thickness on the blow-off time is obtained. The dependence of the boundary viscosity on the distance from the support is determined from the formula

$$\eta = \frac{H}{2}\frac{\Delta p}{\Delta l}\frac{dh}{du(h)} \quad ,$$

where $\Delta p/\Delta l$ is the pressure gradient along the blowing off stream and $u = x/t$, x being the distance from the wetting boundary to the point of observation and t the time from the start of the blowing off to the measurement of the thickness h.

A glass apparatus was used for these experiments;[66] the slit was covered by a prism from which the beam emerged at a definite angle and fell on the insert with the film. In the study of boundary viscosity on glass, a total internal reflection prism was used and the film was deposited on the base of the prism.

A series of organic liquids, effectively wetting metals and glass, were investigated by this method. In the first place, the flow velocity profiles were obtained for liquid paraffin of different grades on a metal and glass. Metallic plates of ShKh-15 steel, polished to class 14 quality, were subjected to additional optical polishing. In all cases rigorously linear velocity profiles were obtained, indicating the absence of an unusual boundary viscosity. Velocity profiles were then recorded for solutions of stearic acid in liquid paraffin.[29,65–67] In order to obtain reproducible results on glass, the latter was cleansed in a gas discharge.[30] Appreciable distortions in the profile were observed at a stearic acid concentration of 0.000021 %. A linear profile with slight steps, whose number and height were not reproducible in different experiments, was obtained. At a concentration of 0.00054 %, an increase in the number of steps is observed (Fig.20) and they are appreciably more pronounced. Their height and number are likewise not reproducible. At a concentration of 0.001 %, inadequate wetting is observed, so that on being blown off the film breaks up into fine drops. This can be explained by the formation of an adsorption layer made up of molecules with vertically disposed methyl groups. At a concentration of 0.01 %, the wetting disappears completely and the solution drains off like water from a greasy surface. This occurs as a result of the completion of an adsorption monolayer of stearic acid, which is not wetted by virtually anything.

Solutions of hydrocarbons, consisting mainly of tetracosane ($C_{24}H_{50}$) with chlorinated methylene groups in the middle section of the chain (mono-, tri-, hexa-, and dodeca-chloroparaffins), in liquid paraffin were tested next.[28,65-67] Steel plates additionally polished and cleaned in a gas discharge in argon served as the supports. In the first place, the velocity profiles were obtained for a solution of monochloroparaffin in D-1 liquid paraffin, after its purification in a chromatographic column, and in liuquid paraffin subjected to acid-alkaline purification. It is seen from the plots (Fig.21*a*) that in the given instance a boundary layer with a modified viscosity, having a thickness of approximately 200 Å, is produced. Trichloroparaffin dissolved in liquid paraffin (Fig.21*b*) yields a result similar to the previous one: a boundary layer approximately 300 Å thick is observed near the wall. The results of the study of the solution of hexachloroparaffin are presented in Fig.21*c*. In this case a velocity profile resembling the previous ones was obtained. A change in viscosity is likewise observed in a boundary layer approximately 250 Å thick. Measurements with dodecachloroparaffin could not be performed because of the absence of wetting.

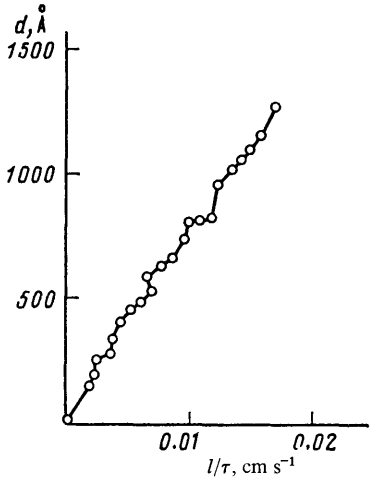


Figure 20. Prifile of a film of 0.00054 % solution of stearic acid obtained on a glass surface during the blow-off process.

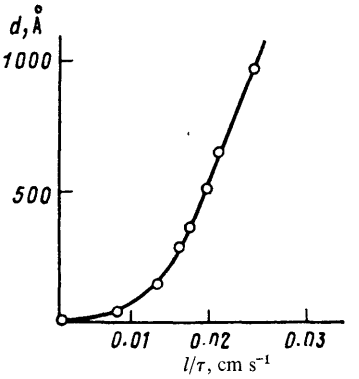


Figure 22. Flow velocity profile of a film of incompletely hydrogenated benzanthrone obtained on a glass surface during the blow-off process.

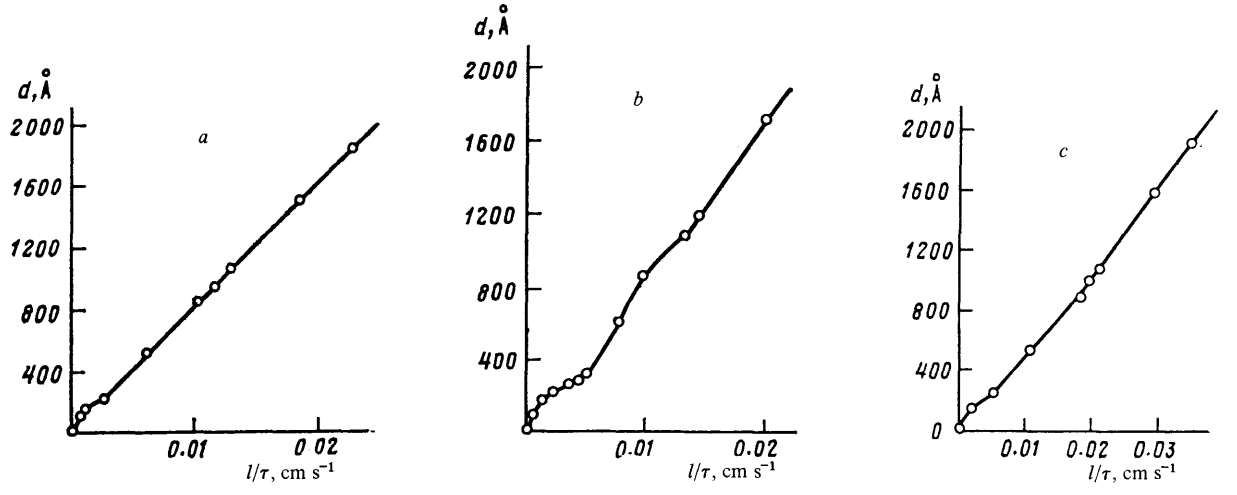
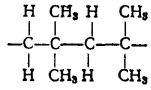


Figure 21. *a*) Profile of a film of 0.01% solution of monochlorotetracosane in liquid paraffin obtained on a steel surface during the blow-off process; *b*) profile of a film of 0.01% solution of trichlorotetracosane in liquid paraffin obtained on a metallic surface during the blow-off process; *c*) profile of a film of 0.01% solution of hexachlorotetracosane obtained on a glass surface during the blow-off process.

Finally, certain individual liquids were blown off. The flow velocity profile was obtained initially (on glass) for the incompletely hydrogenated benzanthrone.[48]§ As the name shows, this substance is not strictly individual. At the start of the experiment, the film was allowed to stand in order that equilibrium should be established in thin layers. Fig.22 illustrates the velocity profile, from which it is seen that, in the immediate vicinity of the wall, the viscosity is appreciably reduced. Above 200–300 Å (naturally this is a very arbitrary figure, since the viscosity varies very smoothly), the viscosity is almost equal to the bulk phase value.

The latest object was polyisobutene, which can be represented by the following formula, for example:



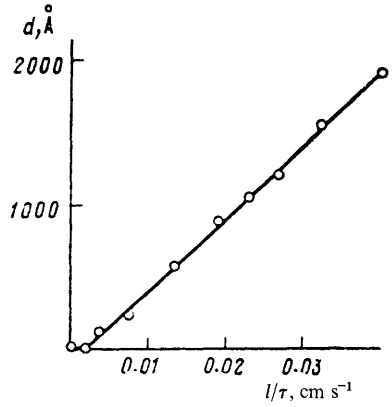


Figure 23. Flow velocity profile of a film of polyisobutene obtained on a metallic surface during the blow-off process.

It is seen from Fig.23 that the velocity profile is close to a linear one; a slip can be seen near the wall. The thickness of the residual film could not be measured. The measurements were performed on a steel plate.[28]

VI. THE STUDY OF THE BOUNDARY VISCOSITY OF VOLATILE LIQUIDS

A limitation of the blow-off method has been hitherto the impossibility of applying it to the study of the boundary viscosity of volatile substances. A modified blow-off method is applicable also to such liquids. In the course of the blowing off of volatile liquids, the film is attenuated also as a result of evaporation. The corresponding theory and method of calculation of the viscosity have been developed by Deryagin and Starov.[34] The viscosity calculations were performed on a computer from the ellipsometrically measured thicknesses of the blown off film at a distance of 2 cm from the initial wetting boundary as a function of time.

The apparatus with a rectangular insert on which the experiment was performed did not differ from the previous ones used to investigate the boundary viscosity by the blow-off method. Hexadecane ($C_{16}H_{34}$), an industrial product of chemically pure grade, was chosen as the test liquid. Specimens subjected to different degrees of chromatographic purification were also tested.

The experiment was performed as follows: a layer of liquid was deposited on the insert as before. Theinset was placed in the apparatus, having determined exactly the position of the wetting boundary, and a stream of air was passed through. The film thickness was determined as a function of time at a fixed site, at a distance l = 20 mm from the wetting boundary; the pressure drop was Δp = 0.0184 mmHg. The corresponding shear stress was 0.4 dyn cm^{-2}. The film thickness was measured as a function of time on an elipsometer using an LG-56 gas laser. Fig.24 presents plots of the dependence of the viscosity on the distance from the support obtained, from which it is seen that the viscosity is reduced in the range of thicknesses from 50 to 200 Å. The reproducibility of the curves in the range of thicknesses as far as 250 Å is complete in different experiments.[34]

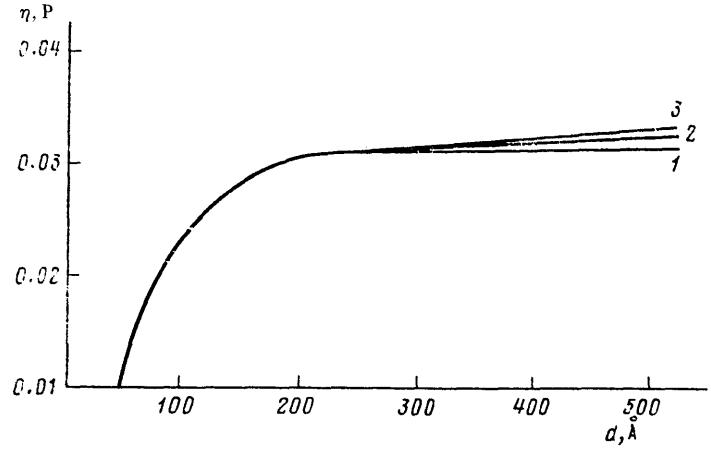


Figure 24. Dependence of the viscosity of hexadecane on the distance from the support.

§This substance was synthesised in A.D.Petrov's laboratory.

The decrease in viscosity which we observed can probably be accounted for by the usual slip of the horizontally oriented molecules. The hexadecane molecule consists of 14 methylene and 2 terminal methyl groups. In the immediate vicinity of the wall, one may expect only a horizontal orientation of the molecules because of their rigidity and fairly considerable length. The horizontal orientation is gradually enhanced as the support is approached owing to the increase in the influence of the force field of the latter.

The results of the application of the blow-off method described show that it provides a unique possibility for discovering the characteristic features of the structure of liquid layers modified under the influence of the adjoining surface of a solid phase, which is reflected by changes in viscosity. Specially rich information is provided by the application of the method to polymers and their solutions. The influence of the support on the structure of the boundary layers of the polymers and also on the stability of the wetting films is observed in this case to a strikingly greater depth, amounting to several micrometers.

Further expansion of the region where the method is applicable will become possible if the procedure can be improved in such a way that evaporation of even a highly volatile liquid can be eliminated during the blowing off of the layer.

REFERENCES

1. B.V.Deryagin, Uspekhi Khim., 1979, **48,** 675 [Russ.Chem.Rev., 1979(4)].
2. B.V.Deryagin and Z.M.Zorin, Dokl.Akad.Nauk SSSR, 1954, **98,** 93.
3. B.V.Deryagin and Z.M.Zorin, Zhur.Fiz.Khim., 1955, **29,** 1010.
4. B.V.Deryagin and Z.M.Zorin, Zhur.Fiz.Khim., 1955, **29,** 1755
5. B.V.Derjaguin and Z.M.Zorin, "II International Congress of Surface Activity", London, 1957, Vol.113, No.2, p.542.
6. N.V.Churaev, Kolloid.Zhur., 1984, **46,** 302.
7. N.V.Churaev and B.V.Derjaguin, J.Colloid and Interface Sci., 1985, **103,** 542.
8. B.V.Deryagin and Yu.M.Popovskii, Dokl.Akad.Nauk SSSR, 1964, **159,** 897.
9. B.V.Derjaguin, "Research in Surface Forces", Consultants Bureau, New York, 1966, Vol.2, p.3.
10. B.V.Deryagin, "Issledovaniya v Oblasti Poeverkhnostnykh Sil" (Studies in Surface Forces), Izd.Nauka, Moscow, 1964, p.3.
11. B.V.Deryagin and Yu.M.Popovskii, Dokl.Akad.Nauk SSSR, 1967, **175,** 385.
12. B.V.Deryagin, Yu.M.Popovskii, and G.I.Silenko, Dokl.Akad. Nauk SSSR, 1972, **207,** 1153.
13. B.V.Derjaguin, Pure and Appl.Chem., 1980, **52,** 1163.
14. B.V.Deryagin, Yu.M.Popovskii, and B.A.Altoiz, Dokl.Akad. Nauk SSSR, 1982, **262,** 853.
15. B.V.Deryagin and Yu.M.Popovskii, Kolloid.Zhur., 1982, **44,** 877.
16. B.V.Derjaguin, Yu.M.Popovskii, and B.A.Altoiz, J.Colloid and Interface Sci., 1983, **96,** 492.
17. Yu.M.Popovskii and B.A.Altoiz, "Poverkhnostnye Sily i Granichnye Sloi" (Surface Forces and Boundary Layers), Izd.Nauka, Moscow, 1983, p.131.
18. B.V.Derjaguin, "Colloid Fluid Interface Phenomena" (Edited by R.Croxton), Wiley, 1986, 739.
19. J.Traube and Siar-Hong-Wang, Z.phys.Chem., 1928, **138,** A102.
20. B.V.Deryagin and N.A.Krylov, "Soveshchanie po Vyazkosti Zhidkostei i Kolloidnykh Rastvorov" (Conference on the Viscosity of Liquids and Colloidal Solutions), Izd.Akad.Nauk SSSR, Moscow, 1944, Vol.2, p.52.
21. A.N.Somov and N.V.Churaev, Kolloid Zhur., 1982, **44,** 614.
22. G.Peschel and K.H.Adlfinger, Colloid and Polym.Sci., 1986, **254,** 1011.
23. B.V.Deryagin and M.M.Samygin, "Soveshchanie po Vyazkosti Zhidkostei i Kolloidnykh Rastvorov" (Conference on the Viscosity of Liquids and Colloidal Solutions), Izd.Akad.Nauk SSSR, Moscow, 1941, Vol.1, p.59.
24. B.V.Deryagin and M.M.Samygin, "Trudy Konferentsii po Treniyu i Iznosu v Mashinakh" (Proceedings of the Conference on Friction and Wear in Machines), Izd.Akad.Nauk SSSR, Moscow, 1941, Vol.11, p.871.
25. B.B.Derjaguin, G.M.Strakhovsky, and D.S.Malysheva, Acta Physicochimica URSS., 1944, **19,** 54.
26. B.V.Deryagin, G.M.Strakhovskii, and D.S.Malysheva, Zhur. Eksper.Teor.Fiz., 1946, **16,** 171.
27. B.V.Derjaguin, V.V.Karasev, and E.N.Khromova, J.Colloid and Interface Sci., 1978, **66,** 573.
28. B.V.Deryagin and V.V.Karasev, Kolloid Zhur., 1953, **15,** 365.
29. B.V.Deryagin and V.V.Karasev, Dokl.Akad.Nauk SSSR, 1955, **101,** 289.
30. V.V.Karasev and G.I.Izmailova, Zhur.Tekh.Fiz., 1954, **24,** 871.
31. B.V.Deryagin, Dokl.Akad.Nauk SSSR, 1943, **39,** 11.
32. B.V.Deryagin and A.S.Titievskaya, Dokl.Akad.Nauk SSSR, 1945, **50,** 307.
33. B.V.Deryagin and A.S.Titievskaya, Zhur.Eksper.Teor.Fiz., 1945, **15,** 119.
34. B.V.Deryagin, V.V.Karasev, V.M.Starov, and E.N.Khromova, Kolloid.Zhur., 1977, **39,** 664.
35. B.V.Deryagin, N.N.Zakhavaeva, S.V.Andreev, and A.N.Khomutov, Kolloid.Zhur., 1962, **24,** 289.
36. N.N.Zakhavaeva, B.V.Deryagin, A.N.Khomutov, and S.V.Andreev, "Issledovaniya v Oblasti Poverkhnostnykh Sil. Doklady II Konferentsii po Poverkhnostnym Silam" (Studies on Surface Forces. Reports at the IInd Conference on Surface Forces), Izd.Nauka, Moscow, 1964, p.173; "Research in Surface Forces", Consultants Bureau, New York, 1966, Vol.2, p.156.
37. B.V.Deryagin and N.N.Zakhavaeva, "Doklady VI Konferentsii po Vysokomolekulyarnym Soedinenyam" (Reports at the VIth Conference on Macromolecular Compounds), Izd.Akad.Nauk SSSR, Moscow–Leningrad, 1949, p.223.
38. B.V.Deryagin and N.V.Churaev "Smachivayushchie Plenki" (Wetting Films), Izd.Nauka, Moscow, 1984.
39. B.V.Deryagin and E.F.Pichugin, Dokl.Akad.Nauk SSSR, 1948, **63,** 53.
40. B.V.Deryagin and E.F.Pichugin, "Trudy II Vsesoyuznoi Konferentsii po Treniyu i Iznosu v Mashinakh" (Proceedings of the IInd All-Union Conference on Friction and Wear in Machines), 1947, Vol.1, p.103.
41. V.V.Karasev and B.V.Deryagin, Dokl.Akad.Nauk SSSR, 1948, **62,** 762.
42. B.V.Deryagin and V.B.Karasev, "Novye Metody Fiziko-khimicheskikh Issledovanii Poverkhnostnykh Yavlenii" (New Methods for Physicochemical Research into Surface Phenomena), Izd.Akad.Nauk SSSR, Moscow, 1950, No.1, p.53.
43. V.V.Karasev, Yu.M.Luzhnov, and N.V.Churaev, Zhur.Fiz. Khim., 1968, **52,** 558 [Russ.J.Phys.Chem., 1968(3)].

44. B.V.Deryagin, V.V.Karasev, Yu.M.Luzhnov et al., "Trudy Moskovskogo Instituta Inzhenerov Zheleznodorozhnogo Transporta" (Transactions of the Moscow Institute of Railway Transport Engineers), Moscow, 1973, No.445, p.115.
45. T.Tuzi and S.Oozima, Papers Inst.Phys. and Chem.Res., Tokyo, 1939, **36**(905), 72.
46. V.V.Karasev, Zhur.Tekh.Fiz., 1952, **22,** 616.
47. B.V.Deryagin, V.I.Gol'danskii, and V.V.Karasev, Dokl.Akad. Nauk SSSR, 1947, **57,** 697.
48. V.V.Karasev and B.V.Deryagin, Kolloid Zhur., 1953, **15,** 365.
49. B.V.Deryagin, V.V.Karasev, I.A.Lavygin et al., Dokl.Akad. Nauk SSSR, 1969, **187,** 846.
50. I.A.Lavygin and I.I.Skorokhodov, Vysokomol.Soed., 1976, **18,** 749.
51. B.V.Deryagin, V.V.Karasev, I.A.Lavygin, et al., "Makromolekuly na Granitse Razdela Faz" (Macromolecules at an Interface), Izd.Naukova Dumka, Kiev, 1971, p.139.
52. B.V.Derjaguin, V.V.Karasev, I.A.Lavygin, et al., Spec.Disc. Faraday Soc., 1970(1), 98.
53. B.V.Derjaguin, V.V.Karasev, I.A.Lavygin, et al., "Research in Surface Forces", Consultants Bureau, New York, 1969, Vol.4, p.227.
54. B.V.Derjaguin and V.V.Karasev, "International Congress of Surface Activity", 1957, Vol.3, p.531.
55. B.V.Deryagin, V.V.Karasev, I.A.Lavygin, et al., "Kompozitsionnye Materialy" (Composite Materials), 1981, No.10, p.51.
56. B.V.Deryagin, V.V.Karasev, I.A.Lavygin, et al., "Poverkhnostnye Sily i Ustoichivost' Kolloidov" (Surface Forces and the Stability of Colloids), Izd.Nauka, Moscow, 1974, p.25.
57. I.A.Lavygin, Vysokomol.Soed., 1976, **18A,** 426.
58. I.A.Lavygin, I.I.Skorokhodov, M.V.Sobolevskii, et al., Vysokomol.Soed., 1976, **18A,** 90.
59. H.W.Fox, P.W.Tabor, and W.A.Zisman, Ind.Eng.Chem., 1947, **39,** 1401.
60. R.Perkel and R.Ullman, J.Polym.Sci., 1961, **54,** 127.
61. K.A.Andrianov and N.N.Sokolov, Khim.Prom., 1955, 329.
62. D.C.Atkins, C.M.Murphy, and C.E.Saunders, Ind.Eng.Chem., 1947, **39,** 1395.
63. D.Delman, M.Landy, and B.Simms, J.Polym.Sci.A, 1969, **7,** 3375.
64. W.Bascom and C.R.Singleterry, J.Coll.Interf.Sci., 1978, **66,** 559.
65. V.V.Karasev and B.V.Deryagin, Zhur.Fiz.Khim., 1959, **33,** 100 [Russ.J.Phys.Chem., 1959(1)].
66. B.V.Derjaguin, V.V.Karasev, N.N.Zakhavaeva, and V.P.Lazarev, Wear, 1958, **1,** 277.
67. B.V.Deryagin, V.V.Karasev, N.N.Zakhavaeva, and V.P.Lazarev, Zhur.Tekh.Fiz., 1957, **27,** 1076.
68. B.V.Derjaguin, V.V.Karasev, and E.N.Chromova, J.Coll.Interf. Sci., 1978, **66,** 573.

Institute of Physical Chemistry,
USSR Academy of Sciences,
Moscow