

REVERSIBLE AND IRREVERSIBLE MODIFICATION OF THE PROPERTIES OF LIQUIDS UNDER THE INFLUENCE OF A LYOPHILIC SURFACE

B. V. DERJAGUIN

*Department of Surface Phenomena, Institute of Physical Chemistry,
Academy of Sciences, Moscow, U.S.S.R.*

ABSTRACT

A review is given of experimental evidence of changes of properties of boundary liquid layers under the action of the surface of a lyophilic substrate, of thermal expansion, specific heat and enthalpy, viscosity and yield value, molecular orientation and structure. It is demonstrated that in some cases the transition from boundary layers to the bulk of the liquid is discontinuous. The corresponding latent heat of transition is measured. Evidence is given of the reversible character of the modification of the properties of liquids under the action of surface forces. Another kind of surface effect is the phenomenon of irreversible, stable and strong modification on liquids on condensation of their vapour. The stable modification of water and the investigation of its properties are described, as also is the mechanism of the stable modification of water in bulk.

CONTACT with a foreign phase, solid or liquid, alters the properties of the boundary layers of liquids to a different depth and to a different extent depending on the nature of the phases and on the molecular nature of their interaction. In a number of cases, e.g. water on metals, or carbon tetrachloride on any substrate, the structure of the liquid does not change substantially, or changes (in the case of water) only within a layer of the order of a few molecules in thickness. In these cases the substrate is said to be lyophobic with respect to the liquid. In other cases, e.g. water-glass, water-quartz, fatty acids-metals, the substrate alters the structure of the liquid and the properties depending on it to a depth of many tens or hundreds of monolayers. The substrate is then lyophilic with respect to the liquid in question.

It is now possible to sum up some of the results of investigations of the changes caused by lyophilic substrates in the adjacent boundary layers of liquids. We shall discuss the results of an investigation of the mechanical, optical and thermal properties of liquid boundary layers by different methods.

1. RHEOLOGICAL PROPERTIES OF SURFACE LAYERS

Attempts to estimate the viscosity of boundary layers have been described in many papers. They are based mostly on observing the resistance of the liquid to flow through fine-pore partitions. Some of the results obtained

have shown unquestionably that in pores with cross sections of 10^{-5} cm and less some liquids display elevated viscosity. However, owing to the irregular geometrical shape of the pores, such observations can yield only semi-quantitative estimates of the average viscosity in pores of a given average radius.

A different approach is to compare viscosity measurements of a suspension with the values calculated theoretically (e.g. by the Einstein formula) under the assumption that the viscosity of the dispersion medium near the surface of the suspended particles does not change. In a number of cases the excess of the experimental viscosity values over the calculated values can be interpreted as the electroviscous effect, which is proportional to the square of the zeta-potential. However, usually only part of the effect can be accounted for in this way, and the rest of it has to be attributed to the specific boundary viscosity due to the structural peculiarities of the boundary layers.

This approach to the determination of the specific boundary viscosity, however, gives still less definite information, because, first, it does not permit the change in viscosity to be attributed to any definite thickness, giving mainly only the product $h\Delta\eta$, where $\Delta\eta$ is the excess of the viscosity above the bulk value, and h is the thickness of the boundary layers, which remains undetermined. Another shortcoming of the method is that the effect is the difference between two values: the experimental and the theoretical viscosities of the suspension. This difference is small for a dilute suspension. With a concentrated suspension, however, theoretical calculations become insufficiently reliable.

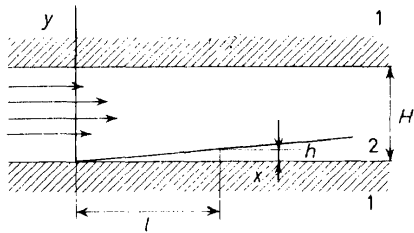


Figure 1. Diagram of the blow-off method.

The blow-off method of measuring the viscosity is the most direct and accurate method and is free from all these shortcomings¹. In this method a stream of air in a plane-parallel slit (Figure 1) sets up a uniform field of tangential (shear) stresses in a liquid layer (several microns thick) covering the part of the lower wall to the right of the wetting line lying at right angles to the direction of the stream. Since the stress field is uniform (due to the absence of volume forces), each liquid layer element moves as an integral whole parallel to the substrate at a velocity v depending on the distance from the substrate y :

$$v = v(y) \quad (1)$$

THE REVERSIBLE AND IRREVERSIBLE MODIFICATION OF LIQUIDS

The viscosity for such a simple unidimensional laminar flow can be found directly by the Newton formula

$$\eta \simeq \frac{T}{(dv/dy)} = T \left(\frac{dy}{dv} \right) \quad (2)$$

During the time of blow-off τ the liquid layer acquires the shape of a gently sloping wedge, the profile of which $x = x(h)$ where $x = v\tau$ represents the displacement of elementary layers during the time τ . Obviously, this profile differs from the velocity profile $v = v(y)$ only in the scale of the horizontal coordinate, by a factor of τ . Hence, having determined the profile of the film after blowing off, the viscosity distribution in the boundary layer can be found from the steepness of the profile according to the formula

$$\eta = T\tau(dh/dx) \quad (3)$$

In this formula T , the tangential stress, can be found if we know the pressure drop along the slit during blowing off and hence the method is absolute and requires no calibration. However, it can easily be verified by taking a liquid of known viscosity and applying formula 3 to distances at which the viscosity has the bulk value. This gives coincidence to one per cent. For this reason the blow-off method can also be used for absolute measurement of the viscosity of microquantities of liquid of the order of 10^{-4} cm^3 .

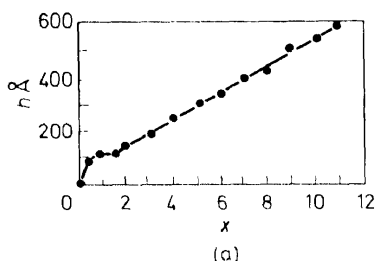


Figure 2(a). Velocity profile in boundary layers of amyl sebacinate.

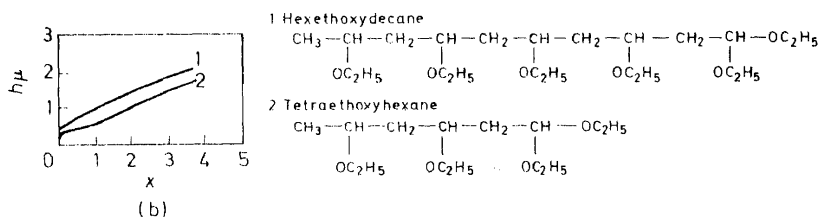


Figure 2(b). Velocity profile in boundary layers of hexaethoxydecane (1) and tetraethoxyhexane (2).

Figures 2 and 3 give the h versus x dependence for a number of organic liquids. Figure 2(a) shows that the viscosity of polar organic liquids sometimes changes jumpwise in the boundary layers at definite distances from the substrate¹. The viscosity may increase or decrease^{2, 3}. An especially sharp

drop is sometimes observed in the direct vicinity of the substrate. All these viscosity changes can be attributed to the specific, possibly oriented, structure of the boundary layers of the liquids. *Figure 3* is for vaseline oil thoroughly purified from polar impurities, and for a solution of amyl sebacinate in it. The linear nature of the curve indicates that the viscosity remains equal to the bulk value even at distances of the order of 10^8 Ångström units from the substrate². It also shows that possible deviations from ideal smoothness of the surface, in view of their smallness could not affect the boundary viscosity values obtained; hence the latter are insensitive to the surface microrelief of our substrates. Despite the very low concentration of amyl sebacinate, the latter has a very strong effect on the viscosity distribution in the boundary layer. As was shown earlier¹, stearic acid has a noticeable effect on the boundary viscosity even at concentrations below 10^{-4} per cent.

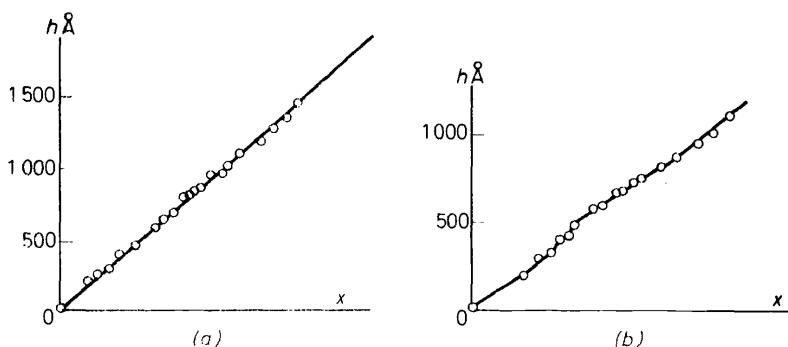


Figure 3. Velocity profiles in boundary layers of pure vaseline oil (a) and of a 0.006 per cent solution of amyl sebacinate in it (b).

It is stated in ref. 4 that such an effect should be attributed to monolayers absorbed at the solution/air surface. Actually this is quite impossible. First, the amount of molecules of organic compounds adsorbed at the air surface is small, and the more so at such low concentrations. Secondly, during blow-off the outer surface of the solution is so strongly extended (to the ratio x/h , i.e. to four or more decimal orders), that an explanation based on the presence of an adsorption layer is out of the question. Since the content of solute molecules in the bulk is also very low and can therefore not change the viscosity directly, the effect can be attributed to nothing but the influence of the monolayer of oriented polar molecules formed on the substrate upon the structure of the boundary layers. The existence of such an influence was assumed fairly long ago⁵, and has been confirmed in a number of other papers, e.g. Cameron⁶ (see also below). It may be accepted that the oriented monolayer is capable of causing a definite orientation of the molecules in the layer arranged just above it. According to the data of Cameron this effect is a maximum when the chain lengths of the adsorbate molecules are close to those of the solvent molecule. Horizontal orientation of the solvent molecules lowers the viscosity, and vertical orientation increases it.

THE REVERSIBLE AND IRREVERSIBLE MODIFICATION OF LIQUIDS

Recently the blow-off method was refined by V. V. Karasev in our laboratory by using a gas laser as the light source during ellipsometric thickness measurements⁷. The use of a laser makes it possible to decrease both the aperture ratio of the rays incident on the film, and the width of the illuminated area. This enables an increase in accuracy of 1–1.5 orders in determining the profile of the wedgelike film.

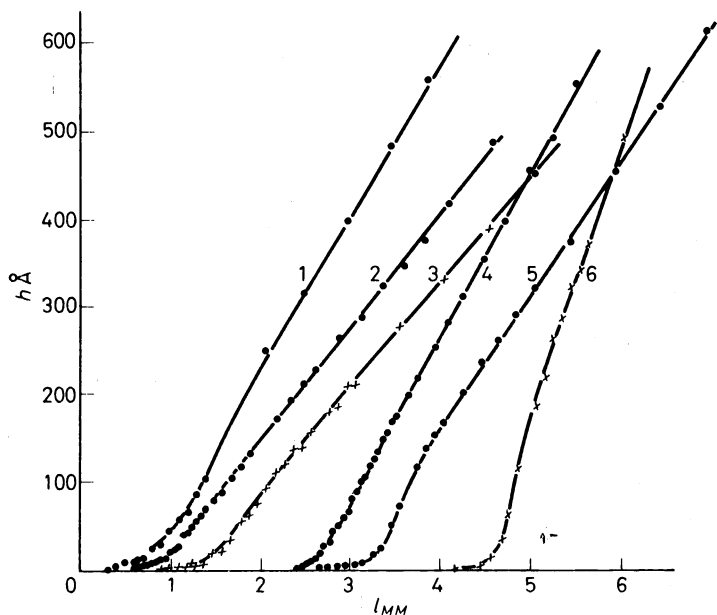


Figure 4. Blow-off profiles of polymethylsiloxanes: 1—PMS 5; 2—PMS 15; 3—PMS 25; 4—PMS 70; 5—PMS 400; 6—PMS 2 000.

The results of these measurements for some siloxane oligomers⁸ are shown in Figure 4. It can be seen that the viscosity is not constant, making it possible to obtain information as to the structural peculiarities of the boundary layers of these oligomers. The jumpwise viscosity changes indicate jumpwise changes in structure and suggest that the boundary phases are separated from the bulk phase by a sharp interface.

Unlike the 'surface phases' introduced purely formally into the thermodynamics of surface phenomena, boundary phases possess the main feature of a phase, namely, they have a sharp interface, and possibly violate the condition of uniformity to the same extent as ordinary phases in an external force field. The difference is that with boundary phases the role of the external force field is played by the molecular-surface forces extending from the substrate. Related to this difference is also the main inherent difference, namely, that the thickness of the boundary phase is not arbitrary, as in the case of ordinary phases, but is a definite function of the temperature. We shall return to this dependence in the following with reference to the boundary phases of nitrobenzene. Sometimes the thickness of the boundary phase may

be just the thickness of an oriented monolayer, a case which is often regarded as typical, though without sufficient grounds.

There are experimental data which can make it necessary to assume that there may be two boundary phases arranged one above the other, the oriented monolayer sometimes, possibly, playing the part of the lower one. Finally, a sort of polymorphism of boundary phases has been observed, for example, by Zorin with benzene on mercury, where islands of one boundary phase of one thickness (≈ 220 Å) coexist in equilibrium with a boundary phase of another thickness (≈ 70 Å). Obviously, these two phases should differ in structure⁹.

Owing to technical difficulties the blow-off method has not been used so far for water and other volatile liquids. However, the viscosity of water was shown to increase near hydrophilic surfaces in a number of other experiments. Of the most recent and convincing of these we may mention measurements of the coefficient of diffusion in water in the pores of a silica gel. The coefficient of diffusion was found to decrease several fold, indicating that the viscosity increases accordingly¹⁰.

Mention is often made of solid or quasi-solid boundary layers of liquids. Measurements by the blow-off method or measurements of diffusion coefficients do not support these assumptions, because they detect only a several-fold increase of viscosity. However, this question appears to be more complicated. In a study by Bazarov, Bulgadaye and myself¹¹, in which oscillating piezoquartz was used as the substrate, it was found that at vibration frequencies of 7×10^4 Hz all liquids, even with low viscosities, display an elasticity of form characterized by an exactly measurable shear modulus of the order of 10^4 dyne cm^{-2} and more. However, the loss angle was sufficiently high, of the order of 10° to 30° . It was found that on approaching a lyophilic substrate (quartz) the shear modulus of polar liquids such as water increases by more than an order of magnitude. Thus, instead of asserting that the boundary layers of liquids are solid, we should rather speak of higher shear modulus values compared to the bulk and possibly of lower loss angles.

This elevated shear modulus value was measured much earlier for water by the present author using a different method¹² at a frequency of the order of 1 to 10 Hz. However, this method was useless for detecting a shear modulus at distances greater than 1000 Å.

Measurements of the shear modulus of liquids with a considerable loss angle do not solve the question of the value and of the very existence of shear strength (yield value). It was shown in papers by N. F. Bondarenko and S. V. Nerpin¹³ that liquids and liquid mixtures with hydrogen bridges between their molecules in quartz capillaries up to 0.2 mm in diameter show deviations from Poiseuille's law at low pressure gradients, and are not only non-Newtonian liquids, but also possess a yield value of the order of 10^{-2} dyne/ cm^2 . The yield value decreases rapidly with rising temperature. However, its value in the boundary layers was found to be several orders higher. This was shown by observation of electroosmosis at elevated potential gradients¹⁴.

With low fields the slip plane remains unchanged and the zeta-potential calculated by classical formulas is constant. However, when the intensity of the external electric field passes through a certain critical value calculated from the velocity of electroosmosis, the ζ -potential increases sharply. Since

the structure of the double layer due to the external field could not have changed substantially under the conditions of the experiment, the increase in ζ -potential can be attributed only to the slip plane shifting closer to the solid wall of each pore. Obviously such a shift becomes possible when the shear stress due to the action of the applied field on the outer part of the ionic atmosphere outweighs the yield value in the region of the boundary layer between the old and new positions of the slip plane. This gives a yield value in the boundary layer of water of the order of 10 dyne/cm², which is three orders higher than its bulk value.

2. STRUCTURAL PECULIARITIES OF BOUNDARY LAYERS

Another property of liquids which is also very sensitive to structure, is their heat conductivity. This value is known to grow sharply on crystallization of the liquid. Metsik showed that the heat conductivity of water films held between sheets of mica in the direction parallel to the sheet planes increases by dozens of times if the thickness is decreased to 0.3 micron or less¹⁵ (see Figure 5). This elevated heat conductivity effect disappears at temperatures above 60°, or if the mica surfaces are coated with adsorption monolayers of organic molecules. The effect is also observed with other polar liquids (e.g. alcohol) but is not observed for carbon tetrachloride.

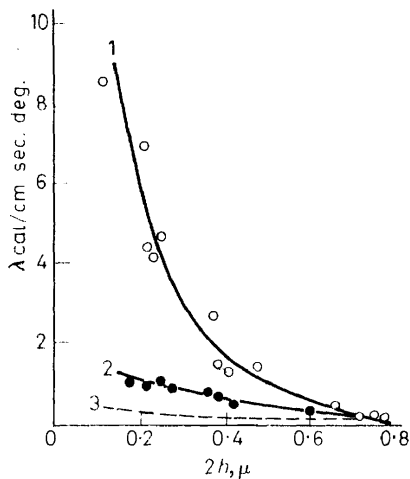


Figure 5. Heat conductivity of liquid layers between mica sheets as a function of the layer thickness $2h$: 1—water films; 2—ditto after treatment of mica in boiling water; 3—glycerol films.

The only explanation for all this is that fresh mica cleavage surfaces give rise to a more regular, evidently oriented structure in the adjacent boundary layers of water. In the case of water the change in structure has a sharp influence on the characteristic course of its thermal expansion. Fedyaikin¹⁶ demonstrated that in glass capillaries of radius less than 300 Å water expands within the interval -10° to $+40^{\circ}$ with a constant coefficient of expansion, not exhibiting even a trace of the volume minimum at 4°C (see Figure 6). Similar

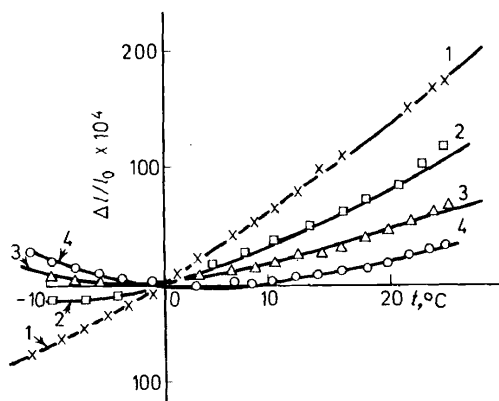


Figure 6. Temperature dependence of elongation of water columns: 1—for $r = 0.02\mu$; 2—for $r = 0.08\mu$; 3—for $r = 0.19\mu$; 4—for bulk water.

results were obtained by Karasev and myself¹⁷ for water in aerosil pores (see Figure 7).

That the effect is not due to contaminations of any kind follows from the fact that after extraction from the aerosil pores the water shows the normal course of thermal expansion characteristic of water in bulk. Since the thermal expansion anomaly of water is due to its loose structure caused by the hydrogen bridges between its molecules, the disappearance of this structure in narrow pores is an indication of a denser structure with a smaller number of hydrogen bonds. The hypothesis of an ice-like structure cannot account for the high coefficient of expansion of water in capillaries.

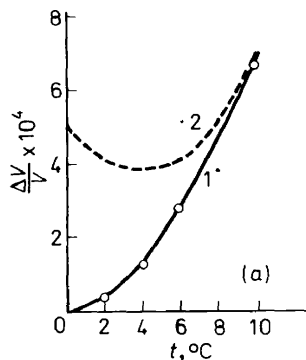


Figure 7(a). Thermal expansion of water in aerosil pores.

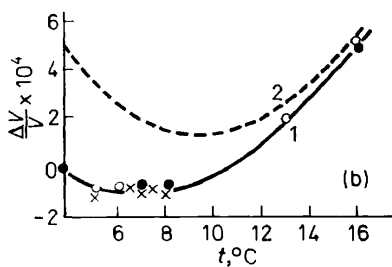


Figure 7(b). Thermal expansion of heavy water in aerosil pores.

3. BOUNDARY PHASES

The existence of 'boundary phases' detected by the blow-off method poses the problem of determining their thermodynamic parameters, primarily

THE REVERSIBLE AND IRREVERSIBLE MODIFICATION OF LIQUIDS

the heat of the phase transition to the bulk. The specific features of this problem are related to the fundamental difference of boundary phases from ordinary ones: it consists in the former having a quite definite thickness which changes only as a function of the temperature. Therefore, no isothermal phase transition is possible with them, and the specific latent heat of this transition λ should be determined by a scheme expressed by the equation

$$Q^* = (M - m_0) c_2 + m_0 c_1 + \lambda(dm_0/dT) \quad (4)$$

where Q^* is the apparent specific heat of a two-phase film consisting of a bulk phase of mass m_0 and a boundary phase of mass $M - m_0$; c_1 and c_2 are the specific heats in the bulk and in the boundary layer, respectively, these quantities being functions of the temperature T .

The problem stated was solved for wetting films of nitrobenzene enveloping particles of a glass or fused quartz powder at uniform thickness¹⁸. This choice was due to the fact that non-additivity of the specific heats of both phases was detected precisely for nitrobenzene-glass powder systems, indicating that the specific heat of nitrobenzene boundary layers changes considerably under the influence of surface forces. The powder was first purified in a glow discharge (without which no change in specific heat of the nitrobenzene boundary layers was observed compared to its bulk value). By means of a special technique the surface of the particles was coated with an even layer of nitrobenzene of the order of 10^{-5} cm thick. The specific surface area of the powder being of the order of $1 \text{ m}^2/\text{g}$, the proportion of nitrobenzene in the 'cuffs' around the points of contact between the particles of the powder was small.

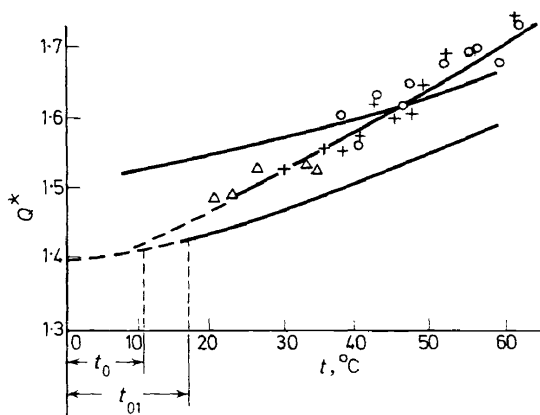


Figure 8. Apparent specific heat of two-phase nitrobenzene film 94 μ thick as a function of the temperature.

Calorimetric measurements revealed that the specific heat of films of thickness less than a certain value h_c , which is a function of the temperature, is approximately 20 per cent smaller than the bulk value and independent of the thickness, in agreement with equation 4. The existence of a heat of transition of the boundary phase into the bulk is evident from Figure 8 where the

apparent specific heat is plotted against temperature for a film $h = 94$ μ thick. The lower curve is the specific heat of the boundary phase and the upper one is that of the bulk phase. The intersection of the curve of the apparent specific heat with that of the bulk specific heat cannot be interpreted without taking into account the last term in formula 4.

Denoting by Q_2 the specific heat of the nitrobenzene film entirely in the boundary phase state

$$Q_2 = Mc_2 \quad (5)$$

and making use of Kirchhoff's equation

$$d\lambda/dT = c_1 - c_2 \quad (6)$$

we reduce equation 4 to the form

$$d(m_0\lambda)/dT = Q^* - Q_2 \quad (7)$$

Integrating equation 4, one gets

$$m_0\lambda = \int_{T_0}^T (Q^* - Q_2) dT \quad (8)$$

where T_0 is a certain temperature of homogenization, on cooling to which

$$m_0 = 0 \quad (9)$$

i.e. the last layer of the bulk phase disappears and the entire film is in the state of a boundary phase of thickness h_c .

The homogenization temperature was always found assuming the nitrobenzene films to be in the two-phase state and while lowering the temperature, because when a single-phase boundary film is heated formation of the bulk phase is retarded and the film becomes overheated and passes into a metastable state. On cooling, this phenomenon naturally does not occur. However, the jump of the apparent specific heat due to disappearance of the term $\lambda(dm_0/dT)$ on reaching the homogenization temperature does cause some difficulty in the method. The effect of this on the experimental determination of the homogenization temperature can be eliminated by the following approximation.

Since the thickness of the nitrobenzene film becomes exactly equal to the equilibrium thickness of the boundary phase h_c at the temperature of homogenization (at a higher temperature $h_c < h$), both h_c and m_0 can be found for the corresponding T values by determining T_0 for various values of h . Owing to certain experimental difficulties and inconveniences this procedure was not employed for obtaining the h_c versus T dependence over the entire temperature range of interest, but only to obtain three 'base' values of $h_c(T)$ for three values[†] of T : $T_1 = 0.3^\circ$, $T_2 = 7.2^\circ$ and $T_3 = 23.7^\circ\text{C}$.

Applying formula 8 to the temperature intervals $T_0 = T_1$, $T = T_2$ and

[†] The temperature 0.3°C is below the melting point of bulk nitrobenzene (5.8°C). The possibility of two-phase existence of nitrobenzene films within the temperature interval 0.3° to 5.8° is due to the supercooled state of these films.

THE REVERSIBLE AND IRREVERSIBLE MODIFICATION OF LIQUIDS

$T_0 = T_2$, $T = T_3$, we were able to obtain two 'base' values of λ , corresponding to the temperatures T_2 and T_3 . These base values of λ were employed for determining λ as a function of temperature by integrating formula 6. The resulting curve is shown in *Figure 9* together with the 'base' values of λ which simultaneously demonstrate the possible error of their determination. Similarly, knowing $\lambda(T)$, we determine $m_0(T)$ from formula 8.

After this the thickness of the boundary phase could be calculated as a function of temperature from the formula

$$h_c = (M - m_0)/\rho S \quad (10)$$

where ρ is the density of nitrobenzene, and S is the total surface area of its layer on the powder. Substituting the results of experiments with three different film thicknesses $h_1 = 106 \text{ m}\mu$, $h_2 = 94 \text{ m}\mu$ and $h_3 = 90 \text{ m}\mu$ (equal to the three 'base values' of h_c) into formula 8 we obtained three versions of

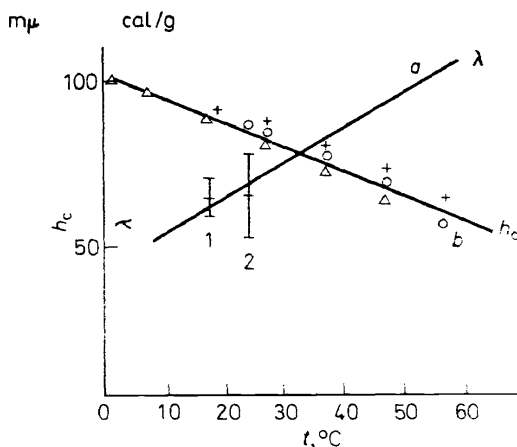


Figure 9(a). Specific heat λ of transition of nitrobenzene boundary phase to the bulk phase (1 and 2—base values of λ) as functions of the temperature. (b) Equilibrium thickness of nitrobenzene boundary layer as a function of the temperature according to experiments with different film thicknesses: $\triangle\triangle\triangle$ $h = 106 \text{ m}\mu$; $++$ $h = 94 \text{ m}\mu$ $\circ\circ$ $h = 90 \text{ m}\mu$.

calculated h_c versus T dependences. Since they were very close to each other, only one curve is shown in *Figure 9*, this being an average $h_c(T)$ curve with the three base values of h_c . The position of the latter confirms the agreement between the results obtained[†]. The possible discrepancies are much smaller than the absolute values of h_c .

It is noteworthy that such a high accuracy of determination of the boundary phase thickness could be obtained on the basis of purely calorimetric determinations. Taking into account the possibly not very large difference between the refractive indices of nitrobenzene in the bulk and in the boundary layers, it would seem very difficult to solve the same problem optically[‡].

[†] The linear drop of h_c with T is in agreement with the results of G. I. Fuks's paper¹⁹.

[‡] The birefringence in the thin liquid layers which form during the intracrystalline swelling of montmorillonite, however, was found to be measurable²⁰.

Recently the difference between the structure of the boundary layers of a liquid near a lyophilic surface and its structure in the bulk was confirmed by using the method of nuclear magnetic resonance²¹.

All the above can be summed up as the ability of boundary layers of liquids situated within the radius of action of surface forces of the adjacent phase to change their structure and properties, i.e. to become 'modified'. There are grounds for assuming that these changes are reversible, i.e. that if the layers are removed to a sufficient distance from the phase interface they recover their normal properties. This can sometimes be proved directly by experiment. For example, according to Karasev¹⁷ water extracted from aerosil pores recovered its usual course of thermal expansion with a volume minimum at 4°C. After passing through the capillaries of a glass filter a liquid has the same parameters as before passing through it. After desorption the vapours of a liquid have the same properties as before adsorption.

Special note should be made of the observation of Bangham and co-workers²² of thick, evidently metastable wetting layers of liquids formed by condensation of water, methyl alcohol or other vapours on the fresh cleavage surfaces of mica. The behaviour of drops of the same liquids placed on these layers shows that the structure and properties of the latter differ greatly from the normal properties of the same liquid in bulk, which is very surprising since their thickness is of the order of microns. However, it was not proved that the peculiarities acquired by the condensate layers could persist after they were removed from the substrate, e.g. by distillation. Nobody can object to the assumption that these layers are boundary phases in a metastable state at which their thickness is larger than the equilibrium thickness, an example of this being the nitrobenzene layers in Popovsky's experiments.

4. IRREVERSIBLE MODIFICATION OF THE PROPERTIES OF A LIQUID ON CONDENSATION OF ITS VAPOURS ON A LYOPHILIC SURFACE

Of a considerably different quite unambiguous nature of irreversible changes is the phenomenon of condensational modification observed during the condensation in glass and quartz capillaries of water, methyl alcohol and acetic acid vapours²³. It was shown that under definite conditions of condensation liquid columns appear with a reduced vapour pressure and an elevated viscosity. It was at first assumed that the anomalous columns differed from normal ones only in molecular arrangement. However, further investigation of this phenomenon in water made it necessary to revise this assumption.

It was found that evaporation accompanied by shortening of the column increases the deviation from the normal state, the viscosity increasing and the equilibrium vapour pressure decreasing to an extremely low value if evaporation is continued for a sufficient length of time. At the same time the column reaches a limiting length which can be further reduced substantially only by raising the temperature above 200°C; up to this temperature the column contracts only slightly, unless evaporation is carried on for many hours. The state attained after prolonged evaporation was called the ultimate anomalous state.

THE REVERSIBLE AND IRREVERSIBLE MODIFICATION OF LIQUIDS

On the other hand, if the anomalous column is diluted with molecules of ordinary water by condensing vapours of the latter on its menisci, or by contact with it, the degree of anomalousness falls off, tending to zero at the limit. This behaviour shows that anomalous water is a solution of the low-volatile component in ordinary water. This conclusion also follows unambiguously from the fact that anomalous water separates into two phases at negative Celsius temperatures. It follows from the phase rule that the system is therefore a two component one. It would be more accurate to call it a quasi-two-component system after Tamman who observed similar behaviour in the system acetaldehyde–paraldehyde, which is chemically a single-component system.

The stability of the anomalous component follows primarily from the fact that evaporation of anomalous water at 300°–400°C and recondensation at the other end of the capillary or in a different capillary does not change the degree of anomalousness.

At first we called the result of phase separation a 'water-in-water emulsion'. Later, detailed observations showed that the drops of this emulsion are actually tiny crystals, evidently of ice. The dispersion medium possesses properties very close to those of the ultimate anomalous state. It does not follow, however, that at a low temperature the system separated completely into two components as a result of the evolution of ice crystals—phase β . It is quite possible that the second, α phase included monomeric water molecules interacting with the polymeric complexes with a bond energy less strong than the bond energy connecting the molecules inside the complexes. This makes it difficult to determine the molecular weight of the anomalous component by the lowering of the vapour pressure and the end melting point of anomalous water. Such determinations made without allowance for possible 'hydration' of polymeric complexes may give too high values for the molecular weight of the latter.

The two-component behaviour of anomalous water gives rise to quite a natural temptation to attribute its appearance and properties to the presence of impurities which volatilize at temperatures above 300°C. Suspicion falls on contamination by water-soluble organic substances. However, this hypothesis is refuted by surface tension measurements of anomalous water carried out by us²⁴. Figure 10 shows the surface tension of anomalous water as a function of the concentration of the anomalous component (calculated proceeding from the mass of the ultimately anomalous residue). Such a

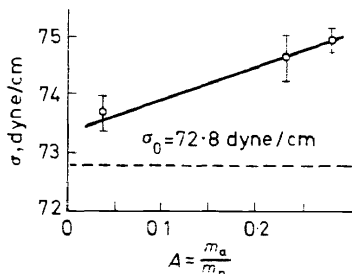


Figure 10. Surface tension of anomalous water vs. concentration of anomalous component A.

substantial rise in surface tension cannot be attributed to organic contaminations, which may either lower σ down to values several times smaller than the tabulated values for water, or, in the case of surface inactivity, hardly change σ at all.

This increased value of σ was measured for anomalous water samples obtained in an apparatus developed by Karasev²⁵ and shown in *Figure 11*. Here the left-hand part of the Pyrex chamber, maintained at temperature T_1 , is separated by a thin glass partition from the right-hand part which is kept at a temperature $T_2 < T_1$. Very pure doubly distilled water of electrical

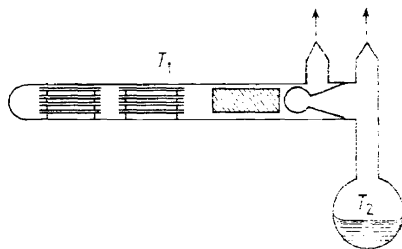


Figure 11. All-fused chamber for production of anomalous water.

conductivity 6×10^{-7} and containing less than 5×10^{-9} mole/litre of organic compounds is placed in the right-hand part and degassed, after which it is frozen and evacuated. Then this part is sealed off from the vacuum line and brought to the temperature T_2 . The left-hand part of the chamber is charged with sets (100 to 300) of freshly drawn quartz capillaries and is then kept at a temperature of 400°C while being evacuated continuously through two liquid nitrogen traps for 48 hours, after which it is cooled. Then the partition is broken by means of a magnetically controlled striker, causing the water vapour to fill the left-hand part, where the anomalous columns form.

I also think it impossible to attribute the rise in surface tension of anomalous water, as well as its other remarkable properties, to the presence of electrolytes. Electroconductivity measurements showed that even in ordinary glass capillaries the electrolyte content in the anomalous water columns is two orders lower than is necessary to account for its properties, e.g. for its density of 1.4, its refractive index of 1.49, and its sharply reduced vapour pressure and lowered melting point. It is all the more impossible to admit the influence of electrolytes when the anomalous columns are produced in freshly drawn quartz capillaries in a chamber without ground joints or cocks after prolonged 48-hour vacuum conditioning while being heated at 400°C .

That even ultimately anomalous columns consist mainly of water is also confirmed by the fact that if its vapours are passed through a heat barrier—a widening in a capillary where the temperature is maintained at 800°C —the condensed product is normal water in an amount corresponding to the mass of the initial column (taking into account absorption of water molecules by the capillary walls in the high-temperature zone).

Another point favouring the impossibility of attributing the anomalous properties to accidental contaminations is that the ratio $\Delta T/A$, ΔT being

the lowering of the melting point, and *A*, the content of the anomalous component, remains constant within the limits of random errors of measurement for samples of water obtained under a great variety of conditions, even for those obtained in less 'sterile' apparatuses having joints and cocks, in which the capillary walls were not free from minor organic contaminations.

In summing up it may be said that the aggregate of experimental facts gives evidence that the condensation of water vapours on glass and fused quartz surfaces gives rise to a new form of water with physical properties, starting with its density which may be as high as 1.4, sharply differing from those of normal water†.

ACKNOWLEDGEMENTS

The author expresses his gratitude to Academician V. I. Spitsin, Director of the Institute of Physical Chemistry of the USSR Academy of Sciences, for his assistance and support in carrying out this work and his interest in it.

REFERENCES

- ¹ B. V. Derjaguin and V. V. Karasev, *Kolloidzshr.* **15**, 365 (1953); *Dokl. Akad. Nauk S.S.S.R.* **101**, 289 (1955); *Proceedings of the Second International Congress of Surface Activity*, Vol. III, p 531 (1957); *Wear* **1**, 277 (1958); *Zh. Fiz. Khim.* **33**, 100 (1959).
- ² N. N. Zakhavayeva, B. V. Derjaguin, A. M. Khomutov and S. V. Andreyev, in *Research in the Field of Surface Forces*, Vol. II, p 173. U.S.S.R. Academy of Science Press: Moscow (1964); Consultants Bureau, New York (1966).
- ³ B. V. Derjaguin, N. N. Zakhavayeva, S. V. Andreev and A. M. Khomutov, *Colloid Jnl, Moscow*, **24** No. 3, 289 (1962).
- ⁴ A. T. Hayward and J. D. Isdale, *Brit. J. Appl. Phys. Sect. 2*, **2**, 251 (1969).
- ⁵ B. V. Derjaguin, *Miner. Syrye (Moscow)*, **2**, 33 (1934).
- ⁶ R. F. Crouch and A. Cameron, *Nature, Lond.* **198**, 475 (1963).
- ⁷ T. C. Askwith, A. Cameron and R. F. Crouch, *Proc. Roy. Soc. A*, **291**, 500 (1966).
- ⁸ V. V. Karasev, Ju. M. Loughnov and N. V. Churaev, *Zh. Fiz. Khim.* **42**, 558 (1968).
- ⁹ V. V. Karasev, B. V. Derjaguin, I. A. Lavygin, I. I. Skorochodov and E. N. Chromova, *Dokl. Akad. Nauk S.S.S.R.*, **187**, N4 (1969).
- ¹⁰ Z. M. Zorin, in *Research in the Field of Surface Forces*, Vol. II, p 146. See ref. 2.
- ¹¹ Z. M. Tovbina, in *Research in the Field of Surface Forces*, Vol. III, p 24 (1967); Plenum: New York (1970).
- ¹² U. B. Bazaron, B. V. Derjaguin and A. V. Bulgadaev, *J. Exp. Theor. Phys.* **51** (No. 10), 970 (1966).
- ¹³ B. V. Derjaguin, *Z. Phys.* **84** (Nos. 9-10), 657 (1933).
- ¹⁴ N. F. Bondarenko and S. V. Nerpin, in *Research in the Field of Surface Forces*, Vol. III, p 401 (1967), See ref. 10.
- ¹⁵ N. F. Bondarenko and S. V. Nerpin, *Dokl. Akad. Nauk S.S.S.R.* **168**, 368 (1966).
- ¹⁶ M. S. Metsik and G. T. Timoschenko, in *Research in the Field of Surface Forces*, Vol. III, p 41, See ref. 10.
- ¹⁷ N. N. Fedyakin, *Dokl. Akad. Nauk S.S.S.R.* **138** (No. 6), 1389 (1961).
- ¹⁸ V. V. Karasev, B. V. Derjaguin and E. N. Chromova, in *Research in the Field of Surface Forces*, Vol. III, p 31, see ref. 10.
- ¹⁹ B. V. Derjaguin and Ju. M. Popovsky, *Dokl. Akad. Nauk, S.S.S.R.*, **175** (No. 3), 549 (1967).
- ²⁰ G. I. Fuks, *Colloid Jnl, Moscow*, **20**, 748 (1958).
- ²¹ B. V. Derjaguin and R. Green-Kelly, *Trans. Faraday Soc.* **60**, 449 (1964).

† The difference between infra-red and Raman spectra was shown in ref. 26. The same paper confirms the main results of our investigations, particularly, the persistence of anomalousness on distillation. See also ref. 27.

B. V. DERJAGUIN

- ²¹ G. A. Johnson, S. M. Lecchini, E. G. Smith, J. Clifford and B. A. Pethica, *Disc. Faraday Soc.* **42**, 120 (1966).
- ²² D. M. Bangham and Z. Saweris, *Trans. Faraday Soc.* **34**, 554 (1938).
- ²³ B. V. Derjaguin and N. N. Fedyakin, *Dokl. Akad. Nauk S.S.S.R.* **147**, 403-406 (1962); B. V. Derjaguin, M. V. Talaev and N. N. Fedyakin, *Dokl. Akad. Nauk S.S.S.R.*, **165**, 597-600 (1965); N. N. Fedyakin, B. V. Derjaguin, A. V. Novikova and M. V. Talaev, *Dokl. Akad. Nauk S.S.S.R.*, **165**, 878-881 (1965); B. V. Derjaguin, I. G. Ershova, B. V. Zheleznyi and N. V. Churaev, *Dokl. Akad. Nauk S.S.S.R.*, **170**, 876-879 (1966); B. V. Derjaguin, N. N. Fedyakin and M. V. Talaev, *J. Coll. Interfac. Sci.* **24**, 132-133 (1967); B. I. Anisimova, B. V. Derjaguin, I. G. Ershova, D. S. Litsnikov, Ja. I. Rabinovich, V. K. Simonova and N. V. Churaev, *Zh. Fiz. Khim.* **41**, 2377-2379 (1967); B. V. Derjaguin, N. V. Churaev, N. N. Fedyakin, M. V. Talaev and I. G. Ershova, *Izvest. Akad. Nauk S.S.S.R., Ser. Khim.*, **10**, 2178-2187 (1967); B. V. Derjaguin, Z. M. Zorin and N. V. Churaev, *Colloid Jnl, Moscow*, **30**, 308-309 (1968); B. V. Derjaguin, I. G. Ershova, V. K. Simonova and N. V. Churaev, *Zh. Teor. Eksp. Khim.* **4**, 527-533, N8 (1968); B. V. Derjaguin, D. S. Lychnikov, K. M. Merzhanov, Ya. I. Rabinovich and N. V. Churaev, *Dokl. Akad. Nauk S.S.S.R.*, **181**, 823 (1968); B. V. Derjaguin, N. V. Churaev and I. G. Ershova, *Dokl. Akad. Nauk S.S.S.R.*, **182**, 368-372 (1968); B. V. Derjaguin, Z. M. Zorin and N. V. Churaev, *Dokl. Akad. Nauk S.S.S.R.*, **182**, 811-815 (1968); B. V. Derjaguin and N. N. Fedyakin, *Dokl. Akad. Nauk S.S.S.R.*, **182**, 1300-1302 (1968); B. V. Derjaguin and N. V. Churaev, *J. Coll. Interfac. Sci.* (November 1970).
- ²⁴ B. V. Derjaguin, Z. M. Zorin, V. V. Karasev and N. V. Churaev, *Dokl. Akad. Nauk S.S.S.R.*, **186**, 1 (1969).
- ²⁵ V. V. Karasev and Ju. M. Loughnov, *Zh. Fiz. Khim.* **42**, 2 (1968).
- ²⁶ L. J. Bellamy, A. R. Osborn, E. R. Lippincott and A. R. Bandy, *Chem. & Ind.* p 686 (24 May 1969); E. R. Lippincott, R. R. Stromberg, W. H. Grant and G. L. Cessac, *Science*, **164**, 1482 (1969).
- ²⁷ B. A. Pethica, *Nature, Lond.* **222**, 159 (1969).