RECENT RESEARCH INTO THE PROPERTIES OF WATER IN THIN FILMS AND IN MICROCAPILLARIES

By B. V. DERJAGUIN

Laboratory of Surface Phenomena, Institute of Physical Chemistry, Academy of Sciences of the U.S.S.R.

Evidence has long since been put forward proving that the properties of polymolecular boundary layers of water and other liquids near their interfaces with other phases differ from those in the bulk of the same liquid. A review of the older literature on this question was published by Henniker (1949). However, the available experimental data are contradictory and many of them are unreliable. A discussion of recent data should therefore be of interest.

The behaviour of the boundary layers of water may exhibit peculiarities because of the van der Waals forces acting in them. Their action becomes appreciable when we have a thin layer of liquid in which the spheres of action of the van der Waals forces at the two surfaces of the thin layer overlap. In this case a force arises which always (if the phases on either side of it are identical) tends to make the liquid layer thinner.

Another well-studied factor influencing the behaviour of boundary and thin liquid layers is the diffuse double ionic layer which gives rise to electrostatic forces. However, neither of these factors—the van der Waals forces which, approximately, diminish with the cube of the distance from the interface, and the electrostatic forces in the diffuse double layer—are evidently strong enough to account for a number of peculiarities in the behaviour of boundary layers. At the same time, these peculiarities are an indication of the existence of structural changes in the boundary layers. We shall assume such structural peculiarities as a working hypothesis in accounting for the new experimental material, which, in its turn, may be regarded as a proof of the existence of these peculiarities.

These new experimental facts are of special interest because the peculiarities detected in the behaviour of boundary and thin water layers may play a substantial part in the equilibrium and movement of water in plant and animal tissues.

One of the most sensitive properties with respect to changes in structure is viscosity. According to the measurements of N. N. Zakhavayeva and the present author (Derjaguin, Zakhavayeva & Lopatina (1961) the rate of

filtration of water through finely ground quartz sand having a specific surface area of 10 m.^{3} g.$^{-1}$ is about three times smaller than can be calculated by the Kozeny–Carman formula based on the bulk viscosity value for water. Thus, the viscosity of water in interlayers about 10^{-6} cm. thick exceeds the bulk value by three times. With increasing concentration of dissolved salts the boundary viscosity changes, approaching the bulk value of 0·01 only at high concentrations of the order of 0·5 N. If the increased viscosity were a result of the electroviscosity effects related to the existence of the double electric layer, the 'normal' rate of filtration would be reached at much lower electrolyte concentrations, when these are sufficient to cause compression of the double layers, especially in the case of ions with high charges. It is difficult to account for the increased viscosities in thin water layers otherwise than by their specific structure.

M. S. Metsik's investigation (1964) of the heat conductivity of stacks of mica sheets about 10 μ thick with interlayers of water of different thickness between them, suggest the same conclusion. His results show that the average heat conductivity of the water interlayers increases as their thickness decreases, reaching values at thicknesses of the order of 0·1 μ, several dozen times higher than the tabulated value for the heat conductivity of water. As the heat conductivity of bodies possessing a regular crystal structure is higher, as a rule, we thus have the right to assert that the water near the mica surface has a more regular structure than in the bulk. The difference in structure of the boundary layers of water should give rise to differences in dielectric properties as well. Of interest among recent data are Zhilenkov's studies (1963) of the dielectric properties of water sorbed in a silica gel. In particular, it was shown that the static value of the dielectric permeability of the adsorbed layers, starting from the second monolayer, equals 8–10 and does not change on further thickening up to 10 or 20 layers. Such a low value of the dielectric permeability is evidence of the small contribution of the orientation effect, which is impossible unless the structure of the water undergoes a change accompanied by a decrease in the freedom of rotation of its molecules. It should be noted that no such changes in dielectric permeability are observed for the boundary layers of water at the interface with metals. This may be assumed to be due to the specific structure of the boundary water layers appearing as a result of interaction, say, through the hydrogen bond with the surface hydroxyl groups of the hydrophilic surface.

Direct proof of the specific and, furthermore, anisotropic structure of thin water layers could be obtained by studying their optical properties. However, direct measurement of refractive index, and even more so of double refraction, for a single thin layer is very difficult. Derjaguin &

Green-Kelly (1964) succeeded in solving this problem by measuring the birefringence of swollen montmorillonite in which the water interlayers between each elementary silicate layer are of equal thickness. Knowing the birefringence of the montmorillonite itself and taking advantage of Wiener's formula (1912), which makes allowance for double refraction due to lamination of the medium, we were able to calculate the birefringence of the water layers from the measured path difference for a beam parallel to the layers. The equilibrium thickness of the water layers in the montmorillonite swollen to equilibrium could be varied by changing the concentration of sodium chloride in the water. It was found that the birefringence does not drop sharply in value with growing layer thickness but remains at about 0·002, a value of the same order as the birefringence of ice. Calculations reveal, moreover, that the Kerr effect of the electric field of the double ionic layers forming on the surfaces of a thin layer, can account for not more than one-tenth of the observed birefringence, even in the most favourable case.

The absence of a pronounced drop in these peculiarities (or their indicators) in water layers as the distance from the interface increases up to a certain thickness, gives grounds for assuming that the specific structure of water (and other liquids) in boundary layers is uniform and changes abruptly, at a certain small distance from the interface, into the normal structure of the bulk liquid phase. Indirect evidence in favour of this assumption is the result of a study of the relation between the viscosities of a number of organic liquids and the distance from a solid wall. It was demonstrated (Derjaguin & Karasev, 1952, 1953, 1955; Derjaguin & Pitschugin, 1948) that at a sufficiently small distance from the wall the viscosity can change its normal bulk value jumpwise.

Theoretically, it is also natural to assume that the structure of liquids in the boundary layer can change only jumpwise, just as is observed in liquid crystals.

Thus, there are grounds to speak of boundary phases separated from the bulk liquid by a sharp interface but differing from conventional phases in that their thickness is definite under given conditions, and that they depend on the nature of the substratum, i.e. adjacent phase. The existence of boundary water phases with specific properties also accounts for a number of other phenomena, e.g. capillary osmosis. The latter was studied (Derjaguin & Milekhina, 1962) with the aid of radioactive tracers for aqueous alcohol solutions in particular. It was shown that if the alcohol concentration on either side of a porous glass filter is different, a flow of solution arises towards the lower concentration. Under definite conditions this flow retained a constant intensity for several days (as long as observed).

The phenomenological theory of this effect, given at an earlier date (Derjaguin, Sidorenkov, Zubashchenko & Kiseleva, 1947) establishes it as depending unambiguously on the difference of concentrations of dissolved molecules in the boundary layer at the pore wall–solution interface and in the bulk, this difference being a consequence of the different solvent structures in them. The direction of the effect indicates that the alcohol concentration in the boundary water layer is lower than in the bulk. A similar phenomenon of capillary osmosis was observed for other mixtures too. Evidently, the cases of 'anomalous osmosis' known in the literature can be attributed to the increase in concentration of the solute near the wall, compared to the bulk—to the formation of diffuse adsorption layers. It should be pointed out that in the case of electrolyte solutions the theory becomes somewhat more complicated, as it must take into account electrokinetic phenomena; on the other hand, advantage can be taken of the distribution of dissolved ions near the wall as given by the Guy–Chapman theory, neglecting the specific properties of the boundary solvent layers.

The direct biological importance of capillary osmosis may lie in its possible role in the movement of water both through biological membranes and in narrow plant micropores. It is significant in this connexion that the linear velocity of capillary osmosis, as in the case of electro-osmosis, remains constant with diminishing capillary radius, down to very small values (however, they must remain substantially larger than the thicknesses of the boundary layers), in contrast to a Poiseuille flow under the influence of an external pressure drop.

It is beyond doubt, however, that the behaviour of water will be still more complicated in microcapillaries with radii of the same order as the thicknesses of the boundary layers, when, therefore, all, or a substantial part of the water filling the capillary, may exhibit unusual properties. For this reason, the investigations undertaken by N. N. Fedyakin of the behaviour of water and other liquids in glass microcapillaries 150 Å and more in radius are of great interest. These investigations became possible owing to the development of a clever technique for obtaining and calibrating such micro-capillaries and an ultramicroscopic method of reading meniscus positions. It was detected, first of all (Fedyakin, 1961), that the thermal expansion of the water columns, when the capillary radius is below 100 Å, begins to deviate perceptibly from the thermal expansion curve of bulk water. At radii of the order of 200 Å and less, the length of the water columns changes with the temperature according to a strictly linear law, not only not exhibiting a minimum at 4° C., but continuing to fall linearly with de-creasing temperature after passing through 0, and down to −12° C.

A similar change in the thermal expansion of water was observed by Derjaguin & Karasev (1962) in aerosil pores.

This behaviour of water in microcapillaries can be attributed to the fact that its structure in the latter is more compact than in the bulk. The result is, that on raising the temperature no break-up and rearrangement of structure occurs such as is responsible for the well-known anomalous thermal expansion of water in bulk from 0°.

Capillary suction may easily be observed by immersing the open end of a capillary with one fused end in a liquid. Suction ceases at the moment equilibrium is established between the capillary pressure of the meniscus and the excess pressure of the air compressed owing to the movement of the meniscus. Therefore, applying the law of Boyle and Mariotte, the capillary pressure of the meniscus can easily be calculated and compared with that which follows from the Laplace formula. It was found (Fedyakin, 1962) that the experimental value of the capillary pressure for capillaries less than 1μ in radius is substantially smaller than that calculated from the Laplace formula. In the case of microcapillaries 200 Å in radius, the difference was as high as several-fold (twofold, for water). Such a difference cannot be accounted for otherwise than by the sharp difference between the thermodynamic properties of the liquid in the microcapillaries and in bulk, which makes the Laplace formula (and simultaneously that of Kelvin) inapplicable.

Despite the depressed value of the capillary pressure, capillary suction occurred at a rate several times higher than that calculated from Wasburn's formula assuming applicability of the Poiseuille equation. The discrepancy with this formula becomes still greater if allowance is made for the true value of the driving force of the process, namely, the capillary pressure. This apparently testifies to the fact that the flow of water (and other liquids) through microcapillaries follows a specific mechanism in which sliding along the walls plays a major role. The existence and role of this sliding was first proved experimentally by D. M. Tolstoy (1952a) for mercury in glass capillaries 0·01 mm in radius. The theory developed by the same author (Tolstoy, 1952b) relates this sliding to the magnitude of the contact angle. In the case of water–glass the contact angle is much smaller, but in Fedyakin's work the capillaries had a radius 10^3 times smaller, which could sharply increase the role of sliding along the walls and result in the discharge of the liquid varying in proportion to the third, rather than the fourth power of the radius—in close agreement with what was observed.

Doubtless in live tissues the contact wetting angle may be much larger owing to the hydrophobic nature of the walls, and the sliding of the water may be of still greater importance.

The results discussed above show that in considering the behaviour of water in plant and animal tissues we must take into account the specific properties and phenomena existing in thin films and narrow capillaries, the study of which is a difficult but essential field of surface phenomena now in a new stage of development.

REFERENCES

DERJAGUIN, B. V. & GREEN-KELLY, R. (1964). *Trans. Faraday Soc.* **256**, 131.

DERJAGUIN, B. V. & KARASEV, V. V. (1952). *J. Phys. Chem., Moscow*, **33**, 100 (in Russian).

DERJAGUIN, B. V. & KARASEV, V. V. (1953). *Kolloid Zh.* **15**, 365 (in Russian).

DERJAGUIN, B. V. & KARASEV, V. V. (1955). *Dokl. Akad. Nauk SSSR*, **101**, 289 (in Russian).

DERJAGUIN, B. V. & KARASEV, V. V. (1962). *Kolloid Zh.* **24**, 471 (in Russian).

DERJAGUIN, B. V. & MILEKHINA, M. M. (1962). *Peredovoy nautschnotechnitschesky put*, 1962, N8. (in Russian)

DERJAGUIN, B. V. & PITSCHUGIN, E. F. (1948). *Dokl. Akad. Nauk SSSR*, **63**, 53 (in Russian).

DERJAGUIN, B. V. SIDORENKOV, G. P., ZUBASHCHENKO, E. A. & KISELEVA, E. V. (1947). *Kolloid Zh.* **9**, 335 (in Russian).

DERJAGUIN, B. V., ZAKHAVAYEVA, N. N. & LOPATINA, A. M. (1961). *Research in the Field of Surface Forces*. Moscow: USSR Academy of Science Press, p. 182 (in Russian). New York Consultants Bureau 1962, p. 141 (in English).

FEDYAKIN, N. N. (1961). *Dokl. Akad. Nauk SSSR*, **138**, 1389 (in Russian).

FEDYAKIN, N. N. (1962). *J. Phys. Chem., Moscow*, **36**, 1450 (in Russian).

HENNIKER, G. (1949). *Rev. mod. Phys.* **21**, 322.

METSIK, M. S. (1964). *Research in the Field of Surface Forces. II*, p. 138. Moscow: Nauka Press (in Russian).

TOLSTOY, D. M. (1952a). *Dokl. Akad. Nauk SSSR*, **85**, 1089 (in Russian).

TOLSTOY, D. M. (1952b). *Dokl. Akad. Nauk SSSR*, **85**, 1329 (in Russian).

WIENER, O. (1912). *Abh. sächs. Ges. (Akad.) Wiss. (Math.-Phys. Kl.)*, **32**, 509.

ZHILENKOV, A. P. (1963). Abstract of Doctor's Thesis, Institute of Physical Chemistry of the Acad. of Sci. of the U.S.S.R.