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1962

SovietRxiv

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Abstract

Full Text

PHYSICAL CHEMISTRY

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SPECIAL PROPERTIES AND VISCOSITY OF LIQUIDS CONDENSED IN CAPILLARIES

One of us showed (^{1}) that a column of water in a sealed capillary with a radius of 1-5 μ gradually shortens owing to the formation and subsequent lengthening, adjacent to it, of another column (or columns) of water. Such migration of water indicates a difference in the chemical potentials, and consequently also in the properties, of the two columns—the initially introduced one and the daughter one. This was confirmed by the discovered (^{1}) difference in the thermal expansion of the two columns: namely, the daughter column of water has a constant coefficient of volume expansion in the temperature interval 20–50°.

A column of water with "special" properties can also be obtained in open glass capillaries by placing them in a chamber with a relative humidity of the air exceeding 93%. The rate of elongation of the forming columns increases monotonically with increasing relative humidity above this threshold. It is evident from this, since the correction to the saturated-vapor pressure for the curvature of the menisci in this case is much less than 7%, that the properties of the anomalous liquid columns, and above all their structure, differ substantially from the properties of bulk liquid water. One of the structure-sensitive properties is viscosity. Measurements of the viscosity of anomalous columns were carried out in the present work. In this connection not only water was investigated, but also a number of other liquids (methyl alcohol, acetone, acetic acid), for which an analogous effect of formation, in sealed glass capillaries, of anomalous columns adjacent to "normal" ones was found.

Fig. 1. Transition of ordinary water into water with altered structure in a cylindrical capillary. $t = 20°$

In Fig. 1 are shown the dependences of the shortening of the column of initially introduced liquid (1) and of the elongation of the daughter liquid column (2) on time; the first becomes linear beginning from a certain moment in time, the latter—from the very beginning. The difference between the ordinates of the two dependences evidently determines the amount of water that has gone into the formation of the adsorption film, since the experiments were usually carried out in freshly drawn capillaries. Thus, the process of pumping the liquid between the columns, once established after formation of the film, proceeds at a constant rate.

Measurement procedure. To measure the viscosity of the column, the capillary containing it was placed in an apparatus whose scheme is shown in Fig. 2. By passing air at different rates through tube 1, we created various pressure differences at the ends of the capillary under investigation; these were measured with a differential manometer. Differential thermocouple 2 monitored the absence of a temperature gradient; by means of a switch, a third junction located in a Dewar vessel could be connected to one of the heads of this thermocouple, and in this way the absolute temperature could be measured at any moment. This apparatus is fastened to

the microscope slide holder in such a way that the column of the liquid under study can be kept continuously in the field of view. By creating different pressures at the ends of the capillary, one can measure the velocity of motion of the investigated column as a function of the pressure difference and from this calculate the viscosity of the liquid.

The motion of a liquid column of length Δl along the capillary channel is equivalent to the motion of a liquid through a capillary of length Δl. For convenience, we shall write the Poiseuille equation in the form

$$8\,\frac{v\Delta l}{r^2} = \frac{1}{\eta}\,\Delta p, \tag{1}$$

where v is the velocity of motion of the liquid column along the capillary channel; Δl is the length of the liquid column, measured with the aid of an ocular scale; r is the radius of the capillary, measured from the capillary pressure (1); Δp is the pressure difference; η is the viscosity.

A liquid with a special structure may turn out to be non-Newtonian, but Bingham, i.e., to possess a limiting shear stress θ. In the case when

$$\theta \ll \frac{r}{2\Delta l}\,\Delta p,$$

instead of equation (1) we have (2)

$$v = \frac{r^2}{8\eta\Delta l}\left(\Delta p - \frac{8\Delta l\theta}{3r}\right). \tag{2}$$

Knowing the intercept a, cut off on the abscissa axis by the straight line expressing the dependence of $8v\Delta l/r^2$ on Δp, one can determine θ:

Fig. 2. Schematic of the apparatus for determining the viscosity of liquids condensed in capillaries. 1 —capillary producing the pressure difference; 2 —differential thermocouple; 3 —leads to the differential manometer; 4 —investigated capillary, in which the motion of the liquid column is observed; 5 —partition; 6 —column of condensed liquid

Figure 2: Fig. 2. Schematic of the apparatus for determining the viscosity of liquids condensed in capillaries. 1 —capillary producing the pressure difference; 2 —differential thermocouple; 3 —leads to the differential manometer; 4 —investigated capillary, in which the motion of the liquid column is observed; 5 —partition; 6 —column of condensed liquid

$$\theta = \frac{3ar}{8\Delta l} \tag{3}$$

In our experiments we studied the motion of columns of length of the order of 1 mm in capillaries with radii of the order of 1μ; thus, the ratio $\Delta l/r$ was of the order of 1000, and the influence of end effects, or of the distances over which the parabolic velocity profile is established, may be neglected.

Fig. 2. Schematic of the apparatus for determining the viscosity of liquids condensed in capillaries. 1 —capillary producing the pressure difference; 2 —differential thermocouple; 3 —leads to the differential manometer; 4 —investigated capillary, in which the motion of the liquid column is observed; 5 —partition; 6 —column of condensed liquid.

Results of the measurements. The results of one of the experiments are shown in Fig. 3. The velocity of motion of a daughter column of water 1.5 mm long was measured on a 4-5 mm section of the capillary. Straight line 1 was obtained during the first motion; straight line 2 was obtained during motion along the same section as the first time and in the same direction, i.e., before this the column had been returned to its initial position. Similarly, in subsequent motions, straight lines 3 and 4 were obtained.

Motion along one and the same section and in one and the same direction is desirable in order to obtain identical conditions, so that the change in velocity could not be explained by any extraneous causes (for example, by the conicity of the capillary).

Figure 4 gives the dependence of the velocity of motion of a daughter column of water in the forward and reverse directions on the pressure difference. Straight line 1 was obtained during the first motion, with no stops being made after the measurements; the pressure was increased at definite intervals of time. Curve 2 was obtained during reverse motion; here, after each measurement, the motion was stopped, and thus the column started from rest in each at every

measurements with ever greater speed. It is seen that, as the initial speed of motion increases, a sharper decrease in viscosity occurs. At speeds on the order

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

of 1 mm/sec the viscosity very quickly reaches its normal value. It should also be noted that if, during the first motion,

Fig. 3. Dependence of the speed of motion of a column of liquid with altered structure on the pressure drop in one and the same section of the capillary and in one and the same direction

Fig. 4. Dependence of the speed of motion on the pressure drop in one and the same section in different directions

having obtained several points, one stops the motion of the column and then again begins with the minimum speed, a limiting shear stress appears, although the viscosity decreases. The limiting shear stress, calculated by formula (3), is on the order of 2 dyn/cm^2.

Measurements of the viscosity of liquids only just drawn into the capillary, as well as of liquids that had remained in it for several days and even months, showed that their viscosities do not differ from the tabulated values within the limits of experimental error ($±$5%), which is due mainly to the inaccurate measurement of the capillary radius. Thus, the increased viscosity of the daughter column of liquid cannot be explained by its prolonged residence in the capillary.

Table 1 gives the results of measurements of the viscosity of water and acetone in the daughter column.

In the table, η_1 denotes the viscosity during the first motion, η_2 the viscosity during the second motion along the same section and in the same direction, and η_t the tabulated value of the viscosity.

The viscosity of water reaches its normal value after 3 or 4 motions (Fig. 3).

The remarkable phenomenon is the restoration of the initial, higher viscosity in the daughter column after it has been significantly reduced as a result of motions, but has not yet reached its bulk value. After twenty-four hours the viscosity becomes the same as it was in the daughter column.

Table 1

r, μ	Δl, mm	η_1, cm · sec · 10^2	η_2, cm · sec · 10^2	$\frac{\eta_t}{r}$, cm · sec · 10^2
Water	**Water**	**Water**	**Water**	**Water**

r, μ	Δl, mm	η_1, cm · sec · 10^2	η_2, cm · sec · 10^2	$\frac{\eta_t}{r}$, cm · sec · 10^2
1.06	0.39	12.5	1.2	1.005
1.03	0.39	12.0	1.2	–
1.78	0.67	15.0	1.5	–
0.94	0.38	11.0	1.2	–
2.64	0.98	8.0	2.0	–
2.13	1.33	10.0	1.2	–
1.37	0.69	12.5	1.1	–
1.85	0.61	12.5	1.3	–
Acetone	**Acetone**	**Acetone**	**Acetone**	**Acetone**
1.4	4.2	0.52	0.34	0.33
1.45	1.64	0.58	0.32	–
1.85	6.58	0.55	0.31	–

For methyl alcohol, no change in viscosity was observed in the columns that formed, but a limiting shear stress was observed, which disappeared when the column moved a distance on the order of a millimeter.

Discussion of the results. The facts described prove

that in glass capillaries at one and the same temperature there may exist, in the form of columns, two different modifications of water, sharply differing in such properties as viscosity, thermal expansion, and elasticity of the saturated vapor, which unambiguously indicates a difference in structure. The appearance of a special structure in the "anomalous" columns is evidently connected with the origin of the latter through the formation of local thickenings of the adsorption film lining the inner walls of the capillary. With a sufficiently large equilibrium thickness of the adsorption layer, obtained in the case of contact with the meniscus of a "normal" column or with vapor close to saturation, the instability of the cylindrical liquid surface known from the theory of capillarity manifests itself; it is not compensated by the stabilizing influence of the disjoining pressure $P(h)$, which depends on the quantity $-\partial P/\partial h$. As a result of the loss of stability of the liquid film, the latter takes the form of an unduloid, which leads to the formation of secondary columns. When the matter ends with the formation and growth only of columns adjacent to the primary one, while other columns are not formed, this alone already serves as proof of the difference in properties—above all of the vapor pressure—between the daughter columns and the primary one.

Taking into account the mechanism considered for the formation of secondary columns, we can interpret their special structure (in those cases where it occurs) as the result of preservation of the structure of boundary layers of liquids when the adsorption layers thicken beyond the equilibrium thickness. In turn, it may be supposed that the special structure of the boundary layers (and, consequently, of the anomalous columns as well) is due to hydroxyl groups on the glass surface, giving rise to chains of liquid molecules united by hydrogen bonds. Consistent with this is the existence of a special structure precisely for liquids with hydrogen bonds (water, acetone). Thus, in anomalous columns the liquid is as it were polymerized under the influence of contact with the glass surface—we have a kind of phenomenon of topochemical long-range action. In this case, in anomalous columns the number of hydrogen bonds per unit volume should be greater than in ordinary water, as a result of which the vapor elasticity in the first case is lower, while the viscosity and packing density of the molecules are greater. During flow, the excess hydrogen bonds apparently may be destroyed and the column acquires the structure and properties of bulk water. In this case the increase in vapor elasticity and, consequently, of the chemical potential and free energy must occur at the expense of the work of external forces expended in the flow of the column, over and above that which is dissipated as heat.

If the process of destruction of the excess bonds has gone sufficiently far, the former state cannot be restored, although a decrease in the chemical potential would correspond to it, since this is hindered by a certain potential barrier. In the opposite case of slight destruction, as experiment shows, the initial anomalous structure is completely restored, evidently because the potential barrier in this case is small owing to the smallness of the regions of disturbed structure.

Thus, in capillaries or pores of porous substances there may exist different modifications of liquids, the possibility of which in boundary layers is theoretically substantiated in work ([5]).

The possibility of the existence of liquids with different structures apparently explains the failure of experiments to verify the applicability to capillary condensation of the Kelvin equation ([3,4]), and is evidently important for understanding the behavior of water in soils and other porous materials.

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Received
2 VI 1962

CITED LITERATURE

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