SLIP OF LIQUIDS IN CAPILLARIES

Corresponding Member of the USSR Academy of Sciences B. V. DERYAGIN, N. N. FEDYAKIN

1968

SovietRxiv

Fig. 1. Dependence of the rate of capillary uptake of water on the reciprocal of the distance of the meniscus from the beginning of the capillary. Capillary radius 0.022 μ

Figure 1: Fig. 1. Dependence of the rate of capillary uptake of water on the reciprocal of the distance of the meniscus from the beginning of the capillary. Capillary radius 0.022 μ

Abstract

Full Text

UDC 532.68

PHYSICS

Corresponding Member of the USSR Academy of Sciences B. V. DERYAGIN, N. N. FEDYAKIN

SLIP OF LIQUIDS IN CAPILLARIES

Earlier ([1]) one of us showed that the rate of capillary uptake of liquids into capillaries with radii less than 0.1 μ is greater than that calculated from the well-known Washburn equation ([2]). The discrepancy increases as the capillary radius decreases. In capillaries with radii of 0.02 μ, the observed rate differs by an entire order of magnitude in comparison with the calculated one and therefore cannot be explained by the slip described in ([3]).

Assuming the realization of the Poiseuille flow regime in the capillaries we investigated, the increase in the uptake rate was explained by a decrease in viscosity.

Indeed, as is evident from works ([4], [5]), in boundary layers of thickness on the order of 100 Å a substantial deviation of the viscosity from bulk values is observed. When liquids move in capillaries with radii much larger than the thickness of the boundary layer, the change of viscosity in it has no substantial effect on the total flow rate of the liquid. The situation becomes different when the capillary radius is comparable with the thickness of the boundary layer.

Fig. 1. Dependence of the rate of capillary uptake of water on the reciprocal of the distance of the meniscus from the beginning of the capillary. Capillary radius 0.022 μ

The present work is devoted to the study of the flow regime of liquids in capillaries with radii in the interval 0.01-0.1 μ. For this purpose, dependences were obtained for the uptake rate v: 1) on $1/x$ (x is the distance between the meniscus and the beginning of the capillary at a given moment in time) at constant pressures p and capillary radius r; 2) on p at constant x and r; 3) on r at constant x and p.

Fig. 2 and Fig. 3: plots of the rate of suction of water in capillaries.

Figure 2: Fig. 2 and Fig. 3: plots of the rate of suction of water in capillaries.

The capillaries were made of thermic glass; the radii were measured by the method described in ([1], [6])*.

To obtain the dependence of v on $1/x$, the time of motion of the liquid meniscus between several divisions of the ocular micrometer of the microscope was measured at various distances x from the beginning of the capillary. Fig. 1 shows an example of such a dependence for a capillary with $r = 0.022\ \mu$. Analogous dependences were obtained in capillaries with larger and smaller radii.

The dependence of v on p was studied in the following way. The rate of motion of the liquid was measured for various x in a capillary sealed at one end. The pressure was determined as

$$p = p_k - p_v, \tag{1}$$

where p_k is the capillary pressure; p_v is the pressure of the compressed air, which is calculated from the Mendeleev-Clapeyron equation.

* In ([7]), a comparison was made of the results of measurements by our method with results obtained with the aid of an electron microscope. The agreement is satisfactory.

The capillary pressure is taken to be equal to the pressure of the compressed air at the moment the meniscus stops. The velocities for various x were reduced to $x = 1$ cm. Fig. 2 shows the dependence of v on p, the capillary radius being $0.046\,\mu$; the velocities are calculated for $x = 1$ cm.

Thus it is shown that the rate of suction of a liquid by a capillary depends linearly on the pressure and is inversely proportional to the distance of the meniscus from the end of the capillary.

Fig. 2. Dependence of the rate of suction of water into a capillary of radius $0.046\,\mu$ on pressure, for $x = 1$ cm

Fig. 3. Dependence of the rate of suction of water on the capillary radius for a pressure drop $p = 30$ atm, $x = 1$ cm

This result is needed in order to calculate the dependence of the velocity of motion of the meniscus on the capillary radius, which is decisive for determining the flow regime. Fig. 3 shows the dependence of the flow velocity of water on the capillary radius at $x = 1$ cm and $p = 30$ atm. The velocity values were obtained by determining, from curves of the type in Fig. 1, the velocity for $x = 1$ cm.

In narrow capillaries the capillary pressure does not obey the Laplace equation, but was measured by the method described in ([1]). Then the velocity was calculated which the liquid would have if the pressure were equal to 30 atm. Similar results are also obtained when measuring velocities in capillaries sealed at one end. In this case the pressure is calculated from formula (1), and the recalculation is carried out in the same manner.

We see that the velocity of motion of the liquid in capillaries with radii smaller than 0.1 μ is proportional to the capillary radius to the first power. Consequently, in such capillaries the flow regime is not Poiseuille, and one may assume that the parabolic velocity profile is absent and that the liquid moves in the form of a plug.

Assuming that the friction force is proportional to the velocity and is determined by a two-term law, for the case of friction between the liquid and the near-wall adsorption layer one may write

$$F_{\text{fr}} = \lambda 2\pi r x v + 2\pi r x f, \tag{2}$$

where v is the velocity of motion of the liquid; λ is the coefficient of friction; f is the limiting shear stress in the slip plane at the liquid–immobile adsorption layer boundary.

The equation of motion of the liquid will have the form

$$\frac{d}{d\tau}(mv) = F_{\text{k}} - F_{\text{fr}}, \tag{3}$$

where F_{k} is the force of capillary suction, $F_{\text{k}} = p_{\text{k}}\pi r^2$; p_{k} is the capillary

pressure $p_k = 2(\sigma_{12} - \sigma_{13})/r$; σ_{12} is the surface tension at the capillary wall—liquid boundary; σ_{13} is the surface tension at the capillary wall—air boundary.

Equation (3) can be written

$$\frac{d^2x}{dt^2} + \frac{\rho}{x}\left(\frac{dx}{dt}\right)^2 - \frac{1}{x}p + \frac{2\lambda}{r}\frac{dx}{dt} + \frac{2f}{r} = 0; \tag{4}$$

for $x \gg r$ the first and second terms may be neglected.

The equation takes the form

$$v = \frac{p}{2\lambda x} r - \frac{f}{\lambda}. \tag{5}$$

How well the equation agrees with the experimental results obtained is seen from Fig. 2. The coefficient of friction is evidently equal to:

$$\lambda = \frac{r}{2x}\frac{1}{\alpha}, \tag{6}$$

where α is the angular coefficient of the straight line.

Table 1

Liquid	t, °C	$10^{-3}\lambda$, $\frac{\text{g}}{\text{cm}^2 \cdot \text{sec}}$
Water	20	2.1
Benzene	20	1.16
Methyl alcohol	20	1.07

The limiting shear stress is also determined from the relation

$$f = p_0 r/2x_0; \tag{7}$$

p_0 is determined by the intercept cut off by the straight line $v-p$ (Fig. 2) on the abscissa axis; x_0 is the capillary length adopted in constructing a dependence of the type shown in Fig. 2. In this case $f = 3.7$ dyn/cm^2.

We also studied the motion of methyl alcohol and benzene in capillaries. For them the straight lines of the type in Fig. 2 pass near the origin of coordinates, i.e., the magnitude of the limiting shear stress is close to zero.

Table 1 gives the values of the coefficient of friction measured by us.

Let us consider theoretically the question of the transition from the Poiseuille flow regime to the "plug" regime.

In sufficiently wide capillaries, in a first approximation, the expression for the tangential stress at the capillary walls, following from the parabolic velocity profile and the Poiseuille regime, is applicable,

$$\tau = 4\eta v/r,$$

where v is the velocity of motion of the meniscus. If this quantity is less than f, there will be no slip of the liquid on the walls.

Consequently, for $r > 4\eta v/f$, viscous flow will not be accompanied by slip.

At smaller radii a mixed regime will be realized. The tangential stress at the wall in the presence of slip is equal to $\tau_s = \lambda v_s + f$, where v_s is the slip velocity.

For sufficiently narrow capillaries, the plug mechanism of flow predominates. The velocity of motion of the meniscus v exceeds v_s by a relatively small quantity $v - v_s = \Delta v$. We can approximately find this difference from the formula

$$\Delta v = r\tau/4\eta \approx r(\lambda v + f)/4\eta.$$

The condition for the smallness of $\Delta v/v$ will be, since in our experiments $f \ll \lambda v$,

$$r\lambda/4\eta \ll 1.$$

For water it follows from this that $r \ll 2 \cdot 10^{-5}$, which agrees with experiment.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
4 VII 1968

REFERENCES

1. N. N. Fedyakin, ZhFKh, **36**, 7 (1962).
2. E. W. Washburn, Phys. Rev., **17**, 26 (1921).
3. D. M. Tolstoi, DAN, **85**, No. 6, 1089 (1952); **85**, No. 6, 1089 (1952).
4. B. V. Deryagin, V. V. Karasev et al., ZhTF, **27**, issue 5, 1076 (1957).
5. B. V. Deryagin, in: *Surface Chemical Compounds and Their Role in Adsorption Phenomena*, 62, Moscow, 1957.
6. N. N. Fedyakin, DAN, **138**, No. 6 (1961).
7. V. D. Sobolev, Z. M. Zorin, *Proceedings of the Third Conference on Surface Forces*, "Nauka," 1967.

Note: Figure translations are in progress. See original paper for figures.