Corresponding Member of the Academy of Sciences of the USSR B. V. DERYAGIN, Yu. SHUTOR,

S. V. NERPIN, M. A. ARUTYUNYAN

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Abstract

Full Text

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Corresponding Member of the Academy of Sciences of the USSR B. V. DERYAGIN, Yu. SHUTOR,
S. V. NERPIN, M. A. ARUTYUNYAN

INVESTIGATION OF THE THERMOOSMOTIC EFFECT FOR WATER IN GLASS CAPILLARIES

In paper (^{1}) it was shown that the difference between the enthalpy in the boundary layers of a liquid and the bulk value should lead to thermoosmosis—the motion of a liquid through a capillary in the presence of an axial temperature gradient. However, the experimental proof of the existence of thermoosmosis in a porous partition in (^{1}) is very imprecise because of the rapid decrease of the effect due to equalization of the temperatures on both sides of the filter as a result of thermal conductivity. Free from this objection is the work (^{2}), but it concerns the motion of wetting films and not the case of completely filled capillaries. Taking into account the importance of thermoosmosis for the behavior of moisture in the surface layers of soil, we undertook the present investigation.

The basic relation for calculating the velocity of thermoosmotic motion v has the form:

$$v = \beta \, dT/dl, \tag{1}$$

where β is the coefficient of thermoosmotic slip; dT/dl is the temperature gradient along the interface.

Fig. 1. Diagram of the apparatus for determining the thermoosmotic coefficient

The present work is devoted to determining the thermoosmotic coefficient for glass capillaries with diameters on the order of several microns. Experiments to determine the thermoosmotic coefficient were carried out on the apparatus schematically shown in Fig. 1. The apparatus consists of a wide capillary 2, at one end of which the thin capillary under investigation 1 is fixed; at the other end of capillary 2 there is a capillary-pressure compensator 3. Part of the wide capillary is placed in a thermostated vessel 4. With the aid of microscope 7, the meniscus of the liquid in capillary 1 is projected onto screen 8. The light beam from the microscope illuminator was passed through a cuvette with water 9, and capillary 1 was blown with a fan to prevent heating.

Before capillary 1 was fixed in the opening of the wide capillary, the capillary-pressure compensator was filled with mercury 6 to half the expansion at the end of the thick-walled capillary. The remaining part was filled with bidistilled water 5; then the capillary under investigation 1 was introduced into the opening of the wide capillary, and the joint was sealed with sealing wax 10.

so that there were no air bubbles between the picein and the water and, as shown in the figure, part of the capillary was placed in a thermostated vessel.

By slowly lowering the cup with mercury of the compensator, the water meniscus in capillary 1 was brought into the field of view of the microscope and, with its aid, projected onto the screen. After the meniscus had equilibrated, the temperature in the thermostated vessel was raised relative to the room temperature, thereby creating a temperature gradient along capillary 1, and the motion of the meniscus under the influence of the resulting thermo-osmotic effect was observed on the screen.

For this case, relation 1 can be rewritten in the form:

$$v = \beta\,\Delta T/l, \tag{2}$$

where ΔT is the temperature difference between the ends of the column of water in the capillary, and l is the length of the column. Formula (2), as is easily shown, is valid regardless of the law by which T varies along the column l, i.e., it is not necessary for this variation to be linear.

For the flow of liquid in the capillary caused by the thermo-osmotic effect, one may write

$$Q_1 = v\pi r^2. \tag{3}$$

When the level of the meniscus changes, hydrostatic equilibrium is disturbed, and in capillary 1 an additional pressure arises, creating a Poiseuille flow in the opposite direction. For the resulting counterflow we obtain the expression

$$Q_2 = \frac{\pi r^4}{8\eta l}\Delta P, \tag{4}$$

where the additional pressure is, obviously, equal to

$$\Delta P = \rho g l - \rho g l_0 = \rho g (l - l_0); \tag{5}$$

here l_0 is the initial length of the column of water in the capillary, and l is that at the moment under consideration.

Since in our case the flows Q_1 and Q_2 are oppositely directed, for the resultant flow Q we obtain

$$Q = Q_1 - Q_2 = v\pi r^2 - \frac{\pi r^4}{8\eta l}\rho g\,(l - l_0). \tag{6}$$

We now pass to the resulting linear velocity of motion of the meniscus, v_r. The observed velocity will be

$$v_r = v - \frac{r^2 \rho g}{8\eta}\,\frac{(l - l_0)}{l}. \tag{7}$$

The velocity v is known from formula (1); therefore

$$v_r = \beta\,\frac{\Delta T}{l} - \frac{r^2 \rho g}{8\eta}\,\frac{(l - l_0)}{l}. \tag{8}$$

Multiplying both sides of equation (8) by l, we obtain

$$l v_r = A - Bl, \tag{9}$$

where the constants A and B are equal to

$$A = \beta \Delta T + l_0 \rho g r^2 / 8\eta, \tag{10}$$

$$B = \frac{r^2 \rho g}{8\eta}. \tag{11}$$

Figure 2 presents the results of observations of the motion of the meniscus for a capillary of radius $7.5\,\mu$ at a meniscus temperature $T_0 = 18^\circ$ and a temperature of the lower end of the capillary, lowered into the thermostat, $T_1 = 20^\circ$, i.e., at $\Delta T = 2^\circ$. The results of the observations, in accordance with the theory, fall on a straight line. The slope of the straight line, found from the experiment, is close to the value of the constant $B = 6.5 \cdot 10^{-5}$, which can be calculated from the for-

formula (11). This proves that the driving force of the thermoosmotic flow, ΔT, was established very rapidly, already by the time of the first reading—

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

approximately after 1 min—and thereafter remained constant throughout the entire course of the process, up to the attainment of the stationary state.

The coefficient β can be calculated from formulas (10), (11)

$$\beta = (A - l_0 B)/\Delta T; \tag{12}$$

here the quantities A and B are determined from the graph in Fig. 2. Processing of the experimental data showed that the quantity β is of the order of $2 \cdot 10^{-5}$ cm^2/sec $\cdot$ deg.

Figure 3 shows the dependence of the initial velocity (at $l = l_0$) on the temperature difference ΔT.

In accordance with the theory, a directly proportional dependence is obtained, corresponding to one and the same value of β.

Let us now consider the influence of the expansion of water on the accuracy of the results obtained. Bidistilled water in the wide capillary is under the action of capillary forces and of forces compensating the capillary forces. Before the thermostat is switched on, these forces are in equilibrium. After the thermostat is switched on, the water is heated. Under the influence of expansion by the amount ΔV, a new equilibrium arises. This leads to an increase of the column of bidistilled water in the capillary under study 1 by an amount Δh_1 and in the compensator cup by Δh_2. In the state of the new equilibrium, for these quantities one may write the proportionality $\Delta h_2 = 13.55\,\Delta h_1$, taking into account that there is mercury in the compensator cup.

Fig. 2

Fig. 3

The equation for the distribution of the resulting increase in the volume of water, ΔV, between the capillary under study and the compensator cup takes the form $\pi r_1^2 \Delta h_1 + \pi r_2^2 \Delta h_2 = \Delta V$, where r_1 is the radius of the capillary under study, and r_2 is the radius of the compensator cup.

Under the condition $\Delta h_2 = 13.55\,\Delta h_1$ and $r_1 = 7.5$, $r_2 = 2.5$ mm, the calculations show that, owing to the expansion of water, the rise of the meniscus is possible only to a height of 131. This rise, in comparison with the rise of the meniscus under the influence of the thermoosmotic effect, may be neglected.

The experiments carried out showed that the thermoosmotic motion proceeds toward the lower temperature, which corresponds to the case when, near solid surfaces, the enthalpy of the liquid is higher than in the bulk. At the same time it is known that, near solid surfaces, the enthalpy of water is lower than in the bulk, which follows from observations of the decrease in its average value as the moisture content of porous bodies decreases. In this connection, assumptions can be made about the reasons for the sign of the observed effect. One of them is the supposition that boundary layers with reduced heat content, possessing elements of shear strength, did not participate in the observed motion, and that beyond the boundary layers the water has an increased heat content in comparison with the bulk.

Note added in proof. In the work of B. V. Deryagin, S. V. Nerpin, and M. A. Arutyunyan ([3]), a method is described for measuring the temperature decrease ΔT at the entry of a flow into the capillaries of a porous filter. Unfortunately, the graphs presented in that article in Fig. 1, as well as formulas (2) and (2′), were included in the article through a gross oversight and do not at all illustrate this ΔT-effect for water.

However, the true observed values of ΔT for water (also of the order of hundredths of a degree) lead, after recalculation based on Onsager' s principle ([1]), to a value of the coefficient of thermo-osmotic slip β of the same order as those measured directly in the present communication.

Agrophysical Institute
of the All-Union Academy of Agricultural Sciences
named after V. I. Lenin

Institute of Physical Chemistry
of the Academy of Sciences of the USSR

Institute of Hydrology and Hydraulics
of the Czechoslovak Academy of Sciences

Institute of Deserts
of the Academy of Sciences of the Turkmen SSR

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