REVIEW

EFFECT OF SURFACE FORCES ON FLUID FLOW IN THIN PORES

N. V. Churaev

The structure of fluids near solid surfaces differs from that in the bulk [1]. In the case of isotropic simple fluids with a spherically symmetric intermolecular interaction potential, these variations extend to several molecular layers. For anisotropic fluid crystals the surface effect is manifested at distances of the order of several micrometers. Polar associated fluids, including water, occupy an intermediate position. Boundary layers of water with varying structure reach nearly hydrophilic, well-wettable surfaces of dozens, sometimes hundreds of angstrom. A worsening of the wetting leads to a decrease in the width of boundary layers. In the case of hydrophobic surfaces, breakdown of the sticking condtion becomes possible, and we have slipping of water over the solid surface.

The change in structure of boundary layers of fluids affects the rate of their flow in thin pores. The effective width of boundary layers is sensitive not only to the state of the solid surface, but also to the solution composition and to temperature. Thus, an enhancement in the concentration of the electrolyte solution and in temperature leads to a breakdown of the special structure of boundary layers and to a decrease in their width. Therefore, one cannot indicate a pore radius common for all cases, for which structural effects must be manifested. For example, for water and aqueous solutions of sufficiently low concentration, these effects become substantial (at ordinary temperature and pressure) in pores of radius R of the order of and smaller than 0.1 μm.

We consider initially the effect on filtration of single changes only of rheological properties of fluid boundary layers. We also track the action of an electric field, of concentration gradients, and of temperature on the flow in thin pores.

As was shown earlier [2, 3], in thin pores of glass membranes (R = 10-50 Å) one observes only an enhancement in the Newtonian viscosity of water without breakdown of Darcy's law:

$$v = K_f P. \tag{1}$$

Deviations from this law were observed in a number of cases, accompanied by a nonlinear dependence of v on P and the appearance of an initial pressure gradient P_0 [4-8]. A different shape for the filtration equation has been suggested [7]:

$$v = K_f P - K_f P_0 [1 - \exp(- P/P_0)]. \tag{2}$$

For $P \gg P_0$ it transforms to the equation often used in practice

$$v = K_f (P - P_0), \tag{3}$$

according to which there is no fluid flow for P smaller than the initial pressure gradient P_0.

The problem of the physical nature of P_0 remains open for discussion. This is usually related to the small, but finite, quantity of limiting shear stress ($\tau_0 \simeq 10^{-2}$-10^{-3} dyn/cm^2) of bulk water or to the enhanced values of τ_0 in the boundary layers of water, considered as a viscoplastic body [4]. Not to be excluded, however, is the possibility that this actually observed effect could be generated by the effect of capillary osmosis or the presence of colloidal particles in the porous moisture, a saturating effect. Thus, in nonsaturated porous bodies, filtration usually obeys Darcy's law [8-10], which also follows from our experiments [2, 3], whose results are shown in Fig. 1. The experimental dependence v(P) for thin porous glass with mean pore radius R ∿ 10 Å is linear in a wide interval of pressure gradients P and passes through the origin of coordinates. The dark and bright points correspond to measurements at enhanced and lowered P values, respectively. The measurement results were independent of the direction of P measurement, and were quite reproducible.
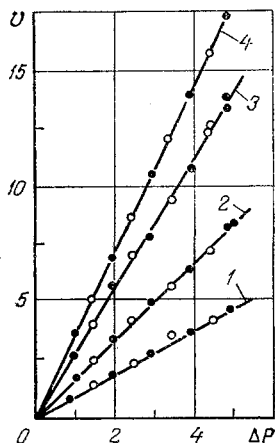
Fig. 1   Fig. 2

Fig. 1. Filtration rate of water v in thin porous
glass as a function of pressure difference ΔP at 20
(1), 40 (2), 60 (3), and 70°C (4). Sample width l =
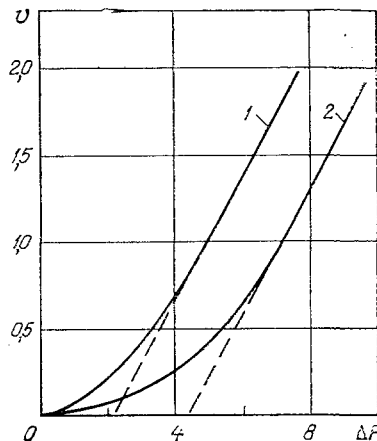0.03 cm. ΔP, 10^5 N/m^3; v, 10^{-8} m/sec.

Fig. 2. Effect of capillary osmosis on the filtra-
tion rate v of a solution through a thin-pore body un-
der the action of various pressure difference ΔP: 1)
$C_0 = 10^{-2}$; 2) $2 \cdot 10^{-2}$ mole/liter. ΔP, 10^5 N/m^2; v,
10^6 m/sec.

The important role of the solution in a moist pore of sodium and potassium silicates,
occurring in compounds of ceramic filters, was demonstrated by Jackson [11]. In several
cases one could simply affect the nontotal wetting by a fluid capillary; from the meniscus
displacement one could measure the fluid deviation. This effect was discussed by Novak [12].

The nonlinear behavior of v(P) is mostly generated by the reversible (and sometimes also
irreversible) change in the mutual position and orientation of the porous body particles un-
der the action of pressure. The nonlinear dependences of v(P) are usually observed in satu-
rated systems [6, 8, 13, 14], where rearrangement of the porous structure is also possible.
The dependence v(P) is in this case formally the same as for flow through a nondeformable
porous body of non-Newtonian fluids.

If the pores have extensions and compressions, the nonlinearity of the dependence v(P)
can be related to the rearrangement of current lines in such a system during the change of
the acting pressure gradient. In this case closed flow lines (circulating flows) can be
generated during the expansions; their configuration depends on the flow rate. This is well
verified both experimentally [15, 16] and theoretically [17, 18].

Often the flow instability in time is located by exact filtration measurements. The
reason can be bacterial activity [19, 20], air extraction from the solution [4], structural
rearrangement of the saturated porous body under the effect of pressure changes, and moisture
content of the compound and dissolved materials [14, 21]. In wide pores an important effect
is due to fall and accumulation of dust particles [22, 23]. Colloidal particles can be in-
hibited in thin pores.

Deviations from Darcy's law during flow in thin pores can be the consequence of genera-
tion of concentration gradients and an electric potential during the flow. The latter effect,
in particular, acquired the name electric viscosity, since it leads to an apparent increase
in the fluid viscosity as a result of damping of flow filtration by electroosmosis. For wide
pores both effects are small and cannot lead to a noticeable change in the pattern of the
fluid flow. Their effect becomes important only for an overlap of diffuse ionic or molecular
layers, belonging to opposite pore surfaces.

The theory of the electroviscous effect in thin pores, where double electric layers (DEL)
overlap, has been developed quite extensively in [24-26]. It has been shown that the largest
relative narrowing of the filtration rate occurs for $\varkappa h \approx 1$. During further decrease of the
pore width, when the DEL overlap to a larger extent, convective flow of ions decreases more

quickly than the electric conductivity of the solvent in the pore. This leads to a lowering of the flow potential and to a falloff in the electric viscosity.

Under stationary conditions the electroviscous effect cannot generate a deviation from Darcy's law, since the relative decrease of the flow rate is independent of the pressure gradient and is determined only by the value of $\varkappa$. Deviations can be observed only when measurements of filtration rates are carried out for preequilibrium values of the flow potential. In this connection it must be noted that relaxation times of the potential can be quite substantial.

An alternate situation occurs when a solvent concentration gradient is generated during filtration. An oppositely directed capillary-osmotic fluid flow is then generated. This is related to the fact that the concentration of outflowing solvent is a function of filtration rate in the case of thin pores.

If the pores are filled by a pure fluid, the effect of surface forces can change the structure of boundary layers, leading to local changes in the density and viscosity values, which become functions of the distance y from the pore surface: $\rho(y)$, $\eta(y)$. The shape of these functions is determined by the nature of acting forces, and in a number of cases satisfies an exponential drop of the ρ and η values with increasing distance from the solid surface [27]. In thin pores, where the boundary layers overlap, there are additional structural changes in the overlap zone.

When the pores are filled by a solution, then besides the structural changes in the solvent mentioned above, there occurs a redistribution of the dissolved material molecules over the pore cross section. The concentration of dissolved molecules also becomes a function of distance to the pore wall $C = C(y)$, differing in this case from the bulk values. The function $C(y)$ is determined by the magnitude and sign of the forces acting between the dissolved material molecules and the pore surfaces through the solution layers.

If the resulting force is repulsive, the solution is lowered, which corresponds to negative adsorption. This situation was observed for many aqueous solutions, and was earlier explained by the existence of "nonsolvent bulk" or by "binding" of water in disperse systems [28]. The effect of concentration lowering of the dissolved material in thin pores is used for separation of solutions (e.g., distillation of water) by the inverse osmosis method [29].

When the resulting force is attractive, positive adsorption takes place, which is not restricted by the formation of an immobile adsorption monolayer. Molecular adsorption layers in solutions have a diffuse structure (as in diffuse ionic layers), which is proved by the effect of capillary osmosis — solution flow under the action of a concentration gradient [30]. As is well-known, capillary osmosis is possible only in the presence of a mobile portion of the adsorption layer. The magnitude of adsorption determines the intensity, and the sign of adsorption (negative or positive) determines the direction of capillary-osmotic flow.

The concentration distribution of the dissolved material over the pore cross section can be found from the Boltzmann equation

$$C(r) = C_0 \exp[-\Phi(r)/kT]. \tag{4}$$

Here $\Phi(r)$ is the potential function, characterizing the interaction energy of dissolved material molecules with the pore surfaces, and C_0 is the bulk solution concentration at the pore limits or in a portion of it (if the pore is wide), where $\Phi = 0$. The values of $\Phi(r)$ are determined by the contributions of the various components of surface forces, and depend on the solution composition and on the sublayer properties. Dispersion forces play a major role in the case of nonaqueous systems. For this case the calculation of the functions $\Phi(r)$ was carried out in [31, 32] on the basis of well-known equations of the macroscopic theory of molecular forces [33].

For aqueous solutions near hydrophilic surfaces the main contribution to the function $\Phi(r)$ is provided by structural forces, generated by the overlap of boundary layers to the pore surfaces with hydrate (in the general case, solvate) shells of polar molecules or ions. In the case of electrolyte solutions, a significant and sometimes decisive contribution to the function $\Phi(r)$ is also provided by Coulomb forces.

Since a rigorous calculation of $\Phi(r)$ is complicated and practically impossible, in solving problems of solution flow through a thin-pore body we can confine ourselves to introducing the effective potential averaged over the pore cross section $\bar{\Phi}_\alpha = (2/R^2) \int\limits_0^R \Phi_\alpha(r)\, r\, dr$, where the

subscript α refers to some component of the solution. Using for an isotropic thin-pore body also the mean concentration across the pore C_α and the diffusion coefficient D_α, one can reduce the problem of solution flow to a one-dimensional problem. The stationary flow of component α (in the absence of an electric field) can be found by solving the Nernst-Planck equation for convective diffusion of dissolved material molecules in the field of surface forces:

$$J_\alpha = C_\alpha v - D_\alpha \left(\frac{\partial C_\alpha}{\partial x} + C_\alpha \frac{\partial \overline{\Phi}_\alpha}{\partial x} \right) = \text{const.} \tag{5}$$

The solution of these equations, under conditions in which the output at the porous body occurs with constant outflowing solution with concentration C_0, leads to the following expression for the outflowing solution concentration C_f [32]:

$$C_f = \frac{C_0}{1 + (\exp \overline{\Phi}_\alpha - 1)[1 - \exp(-vl/D_\alpha)] \exp(-v\delta/D_0)}, \tag{6}$$

where δ is the width of the laminar sublayer at the output of the porous body, being a decreasing function of the mixing intensity.

As seen from this equation, for $\overline{\Phi}_\alpha > 0$ the concentration of outflowing solution is lowered, which corresponds to negative adsorption of the dissolved material, while for $\overline{\Phi}_\alpha < 0$ it is enhanced, corresponding to positive adsorption. In the equilibrium state (when $v = 0$) the concentrations due to diffusion are equated, and $C_f = C_0$. The same situation also occurs for $\overline{\Phi}_\alpha = 0$, when there is no adsorption and the solution concentration at the pore does not differ from the bulk concentration of the solution.

Calculations show that for thin-pore bodies with mean pore radius 10-20 Å the values of the effective potential are approximately $\overline{\Phi}_\alpha \leqslant 0.5$ kT for nonaqueous solutions, where the interaction is due to relatively weak dispersion forces. For aqueous solutions the values of $\overline{\Phi}_\alpha$ are higher by an order of magnitude (4-5 kT), which is related to the action of the more powerful forces of structural repulsion.

The generation of a concentration gradient during solution filtration through thin pores leads to the development in the porous body of a counter capillary-osmotic flow under the action of the generated concentration difference. This counter-flow brakes filtration, which leads to deviations from Darcy's law for solutions during their flow through a thin-pore body, where $\overline{\Phi}_\alpha \neq 0$. The resulting flow rate of the solution is obtained by the equality [32]

$$v = K_f P - K_f R_0 T \Delta C [1 - \exp(-\overline{\Phi}_\alpha)]. \tag{7}$$

The concentration difference at the pore edges ΔC, however, is not equal to $C_0 - C_f$, due to the effect of concentration polarization, leading to concentration enhancement at the output of the porous body in comparison with C_0. Calculations of the quantity ΔC, being a function of the flow rate v and of the mixing intensity of the solution, were carried out by solving Eq. (5) and finding the concentration distribution $C(x)$ in the porous body and behind it [32]. These calculations lead to the following theoretical dependences $v(P)$, shown in Fig. 2 for two different solution concentrations C_0, outflowing in a thin-pore body with mean pore radius $R = 20$ Å. In these calculations we used: $K_f = R^2/8\eta l = 2.5 \cdot 10^{-9}$ cm³/dyn·sec; $l = 0.02$ cm; $\overline{\Phi}_\alpha = 3.3$ kT; $D_\alpha = 5 \cdot 10^{-6}$ cm²/sec; $T = 300°$K; $\delta = 10^{-3}$ cm; $\eta = 0.02$ P.

As seen from Fig. 2, the effect of the counter capillary-osmotic flow leads to noticeable deviations from Darcy's law. Thus, the nonlinearity of the filtration dependence may be related to not only deformation effects of the porous body. At high filtration rates the dependence $v(P)$ becomes linear, but does not pass through the origin of coordinates, intersecting, as shown by the dotted lines, on a segment of the pressure axis equal to the osmotic pressure of an ideal semipenetrable membrane (for which $\overline{\Phi}_\alpha = \infty$): $P_0 = R_0 T \Delta C$. For low concentrations of outflowing solution the ΔC values practically coincide with C_0. This pressure P_0 can be erroneously interpreted as some dynamic limiting shear stress of the flow if the effect of capillary osmosis is not taken into account.

It is interesting to note that Eq. (7), taking into account the effect of capillary osmosis on solution filtration, coincides in form with the empirical equation (2), earlier suggested by Swartzendruber [7] for describing filtration experiments with thin-pore bodies.

Important information on structural changes of fluids in thin pores can be extracted by observing osmotic transfer of different nature, more precisely, thermoosmotic fluid flow.
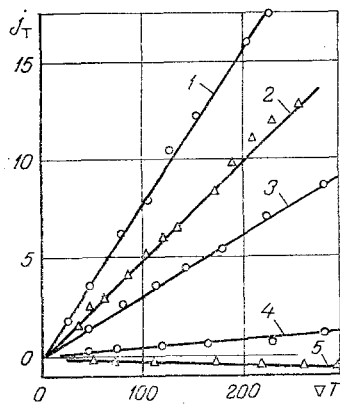
Fig. 3   Fig. 4

Fig. 3. The thermoosmosis rate j_T as a function of tempera-
ture gradient ∇T for thin-pore glasses with varying mean pore
radius: 1) R = 4.5 nm; 2) 8.3; 3) 10; 4) 55 nm; 5) 1.5 μm; j_T,
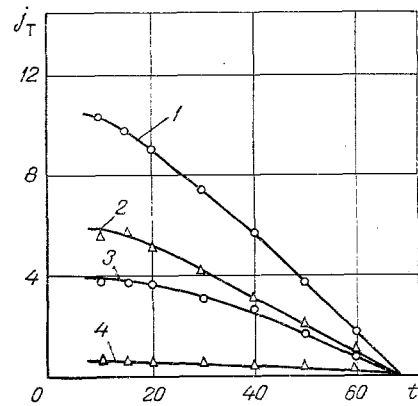10^{-9} m/sec; ∇T, 10^{-2} deg/m.

Fig. 4. Effect of mean temperature t (°C) on thermoosmosis
rate j_T (for ∇T = 1.2 deg/m) in porous glasses with varying
mean pore radii: 1) R = 4.5 nm; 2) 8.3; 3) 10; 4) 55 nm. j_T,
10^{-9} m/sec.

The effect of thermoosmosis was first observed by Deryagin [34], and was explained by the
difference in specific enthalpy of boundary layers ΔH from its value for a bulk fluid. The
following expression was obtained for the coefficient of thermoosmosis [34] from calculations
of isothermal heat transport on the basis of thermodynamics of irreversible processes:

$$\chi = -\int_0^\infty \frac{\Delta H (y) \, y dy}{\eta (y)}, \text{ cm}^2/\text{sec}, \tag{8}$$

determining the rate of thermoosmotic transport:

$$j_T = \chi \frac{\nabla T}{T}, \text{ cm/sec}. \tag{9}$$

Equation (8) was written for a wide pore, when the width of boundary layers with varying
specific enthalpy is much smaller than the pore width. The coordinate y in Eq. (8) is meas-
ured from the normal of the solid wall.

In thin pores, where the boundary layers overlap, to integrate Eq. (8) (since the shapes
of the functions $\Delta H(y)$ and $\eta(y)$ were earlier unknown) one may use another simplifying assump-
tion [35]. Introducing the mean values over the thin-pore cross section $\overline{\Delta H}$ and $\overline{\eta}$, we obtain
the following expression for a slit pore:

$$\chi = -\frac{2h^2\overline{\Delta H}}{3\overline{\eta}}. \tag{10}$$

This equation makes it possible to estimate the change in the specific enthalpy $\overline{\Delta H}$ from rate
measurements of the thermoosmotic flow j_T, knowing the mean pore size h and the mean fluid
viscosity in a thin slit pore η.

Figure 3 shows measurement results of the thermoosmosis rate j_T as a function of the
temperature gradient ∇T for five samples of porous glasses with varying mean pore radius
(from 45 Å to 1.5 μm) [35, 36]. The experimental dependence $j_T(\nabla T)$ is in good agreement with
the theoretical values from Eq. (9). The magnitude and sign of the thermoosmosis coefficient
χ depend on the pore size. In wide pores, where the boundary layers do not overlap (line 5),
the thermoosmotic flow is directed toward the hot side ($\chi > 0$). This corresponds to lowering
of the specific enthalpy of identical boundary layers of water ($\Delta H < 0$), i.e., enhancement of
the mean energy of intermolecular hydrogen bonds. In thinner pores the thermoosmotic flow
is directed toward the cold side ($\chi < 0$), which corresponds (on the average) to enhancement of

the specific enthalpy of water in thin pores. The negative χ values and, correspondingly, the positive ΔH values increase with decreasing pore size. This result can be explained by the progressive destruction with boundary-layer overlap in intermolecular binding in water in the overlap zone. The weakening of intermolecular hydrogen bonds in water, found in thin pores of polymer membranes and clays, was verified by IR [37] and NMR [38] spectroscopic methods.

The changes in specific enthalpy ΔH, obtained in experiments with thin-pore glasses, vary in order of magnitude from 10^{-3} to 10^{-1} cal/mole. They are very small, e.g., in comparison with the specific melting heat of ice-1, equal to 1440 cal/mole. This implies that very small changes in the structure of water under the influence of surface forces are sufficient for organizing measurements of thermoosmosis rates.

As seen from Fig. 4, j_T values drop with increasing mean temperature, which implies thermal destruction of the peculiar structure of water in thin pores. At a temperature above 65-70°C no thermoosmotic flow is registered: $j_T = 0$.

The same comclusion also follows from analyzing measurement results of filtration rates of water at varying temperatures (see Fig. 1). Comparing the slopes of the straight lines $v(P)$ on this figure, proportional to the mean viscosity of water $\bar{\eta}$ in thin pores, it can be discovered that the η values decrease faster with increasing temperature than the corresponding values of the bulk viscosity of water.

The breakdown of boundary layers of water may be generated not only by heating, but also by enhanced electrolyte concentration. Total breakdown occurs, e.g., at a KCl concentration near 20 mass % [2]. Hydrophobization of surface pores [35] leads to the same destruction of the peculiar structure of water in thin pores, determined by the cessation of thermoosmosis.

When the pore moisture contains an electrolyte, the results of thermoosmosis measurements can be distorted by the effect of electroosmotic flow, generated under the action of the thermal diffusion potential [39, 40]. In the general case the effect of a surface charge can provide an additional contribution to the effect of proper thermoosmosis, since polarization of water molecules in the electric field of the sublayer also leads to a change in the specific enthalpy of the fluid in the DEL zone [41]. However, this contribution to the ΔH values in hydrophilic porous bodies is usually significantly smaller than the contribution due to structural changes of the boundary layers of water.

The χ values for water in experiments with thin-pore glasses ($R \leqslant 550$ Å) were of the order of $-(10^{-6}-10^{-7})$ cm^2/sec. Similar values in order of magnitude $\chi = -10^{-7}$ cm^2/sec were obtained for water in acetate cellulose membranes [42], where, as in the case of porous glasses, there was no noticeable effect of the thermodiffusion potential. For aqueous solutions of an electrolyte, in connection with the generation of thermodiffusion potentials and DEL polarization effects, the χ values vary within very wide limits; their sign and magnitude depend on the temperature gradient [42, 43]. In clays the interpretation of thermoosmotic measurements is rendered complicated not only by the presence of electrolytes, but also by the nonlinearity of filtration characteristics [44], related, as can be expected, with deformation processes of the porous structure. In many systems, even thin-porous, thermoosmosis generally cannot be observed [45], if their surface is insufficiently hydrophilic for creating boundary layers of substantial attraction and with a sufficient amount of structural changes.

As follows from this review, the action of surface forces, leading to formation of structurally changed boundary layers of the solvent and diffuse layers of ions and neutral molecules, substantially changes the pattern of filtration in thin pores in comparison with the flow in wide-pore bodies. In a number of cases one succeeds in carrying out a theoretical refinement of the equations of mass transfer with account taken of the electric field, concentration, and temperature gradient generated during the fluid flow.

A large amount of experimental data has been accumulated concerning the physical properties of fluids in thin pores [1]. Thus, e.g., it was shown that the viscosity of water increases with decreasing pore size. Deviations of the viscosity of water from the bulk values η_0 start being felt at capillary radii less than 0.5 μm. However, most deviations of the water viscosity in thin pores do not exceed $(1.6-1.8)$ η_0. Still smaller is the scale of variation of water density: in pores with a mean radius around 50 Å, the density of water is enhanced by approximately 1.5%. In still thinner zeolite micropores the enhancement in water density reaches 7-10% [46].

The presence of dissolved molecules and ions substantially complicates the pattern of fluid flow in thin pores. This generates the necessity of further experimental studies, initially on model systems, as well as of developing theories which take into account the effect of surface forces on the kinetic characteristics and transport mechanisms of the components of a porous solution.

NOTATION

v, filtration rate; K_f, filtration coefficient; P, pressure gradient; $1/\varkappa$, Debye radius of the DEL; h, width of a planar pore; ρ, fluid density; η, fluid viscosity; k, Boltzmann constant; T, temperature; C, concentration; r, radial coordinate; R, pore radius; x, coordinate in the fluid flow direction; l, thickness of a porous body; D_0, diffusion coefficient of the dissolved material in a bulk solution; R_0, gas constant; ∇T, temperature gradient.

LITERATURE CITED

1. B. V. Derjaguin and N. V. Churaev, "Structure of the boundary layers of liquids and its influence on the mass transfer in fine pores," in: Progress in Surface and Membrane Sci., 14, 69-130 (1981).
2. V. I. Lashnev, V. D. Sobolev, and N. V. Churaev, "Viscosity of fluids in pores of separating membranes," Teor. Osn. Khim. Tekhnol., 10, 926-930 (1976).
3. N. E. Khadakhane, V. D. Sobolev, and N. V. Churaev, "Filtration of water through porous glass membranes," Kolloidn. Zh., 42, 911-916 (1980).
4. N. F. Bondarenko, Physics of Motion of Underground Water [in Russian], Gidrometeoizdat, Leningrad (1973).
5. S. P. Li, "Measuring extremely low flow velocity of water in clay," Soil Sci., 95, 410-415 (1963).
6. R. I. Miller and P. F. Low, "Threshold gradient for water flow in clay systems," Soil Sci. Soc. Am. Proc., 27, 605-609 (1963).
7. D. Swartzendruber, "Modification of Darcy's law for the flow of water in soils," Soil Sci., 93, 22-29 (1962).
8. D. A. Russell and D. Swartzendruber, "Flux-gradient relationships for saturated flow of water through mixtures of sand, silt, and clay," Soil Sci. Soc. Am. Proc., 35, 21-26 (1971).
9. E. C. Childs and E. Tzimas, "Darcy's law and small potential gradients," J. Soil Sci., 22, 319-327 (1971).
10. H. W. Olsen, "Darcy's law in saturated kaoline," Water Resources, 2, 287-295 (1965).
11. R. D. Jackson, "Osmotic effects on water flow through a ceramic filter," Soil Sci. Soc. Am. Proc., 31, 713-715 (1967).
12. V. Novak, Vodohosp. Casopis, 20, 213-233 (1972).
13. H. W. Olsen, "Hydraulic flow through saturated clays," Clays and Clay Minerals, 11, 131-142 (1962).
14. V. Novak, "Hysteresis of flux-gradient relations for saturated flow of water through minerals," J. Soil Sci., 23, 248-258 (1972).
15. V. A. Nelidov, "Reasons for generation of 'effective' porosity in granular media," Inzh.-Fiz. Zh., 21, 1017-1023 (1971).
16. R. Skawinski and A. Lasowska, "Non-Darcian flow of water solutions in an artificial porous medium," Bull. l'Acad. Polonaise Sci., Ser. Sci. Tech., 22, 235-238, 307-311 (1974).
17. L. M. Simuni, "Numerical solution of the problem of fluid motion in a rectangular well," Zh. Prikl. Mekh. Tekh. Fiz., No. 6, 106-108 (1965).
18. V. S. Golubev, "Equation of motion of a fluid in a porous medium with stagnant zones," Dokl. Akad. Nauk SSSR, 238, 1318-1321.
19. R. P. Gupta and D. Swartzendruber, "Flow-associated reduction on the hydraulic conductivity," Soil Sci. Soc. Am. Proc., 26, 6-10 (1962).
20. A. Poulovassilis, "The changeability of the hydraulic conductivity of saturated soil samples," Soil Sci., 113, No. 12, 81-87 (1972).
21. N. V. Churaev, "Effect of structure-formation processes on water filtration in disperse systems," Kolloidn. Zh., 25, 718-723 (1963).
22. G. A. Nikitin, "Some features of fluid flow through a clearance of microscopic size," Izv. Vyssh. Uchebn. Zaved., Aviats. Tekh., No. 4, 38-45 (1965).
23. A. T. J. Hayward and J. D. Isdale, "Rhelogy of liquids near a solid wall," Brit. J. Appl. Phys., D2, 251-259 (1969).

24. N. V. Churaev and B. V. Deryagin, "Theory of electrokinetic effects in thin layers of electrolyte solutions," Dokl. Akad. Nauk SSSR, 169, 396–399 (1966).
25. C. L. Rice and R. Whitehead, "Electrokinetic flow in a narrow cylindrical capillary," J. Phys. Chem., 69, 4017–4022 (1965).
26. S. S. Dukhin, Electric Conductivity and Electrokinetic Properties of Disperse Systems [in Russian], Naukova Dumka, Kiev (1975).
27. P. F. Low, "Nature and properties of water in montmorillonite–water systems," Soil Sci. Soc. Am. Proc., 43, 651–658 (1979).
28. A. V. Dumanskii, Lyophility of Disperse Systems [in Russian], Izd. Akad. Nauk Ukr. SSR, Kiev (1960).
29. Yu. I. Dytnerskii, Inverse Osmosis and Ultrafiltration [in Russian], Khimiya, Moscow (1978).
30. B. V. Deryagin, G. P. Sidorenkov, E. A. Zubashchenko, and E. V. Kiseleva, "Kinetic effects in boundary fluid films," Kolloidn. Zh., 9, 335–348 (1947).
31. B. V. Deryagin and N. V. Churaev, "Disjoining pressure in thin layers of binary solutions of nonpolar fluids," Dokl. Akad. Nauk SSSR, 222, 554–556 (1975).
32. G. A. Martynov, V. M. Starov, and N. V. Churaev, "Theory of membrane separation of solutions," Kolloidn. Zh., 42, 489–499, 657–664 (1980).
33. B. V. Derjaguin, I. E. Dzyaloshinski, M. M. Koptelova, and L. P. Pitajevskij, "Molecular surface forces in binary solutions," Disc. Faraday Soc., 40, 246–252 (1965).
34. G. V. Deryagin and G. P. Sidorenkov, "Thermal osmosis at ordinary temperatures," Dokl. Akad. Nauk SSSR, 32, 622–628 (1941).
35. P. A. Voznyi and N. V. Churaev, "Thermoosmotic flow of water in porous glasses," Kolloidn. Zh., 39, 264–270, 438–443 (1977).
36. P. A. Voznyi, V. P. Dushchenko, and N. V. Churaev, "Thermoosmotic flow of water in porous glasses," in: Surface Forces in Thin Films [in Russian], Nauka, Moscow (1979), pp. 109–113.
37. C. Toprak, J. N. Agar, and M. Falk, "State of water in cellulose acetate membranes," JCS Faraday Trans. I, 75, 803–815 (1979).
38. V. V. Mank, Z. E. Suyunova, Yu. I. Tarasevich, and F. D. Ovcharenko, "Study of states of water in disperse Li- and Na-montmorillonite by the NMR method," Dokl. Akad. Nauk SSSR, 202, 117–121 (1972).
39. C. W. Carr and K. Sollner, "New experiments on thermoosmosis," J. Electron. Soc., 109, 616–622 (1962).
40. Y. Kobatake and H. Fujuta, "Osmotic flows in charged membranes," J. Chem. Phys., 41, 2963–2970 (1964).
41. N. V. Churaev, B. V. Deryagin, and P. P. Zolotarev, "Thermoosmosis of electrolyte solutions in porous bodies," Dokl. Akad. Nauk SSSR, 183, 1139–1143 (1968).
42. M. P. Dariel and O. Kedem, "Thermoosmosis in membranes," Isr. At. Energy Commis., No. 1262, 105–110 (1971); J. Phys. Chem., 79, 336–342 (1975).
43. J. W. Lorimer and S. R. Chan, "Thermoosmosis in ion-selective membranes," Preprint Int. Symp. Macromol., Helsinki (1972), Vol. 3, Sec. 2, p. 219.
44. R. C. Srivastava and A. K. Jain, "Thermoosmosis of water through bentonite," Indian J. Chem., 12, 1276–1279 (1974).
45. J. Reekie and J. Aird, "Flow of water through very narrow channels," Nature, 156, 367–368 (1945).
46. B. Kh. Rakhmukov, I. I. Seliverstova, V. V. Serpinskii, and A. A. Fomkin, "Adsorption on a microporous adsorbent," Izv. Akad. Nauk SSSR, Khim., No. 11, 2419–2422 (1979).