If it is necessary to distinguish isolated clusters in explicit form, as well as infinite clusters, Eq. (9) for the third variation of the basic model may be used, bearing in mind that the results of the calculation will be overestimated.

NOTATION

m_1, volume concentration of the first component; m_c, threshold concentration (flow threshold); $\bar{l}_1$, $\bar{l}_2$, L, l', linear dimensions of the cluster model; S_1, S_2, S_3, S_4, ΔS, cross-sectional areas of cluster; V_{IC}, V_C, total volume and core volume of isolated cluster; Λ, conductivity of inhomogeneous medium; Λ_1, Λ_2, ν, conductivity of first and second components and their ratio; H, correction function; α, proportionality factor; σ, conductivity of elementary cell; R_i, thermal resistance of i-th section of elementary cell.

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EFFECT OF ELECTROLYTES ON THERMAL MOISTURE TRANSPORT IN CAPILLARY-POROUS MEDIA

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Experimental data on the effect of electrolytes upon thermal moisture mobility in quartz sand and cellulose are presented. The results are interpreted from the viewpoint of change in properties of moisture boundary layers.

As is well known [1], as the moisture content of a material U varies, the thermogradient coefficient $\delta = dU/dT$ passes through a maximum, corresponding to the greatest mobility of moisture acted upon by a temperature gradient. As $U \to 0$ the moisture mobility decreases due to an increase in the binding energy of surface forces, while as $U \to U_0$ the possibility of change in mass content dU under the action of dT decreases. Thus, for example, at $U = U_0$ only thermal circulation of the mass is possible, with no redistribution over the body volume ($dU = 0$), which corresponds to $\delta = 0$. Moreover, with increase in U there is a decrease in the liquid–gas interface surface, which determines thermal moisture transport under the influence of a surface tension gradient $\partial\sigma/\partial T$. The latter induces a flow of capillary moisture caused by a capillary tension gradient, as well as a film thermocapillary flow.

Thus, the largest values of δ correspond to a liquid state in a porous body in which the pores are not completely filled by moisture and there is a sufficiently developed liquid–gas

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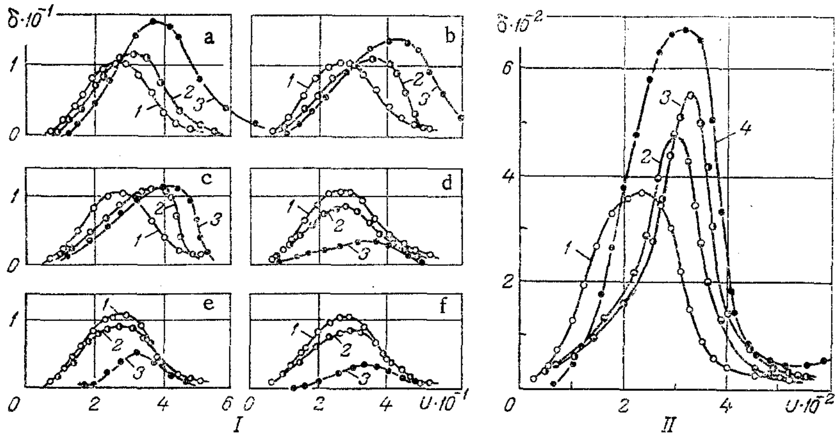

Fig. 1. Effect of electrolyte nature on moisture content U (kg/kg) dependence of thermogradient coefficient δ(deg^{-1}) for cellulose (ρ = 500 kg/m^3, U_i = 0.3 g/kg) (I) and quartz sand ($U_n = 3 \cdot 10^{-2}$) II): I) electrolyte concentration: 1) C = 0; 2) 0.01, 3) 0.1 mole/liter; a) KOH, b) NaOH; c) LiOH; d) KCl; e) LiCl; f) NaCl; II) electrolyte concentration: 1) C = 0.1 mole/liter; a) water; 2) LiOH; 3) NaOH; 4) KOH.

interface to which there is applied a tangential shear stress $\tau = \partial\sigma/\partial T$, producing a liquid flow. In the case of incomplete filling of the pore space by moisture the capillary liquid usually is divided by short film segments (due to inhomogeneity in pore size). The maximum value of the coefficient δ will then depend on the thermal mobility of these segments. Therefore measurement of δ values for pore solutions of various compositions is important in the study of thermal moisture transport mechanisms in porous bodies.

Experiments were performed with quartz sand (0.1 — 0.25 mm fractions) and cellulose strips of color photographic print paper (3 × 16 cm) in a stack 0.5 cm high. The sand was washed with 0.1 N HCl solution, followed by lengthy rinsing in distilled water (until a neutral reaction was obtained).

The specimen materials were placed in planar cassettes providing a moisture barrier to the surrounding medium. The studies of thermal moisture transport were then carried out with the equipment described previously in [2].

The sand was wetted by spraying with a solution V = (2.5•Y) ml per 100 g of dry material, where $Y = V_1/V_0$ is a coefficient characterizing the change in volume of distilled water V_0 upon solution therein of a corresponding quantity of salts V_1. The sand was then carefully mixed and placed in the cassettes.

The cellulose was wetted by solutions which were dripped from a micropipette uniformly over the surface of the paper strips. The strips were then rapidly stacked into a pile, pressed, and placed in the cassettes. The initial moisture content U_i and dry material content were the same in all experiments. Only the electrolyte composition and concentration were varied.

The cassettes with sand were maintained at room temperature for 24 h, those with cellulose, 96 h, in order to establish equilibrium moisture distribution over the material volume. Then the cassettes were maintained in a temperature field with constant gradiant dt/dX = 1 deg/cm for 30 days. As the observations of [2] revealed, such a period is sufficient to establish a steady-state moisture distribution in the specimens.

The values $\delta = DU/dT = (dU/dX)/(dT/dX)$ were found by graphical differentiation of curves of U(X), the moisture distribution over specimen length. Measurements were repeated 3-4 times.

Figure 1 I shows δ(U) curves obtained for cellulose. The curves numbered 1 in all graphs are for experiments with pure water, while curves 2 and 3 represent increasing electrolyte concentrations. As is evident from the figure, in alkaline media (Fig. 1 I, a, b, c) the values generally increase. This can be explained by ion-electrostatic stabilization

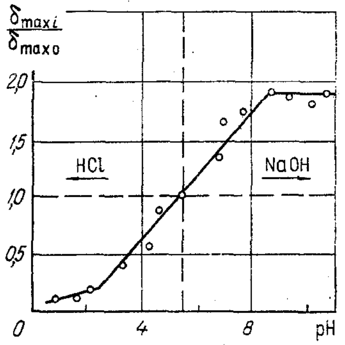

Fig. 2

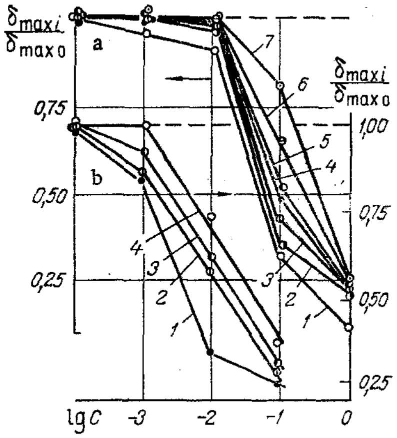

Fig. 3

Fig. 2. Effect of pH of dispersed quartz sand medium ($\rho = 1650$ kg/m^3) on maximum value of thermogradient coefficient δ(deg^{-1}).

Fig. 3. Maximum value of quartz sand thermogradient coefficient δ(deg^{-1}) versus electrolyte concentration (mole/liter) in dispersed medium: a) $U_i = 2.5 \cdot 10^{-2}$ kg/kg; 1) HCl; 2) KI; 3) KBr; 4) KCl; 5) NH_4Cl; 6) NaCl; 7) LiCl; b) $U_i = 3 \cdot 10^{-2}$ kg/kg; 1) $AlCl_3$; 2) $Al_2(SO_4)_3$; 3) $CaCl_2$; 4) $Ca(NO_3)_2$.

of the wetting films. The increase in their thickness with increase in pH is due to increase in negative electrical potential of the cellulose surface due to adsorption of potential-determining OH^- ions [3].

Increase in concentration of a neutral electrolyte (Fig. 1 I, d, e, f), as is well known, leads to a reduction in the cellulose surface potential due to decrease in the Debye radius of the diffuse ionic atmosphere. The reduction in wetting film thickness which this causes (with approximately the same moisture content, since the capillary moisture volume remains practically constant) leads to a reduction in film mobility and decrease in δ. The results obtained agree well with known data on the effect of electrolytes on wetting film thickness [4, 5].

In all cases the position of the δ maximum shifts toward higher moisture content with increased electrolyte concentration. However the reasons for this are different in alkaline and neutral solutions. With increase in wetting film thickness, the amount of moisture coresponding to separation of capillary menisci by films or the state of maximum thermal conductivity increases. Therefore, increase in pH should shift the point δ_{max} toward higher U. In the case of neutral solutions, to maintain high thermal conductivity of the film as it decreases in thickness (with increased electrolyte concentration), it is necessary to increase the moisture content, thus decreasing the length of the film segments separating the capillary moisture.

As is evident from Fig. 1 II, similar results were obtained for quartz sand. In alkaline media δ increased markedly due to increase in wetting film thickness. This is shown especially clearly by Fig. 2, which shows the ratio $\delta_{max\ i}/\delta_{max\ o}$ as a function of pH of the pore solution for a sand fraction <0.1 mm. Here $\delta_{max\ o}$ is the maximum δ value obtained in experiment with distilled water having a pH = 5.5. The pH of the pore solution was changed by introducing NaOH or HCl into the water used to wet the sand.

The stabilization of $\delta_{max\ i}$ values at pH > 8 can be explained by competition between two processes: increase in the negative potential of the surface due to adsorption of OH^- ions and concentration depression due to increasing ionic force of the solution. Addition of acid reduces the value of the thermogradient coefficient almost to zero when the quartz surface reaches an isoelectric state at pH = 2 [6], where the wetting film thickness decreases abruptly.

Figure 3 shows the effect of concentration of various electrolytes on the value of the ratio $\delta_{max\ i}/\delta_{max\ o}$. It is evident form the figure that the $\delta_{max\ i}$ values begin to fall sharply at electrolyte concentrations above 10^{-2} mole/liter (Fig. 3a), where there is a fall in the quartz surface potential. With increase in ionic charge (Fig. 3b) the drop in δ occurs at lower electrolyte concentration ($C \geq 10^{-4}$ mole/liter). Multivalent ions reduce the quartz surface potential and wetting film thickness significantly more intensely at the same concentration. Thus, the trivalent ions Al^{+3} (Fig. 3b, curves 1, 2) reduce δ more than the bivalent ions (Fig. 3b, curves 3, 4).

Thus, the studies performed have established a good correlation between values of the coefficient δ and electrolyte composition. The similarity observed in the dependence of δ on concentration and pH of the pore solution, on the one hand, and on wetting film thickness, on the other, confirms the proposition that thermal mobility of moisture with material pore space not completely filled is determined by the mobility of wetting films which separate the capillary moisture. This indicates possible methods of controlling thermal moisture transport in a required direction by adding electrolytes.

High thermal mobility of moisture in the pore space can be achieved at a high film thickness, which requires creation of the highest possible potentials of identical sign on the film surfaces bordering the solid and gas phases [7]. The use of surfactants opens up especially broad possibilities, since they manifest a selective capability for intensive adsorption levels. To produce high thermal moisture mobility with incomplete saturation of the porous body, use of ionogenic surfactants is preferable [2].

NOTATION

U_0, U_i, material moisture content for complete filling of pores by moisture, and initial moisture content; $\delta_{\max i}$, $\delta_{\max o}$, maximum values of thermogradient coefficient in experiment with electrolytes and with distilled water; σ, surface tension; T, temperature; τ, tangential shear stress; V_0, V_i, distilled water volume before and after solution of electrolyte; Y, coefficient describing water volume change upon electrolyte solution; X, longitudinal coordinate; C, concentration; pH, negative log of hydrogen ion concentration in medium; ρ, density of dry substance in unit volume of moist substance.

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