

MASS TRANSFER AND OSMOTIC PHENOMENA IN SWOLLEN ORGANIC SUBSTANCES

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The mechanisms of mass transfer under the action of the hydrostatic-pressure, temperature, and dissolved-salt concentration gradients and electroosmosis in swollen heterogeneous organic materials have been considered. Mass transfer is similar to the migration of water and solutes in ordinary solutions and represents discrete translational displacements of particles. It is accompanied by ion-exchange processes and leads to a change in the structure of the material.

Introduction. Many swollen organic substances are heterogeneous gels. They represent concentrated aqueous solutions of high-molecular compounds, their complexes (associates), and mineral components of different dispersity. Gels differ substantially from dispersions of solid particles. Among them are foodstuffs (in particular, starch and gelatin), some polymers, peat, and other materials. Most of them do not have continuous channels-capillaries.

When solutions are transported through columns with a swollen gel, the solutes interact with its organic and mineral ingredients. All these ingredients are bonded by intermolecular bonds and form a spatial matrix (skeleton) of the organic substance. The ordered structures are organic crystals, and the disordered structures constitute the amorphous parts of the gel. The disordered macromolecules have a higher conformation mobility than the molecules in the crystals.

Pure water consists of ordered associates ("flickering groups" and clusters) and "unbound" molecules. Clusters in a gel cannot move readily. In it, there is no continuous (molar) liquid motion and there take place discrete translations of an aggregation of its most weakly bound molecules [1].

An increase in the temperature of a gel increases the number of unbound molecules in it. The number of unbound molecules also increases under the action of external force fields. Some hydrogen bonds between the water molecules in the clusters break under the action of an external pressure, with the result that the number of unbound molecules and, accordingly, the liquid flow (in the case where there are pressure gradients) increase.

In acid and salt solutions, water molecules form hydration sheaths around the ions and become dynamically bound. The number of bound water molecules increases with increase in the concentration of solutes.

Physical-Mathematical Model. External water molecules diffused into the matrix of an organic substance interact with the main-chain links. Some water molecules are sorbed on the polar groups of macromolecules. The main part of the absorbed water represents an osmotic moisture. It "expands" the matrix network at the expense of the osmotic pressure and thus causes swelling of the gel. The osmotic moisture is entropically bound.

In the case of mixing, the molar increment of the entropy is equal to

$$\Delta S_{\text{mix}} = -R \sum_{i=1}^m n_i \ln N_i. \quad (1)$$

The value of $\Delta S_{\text{mix}} > 0$ is mainly dependent on the ratio between the first and second components. In the case where the moisture content is low ($i = 1$) or the dissolution of the organic substances is infinitely high ($i = 2$), the increment of the molar entropy ΔS_{mix} tends to zero. ΔS_{mix} has a maximum value at a certain ratio between these components.

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The processes of swelling and absorption of substances occur until the osmotic pressure is compensated by the elastic stresses arising in the spatial structure of the matrix.

At a high moisture content and constant values of the external (barometric) pressure and temperature, the change in the Gibbs potential for a mole of the solvent can be written as

$$\Delta G = \Delta H - T\Delta S = RT \ln (p/p_s) . \quad (2)$$

The process of swelling is not accompanied by heat release [2]; this being so, the change in the molar enthalpy $\Delta H = 0$. Assuming that $\Delta S = \Delta S_{\text{mix}}$, we obtain a formula for calculating the intramatrix osmotic pressure

$$\pi = -\Delta G/V_0 = (T/V_0) \Delta S_{\text{mix}} = (RT/V_0) \ln (p_s/p)^{*}) . \quad (3)$$

The osmotic pressure can reach several hundred atmospheres [3], which is much higher than the capillary pressure. The water found in the macropores between the macromolecular associates and mineral particles in an organic substance can be considered as its capillary moisture. It is directly related to the osmotic moisture, and the latter is related to the sorbed moisture.

In swollen hydrophilic materials dissociation of functional, polar groups occurs. Ion exchange arises when the extramatrix acid or salt solution is changed. As a result of these processes, the composition of the ions absorbed by the material, its structure and volume, the moisture content in it, and the form of the bound moisture are changed [4, 5].

The dissociated functional groups (bound anions) found on the macromolecules composing the matrix of a gel and the mobile cations are hydrated once the dissociation is completed [6]. Since the matrix is a three-dimensional "sieve," the movement of hydrated ions through the gel depends on the size of the pores. If this size is smaller than the diameter of a hydrated ion or the degree of connectivity of the water molecules inside the pores is high, the movement of ions decreases sharply or terminates completely. This makes it possible to remove solutes from the water by passing a solution through fine-pored membranes under pressure (reverse osmosis).

In investigating the process of electroosmotic transfer in heterogeneous organic gels, their features must be taken into account.

1. A capillary model is inapplicable to an aggregation of swollen contacting particles and bound associates of macromolecules; in such materials there are no through pore channels; at the sites of connection of associates, cations of the diffuse shells move to the intraassociate solutions of contacting particles due to the electrostatic repulsion, and the boundary potential at the points of contact decreases to zero; in the system of these contacting particles, cations migrate in the direction of the external electric field vector to the cathode.

2. Because of the high field strength at the associate-external solution boundary ($E_b \sim 10^8$ V/m [7]), the transfer of cations along the normal to the part of the outer contour of an associate, where there is no contact with other associates, does not readily occur.

3. In the system of bound macropores, if any, ions of both signs are transferred in the same manner as in a plating bath.

4. The process of ion transfer is accompanied by ion exchange and causes a change in the resistance of the sample along its length where electroosmosis occurs [8, 9].

The solid ingredients present in a gel decrease the flow section δ . The solvent molecules are scattered on these ingredients in the process of translations. The water molecules found within the associates have a certain energy of binding to the material. Therefore, the potential barrier for translations of water molecules and ions is higher in gels than in ordinary solutions.

An expression for the diffusion coefficient in a swollen gel has the form

$$D = (\delta a^2 / 6\tau_0) \exp (-W/RT) . \quad (4)$$

*) It is the authors' opinion that the calculation of the osmotic pressure by formula (3) is more general as compared to the calculation presented, for example, in [2] (see Vol. 1, p. 244). The Van't Hoff and Raoult relations for diluted solutions follow from it (see below).

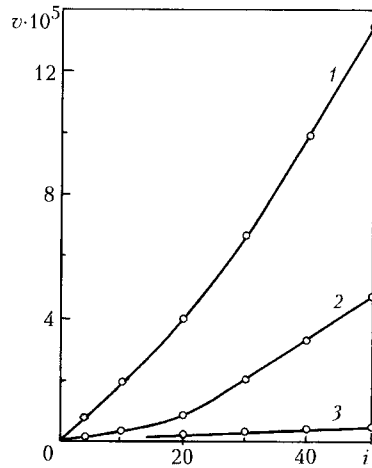


Fig. 1. Dependence of the rate $v \cdot 10^5$ of mass transfer on the pressure gradient i in the sedge peat at a porosity of 0.913 (1), 0.909 (2), and 0.872 (3). v , cm/sec.

A one-dimensional equation of moisture transfer can be written as

$$q_1 = -\gamma_0 \frac{d(Du)}{dx}. \quad (5)$$

Taking into account Eq. (4) and performing differentiation, we bring the equation of a liquid flow to the form

$$q_1 = -D\gamma_0 \left[\frac{du}{dx} - \frac{u}{RT} \left(\frac{dU}{du} \frac{du}{dx} - \frac{U}{T} \frac{dT}{dx} \right) \right]. \quad (6)$$

In the case where there are pressure drops along the length of a gel sample, there arises filtrational mass transfer of liquid, which will be represented as

$$q_2 = -k dP/dx. \quad (7)$$

The coefficient of mass transfer k changes along the length of the sample because of the inhomogeneous compressive deformation and compaction of the skeleton (matrix) of the gel and the partial destruction of the associates of water molecules. As a result of these processes, the diffusion coefficient (4) changes because of the irregular decrease in the values of a and δ along the length of the sample. In practical calculations, the value of k is averaged along the entire length of the sample. The pressure drop is considered only in relation to the moisture transfer without regard for the change in the water and gel structure and the water permeability of the gel under the action of this pressure.

Results and Discussion. The experiments were conducted on a setup making possible separate and simultaneous investigation of filtrational mass transfer under the conditions of thermal moisture transfer, salt osmosis, and electroosmosis [10, 11]. A gel sample of length 4 cm and cross section 16.5 cm^2 was positioned in a metallic cylindrical housing, to both faces of which additional chambers filled with water were connected. The necessary head difference was formed by changing the levels of the liquid in the funnels connected to the right and left reservoirs by flexible hoses. Equal or different temperatures in them were maintained with the use of two thermostats. For investigation of electroosmosis, the current from a universal current source was supplied to the spiral, wire platinum electrodes installed in the additional reservoirs. Liquid flows were measured with the use of flow meters or measuring capillary tubes connected to the additional chambers.

Distilled water was filtrated through the gel sample. Experiments were begun when the ionic and dispersion equilibrium was established within the gel sample, which was attained after 10–20 days of filtration of distilled water through the sample. The rate of liquid flow and the acidity index pH were stabilized during this period. In this case, cations Na^+ , K^+ , Mg^{2+} , and Ca^{2+} of total concentration 5.5 mg/liter and anions Cl^- , $(\text{HCO}_3)^-$, and $(\text{SiO}_2)^{2-}$, corre-

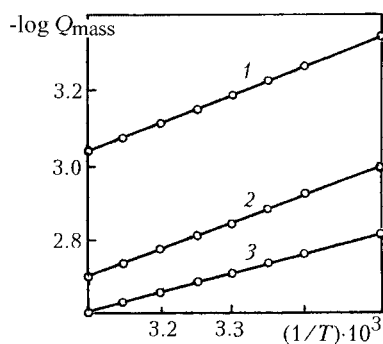


Fig. 2. Dependence of the mass-transfer flow logarithm $\log Q_{\text{mass}}$ ($Q_{\text{mass}} \cdot 10^3$ cm³/sec) on the reverse temperature $(1/T) \cdot 10^3$ (K⁻¹) for the peat (1), humified soil (2), and pure quartz sand (3).

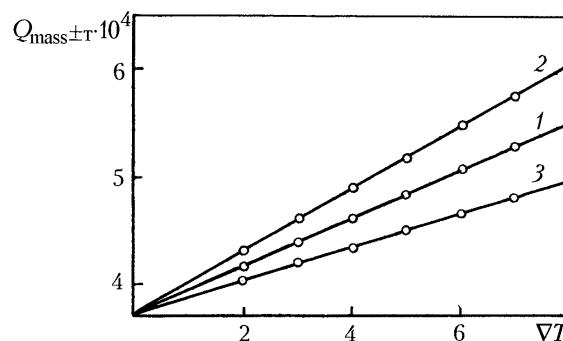


Fig. 3. Dependence of the mass-transfer flow $Q_{\text{mass}} \cdot 10^4$ in the gel on the temperature gradient ∇T at a pressure gradient $i = 3$ (1) and in the case of existence of parallel $Q_{\text{mass+th}} \cdot 10^4$ (2) and antiparallel $Q_{\text{mass+th}} \cdot 10^4$ (3) thermal transfer of moisture. Q_{mass} , $Q_{\text{mass+th}}$, cm³/sec; ∇T , K/cm.

sponding to the above cations in total charge, were left in the filtrate. For investigation of salt osmosis, a salt solution was filled in one of the additional chambers.

The investigation object was a mechanically dispersed, swollen valley sedge peat with a degree of decomposition of 30–35%, ash content of 3.7%, and number of absorbed cations of 1.29 mg-eq/g of dry basis. Cations of calcium (1.09 mg-eq/g of dry basis), sodium, potassium, magnesium, iron, and aluminum were present in the absorbed complex.

On the graphs of the rate of mass transfer of water v through the peat-gel sample versus the pressure gradient i (Fig. 1) there is a nonlinear portion corresponding to small values of $i < 20$. The rate of mass transfer v was calculated as the ratio of the mass-transfer flow Q_{mass} to the cross section of the sample F , and the pressure gradient was calculated by the formula $i = (H_1 - H_2)/l$.

At $i < 20$, the gel is compressed and the water structure has failed. Only a small part of the applied pressure is transferred to the unbound water molecules, with the result that they execute translations in the direction from higher to lower pressure. As the matrix (skeleton) of the gel densifies at the expense of the absorbed gas phase, its resistance to the external pressure increases and the main part of the pressure difference applied to the faces of the sample is transferred to the liquid. As a result, the failure of clusters intensifies and the number of translations of unbound water molecules in the gel sample increases.

At $i > 20$, the swollen gel is consolidated and the compression of the matrix is terminated. In this case, the applied pressure difference is transferred predominantly to the liquid. Therefore, the dependence $v = f(i)$ is linear.

The sample was additionally compressed perpendicularly to the liquid flow with the use of an outer rubber housing into the inner closed volume of which a gas was supplied under pressure. As the pressure increases to 0.1 MPa, the rate of mass transfer decreases. This decrease becomes more marked at a pressure of 0.15 MPa, which is explained by the significant compaction of the gel and, as a consequence, the decrease in the values of δ and the diffusion coefficient (4).

In Eq. (7) the coefficient $k \sim D \sim \exp [-W/(RT)]$; therefore, the experimental dependences $\log Q_{\text{mass}}(T^{-1})$ are linear for the values of i from 1 to 9 in the temperature range 293–313 K. The energy of binding of molecules together and to the polar centers of gel sorption W changes in the range 14–22 kJ/mole. As the gel is compacted, a higher activation energy is required for translations of water molecules. At a constant value of $i = 3$, the activation energies of self-diffusion of water molecules in the peat gel, humified soil, and sand are equal to 18, 16, and 14 kJ/mole, respectively, (Fig. 2). These values approximately correspond to the energy of breaking of one hydrogen bond and the energy of translations of water molecules [6].

At a constant pressure gradient ($i = 3$), the mass transfer increases linearly (Fig. 3, curve 1) with increase in the average temperature of the gel. According to Eq. (6), the diffusion coefficient (4) and the flow Q_{mass} increase with

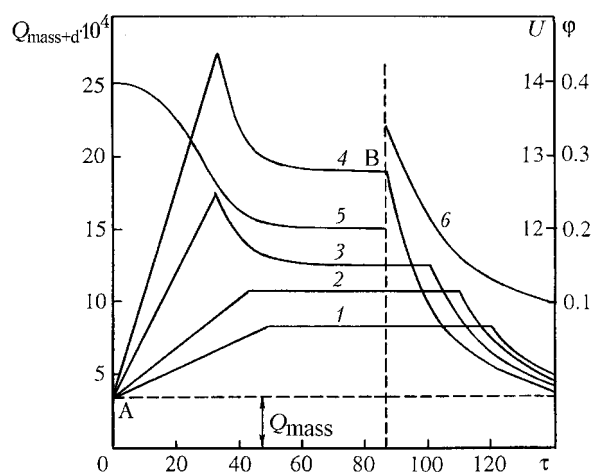


Fig. 4. Change in the total water flow $Q_{\text{mass+el}} \cdot 10^4$ under the action of the hydrostatic pressure Q_{mass} and electroosmosis Q_{el} at the values of the constant current J : 1 (1), 1.5 (2), 2.5 (3), and 5 (4), in the voltage U after switching on the current (5), and in the residual potential ϕ after switching off the current (6) with time τ [A switching on; B switching off]. τ , min; $Q_{\text{mass+el}}$, cm^3/sec ; U , ϕ , V; J , mA.

increase in the heating temperature and the temperature gradients in the sample. The experimental dependence $Q_{\text{mass}} = f(\nabla T)$ is linear in the temperature range 297–309 K. As ∇T increases (Fig. 3, curve 2), the combined flow $Q_{\text{mass+th}}$ is larger than Q_{mass} if the thermal transfer coincides in direction with the filtrational transfer and $Q_{\text{mass+th}}$ (curve 3) is smaller than Q_{mass} if they come from opposite directions to meet each other. At $\nabla T = 8$ K/cm, the flow of thermal transfer accounts for $\sim 11\%$ of Q_{mass} , which agrees with the results of earlier investigations [12].

In the experiments with salt osmosis, distilled water was filled in the left chamber and an MgCl_2 salt solution of different concentration was filled in the right chamber. The rate of osmotic transfer of moisture v is proportional to the concentration of the MgCl_2 solution. Since the rate of diffusion of solvated ions through the extremely swollen gel is much smaller than that of water molecules, the solvent is predominantly transferred at the initial stage of the process. In this case, the gel sample serves as a semipermeable membrane [2].

The increment of the entropy of mixing and the osmotic pressure at the beginning of the process are equal to zero in the left chamber and $\Delta S_{\text{mix}} > 0$ in the right chamber. At $\Delta S_{\text{mix}} \rightarrow 0$, a dynamic equilibrium is established everywhere in the system. This can be attained by decreasing the concentration of the solute in the right chamber up to zero by means of osmotic transfer (intake) of the liquid from the left chamber, in which the concentration of the solvent molecules is higher.

Let us assume that the solution in the right chamber consists of two ingredients: n_1 , water, and n_2 , inorganic solute. $n_2 \ll n_1$ for diluted solutions. Assuming that $\Delta S_{\text{mix}} \approx Rn_1 \ln [n_1/(n_1 + n_2)] = Rn_1 \ln (1 + n_2/n_1) \approx Rn_2$ in relation (1) and taking into account equality (3), we obtain the Van't Hoff–Raoult equation [2]: $\pi \approx RTn_2/V_0 = RTC_2 = (RT/V_0) \ln (p_{0s}/p_0)$. $\pi = gRTC_2$ for real solutions [2]. The osmotic coefficient g accounts for the degree of dissociation and association of the solute and solvent molecules and ions and the hydration of ions.

The flow of osmotic transfer of the solvent (and, accordingly, its velocity v) is proportional to the concentration gradient C_2/l . Consequently, v is proportional to C_2 , which is supported by the experiment [11].

The process of salt transfer is terminated when the salt concentrations in the right and left chambers and in the solution found within the associates of the sample become equal. Such a dynamic equilibrium is established during a long period of time after the ion exchange in the gel membrane is completed. This process is accompanied by amalgamation and compaction of associates, which leads to coagulation of the gel and causes a change in its structure and in the pH index of the solution. The fact that the gel structure changes substantially in the process of mass transfer is supported by the results of the experiments on filtration of distilled water as well as acid and salt solutions through the peat-gel samples [10].

The platinum electrodes positioned in the distilled water have a contact potential at the Pt–water boundary, which is due to the transfer of electrons from the metal to the environment. With an external current source, the concentration of these electrons on the anode is much smaller than on the cathode.

Electrons on the cathode are absorbed by water molecules. This process corresponds to the reaction $4\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- + 2\text{H}_2\uparrow$. The absorption of metal electrons on the cathode can occur for a long time if an equal number of electrons enter the anode.

The reaction $2\text{H}_2\text{O} - 4e^- = 4\text{H}^+ + \text{O}_2\uparrow$ proceeds on the anode if it is positioned in a neutral or an acidic medium [2]. Hydrogen nuclei (protons) interact with the surrounding water molecules and form hydroxonium ions $(\text{H}_3\text{O})^+$. As a result, an acidic medium arises in the near-anode zone at pH 3–4 according to the experiments, an alkaline medium arises in the near-cathode zone at pH 11–12, and molecules of oxygen and hydrogen, respectively, are absorbed on the electrodes. Besides the above-described mechanism of obtaining a current, free cations, as noted above, carry electric charges.

Distilled water enters the left additional reservoir, and cations are carried from the gel sample to the right reservoir. This has been established in the experiments conducted in [13]. As the concentration of cations in the right chamber increases, the osmotic transfer of water molecules through the gel sample intensifies. The outflow of cations is proportional to the current J , time t , osmotic pressure π , and, accordingly, flow Q_{el} of water migrating through the sample (gel membrane) of thickness l . Therefore, the ratio Q_{el}/J should be approximately constant, which follows from the experiments (Fig. 4).

Ions move together with their hydration sheaths and in doing so partially carry more distant water molecules. All the mobile ions acted upon by an external constant electric field add to the failure of the water structure. Under the action of the electric field, functional polar groups and water molecules are oriented and macrodipoles are formed due to the local transfer of protons along the field vector, which leads to the distortion and breaking of hydrogen bonds in the associates of water molecules. This serves to shift the dynamic equilibrium to the region where the number of unbound molecules is increased.

The larger the potential difference (and, accordingly, the current J) applied to the electrodes, the more intensive the failure of the water structure and the larger the decrease in the average energy U necessary for translations of water molecules. This is seen from the experimental graphs $\log Q_{\text{el}} = f_1(T^{-1})$ and $\log Q_{\text{mass+el}} = f_2(T^{-1})$, which are linear in the temperature range 273–313 K.

From these graphs we have determined the energies U necessary for transfer of liquid molecules in the process of electroosmosis: 9.6, 7.1, 6.7, and 6.3 kJ/mole. To these energies correspond the currents 0.5, 1, 1.5, and 3 mA. The energy necessary for filtrational transfer ($i = 3$) is equal to 18 kJ/mole. For the combined parallel filtrational-electroosmotic flow $Q_{\text{mass+el}}$, the values of U are equal to 13.4, 11.3, 10.5, and 8.4 kJ/mole at the same values of the current, respectively.

Cations reaching the cathode are neutralized. Atoms of alkaline metals (Na, for example) actively interact with water and form alkali, which dissociates into sodium ions and hydroxyls. Moreover, there appear hydrogen molecules, a part of which is apparently adsorbed on the cathode surface and the remaining part of which is carried by the electroosmotic flow from the near-cathode zone and then is dissolved in water. For this reason, the adsorption of gases on the spiral, wire platinum electrodes is small.

Hydroxyls and free anions, found in a flow migrating through the sample, move to the anode. Hydroxyls give up electrons to the anode by the following scheme: $4\text{OH}^- = 2\text{H}_2\text{O} + \text{O}_2 + 4e^-$. Oxygen molecules arising as a result of this reaction are additionally adsorbed on the anode and partially dissolved in water. Hydroxyls can also combine with hydrogen ions with the resulting formation of water molecules.

Such reactions occur when water molecules interact with ions of alkali-earth metals. The latter can form ion associates: $[\text{CaOH}]^+$, $[\text{MgCl}]^+$, and others [14]. The polyvalent ions have a higher energy of binding to the dissociated polar functional groups of macromolecules and therefore a lower degree of dissociation as compared to that of the univalent cations. The polyvalent cations are kept stronger by the matrix, and the univalent cations forced out in the process of ion exchange migrate to the cathode. Iron ions combine with free anions and also form ion associates. The interaction of Fe^{3+} with hydroxyls brings about the formation of a partially soluble compound — $\text{Fe}(\text{OH})_3$, which precipitates out of solution. Therefore, the iron ions are of little importance in the charge transfer.

Because of the outflow of cations from the sample to the near-cathode zone, in the left part of the sample there arises a negative charge compensated by the inflow of the most mobile H ions and other free cations from the solution in the near-anode zone. Hydrogen ions migrate over the system of water molecules bound together in the gel. They are also transferred to the cathode, and hydroxyls are transferred to the anode.

The higher mobility of the hydrogen ions is due to the exceptional mechanism of their transfer: protons are translated in the direction of the electric field vector from one water molecule to another with the successive formation of hydroxonium ions (H₃O)⁺. Hydroxyls are also transferred in the relay-race manner; however, in this case, a proton jumps from a water molecule to a hydroxyl. As a result, a hydroxyl and a water molecule are formed once again: H₂O + OH⁻ → OH⁻ + H₂O. The mobility of the hydroxyls is lower than the mobility of (H₃O)⁺ [2].

All these processes occur within the sample and in the near-electrode zones in the case where the system is electrically neutral in any local volume of it. In this case, a dynamic equilibrium is established. A change in the concentration of ions or molecules in any part of the system causes their reverse diffusion occurring until a new equilibrium state is established^{*)}.

At the beginning of the combined transfer of water under the action of the hydrostatic pressure Q_{mass} and electroosmosis Q_{el} , $Q_{\text{mass+el}}$ first increases linearly (Fig. 4). Cations are carried to the near-cathode zone, and their concentration in the right chamber increases. At a current $J < 1.5$ mA, past the linear portion on curves 1 and 2 (Fig. 4), the electroosmotic flow becomes constant. At $J > 1.5$ mA, past the linear portion on curves 3 and 4, $Q_{\text{mass+el}}$ decreases and the liquid flow stabilizes. The decrease in the flow is caused by the reverse transfer of cations, neutral atoms, and molecules to the sample, with the result that salt osmosis arises. The osmotic transfer of water to the right reservoir decreases because of the decrease in the concentration of cations in the near-cathode region.

A steady electroosmotic flow is formed when the direct inflow of cations to the near-cathode zone becomes equal to the reverse flow of particles to the sample. At a high current the filtrational transfer Q_{mass} is of little importance as compared to the electroosmotic flow, and it is of considerable importance at a low current, because the relative contribution of the convective transfer of ions to the near-cathode zone increases and their reverse diffusion to the sample decreases.

When the current is switched off (Fig. 4, point B), the combined flow $Q_{\text{mass+el}}$ decreases to the filtrational flow Q_{mass} . At a weak current J (Fig. 4, curves 1 and 2) a steady flow exists for 30–40 min after switching off the current due to the convective transfer of cations by the filtrational flow to the near-cathode zone and the residual potential ϕ .

During the period of stabilization of the electroosmotic flow (Fig. 4, curve 1) the voltage across the electrodes decreases (curve 5) and, as a result of stabilization, the number of cations reaching the cathode and, accordingly, the electrical resistance of the gel become constant.

After switching off the external current, a residual potential of ~ 0.35 V remains on the electrodes (Fig. 4, curve 6). The residual potential ϕ on the electrodes, around which liquid flows, is low because, as mentioned above, the number of adsorbed hydrogen and oxygen molecules on them is small. Their movement in the form of H⁺ and OH⁻ ions from the surface of the cathode and anode to the alkaline and acidic media, respectively, generates a current [2]. As a result of interaction of H⁺ ions with hydroxyls and OH⁻ ions with hydrogen ions, water molecules are formed. The current from the secondary source flows in the outer circuit in the direction from the anode to the cathode. The residual potential ϕ relaxes and reaches zero within 2–10 h.

At a degree of dissociation of polar functional groups $\alpha \rightarrow 1$, the entropy of mixing of swollen gels reaches a maximum value when the concentration of all the solutes and the solvent becomes constant everywhere in the volume of the gel. At currents of 0.5–10 mA, an ionic equilibrium is established over a period of 16–36 h, respectively. For this time, there takes place a reverse outflow of cations from the near-cathode zone until they are uniformly distributed along the length of the sample. This process is accompanied by ion exchange, in which hydrogen ions are substituted for metal ions, and causes a change in the structure of the gel. The subsequent migration of H⁺ ions to the cathode and of hydroxyls from the cathode zone to the anode adds to the operating time of the secondary source. The larger the difference between the pH values at the cathode and anode, the more intensive the ion transfer and, accord-

^{*)} The authors believe that under the conditions of steady-state processes, any local volume is electrically neutral. Under the condition of a transient process, the electroneutrality is disrupted and mass transfer arises, as noted in this paragraph.

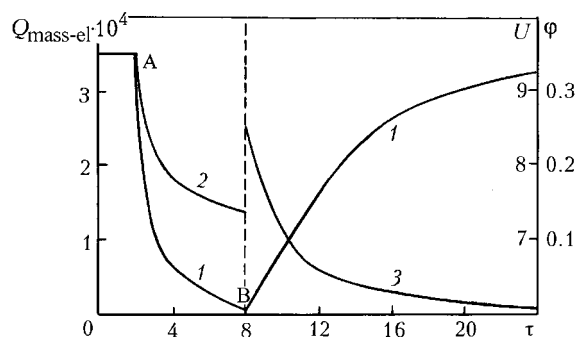


Fig. 5. Change in the total $Q_{\text{mass-el}} \cdot 10^4$ water flow under the action of the hydrostatic pressure Q_{mass} and the reverse electroosmotic flow Q_{el} (1), in the voltage U after switching on the current (2), and in the residual potential ϕ after switching off the current (3) with time τ [A] switching on; b) switching off]; $J = 1$ mA). $Q_{\text{mass-el}}$, cm^3/sec ; U , ϕ , V; τ , h.

ingly, the lower the residual pressure. Allowance must also be made for the fact that, especially at weak currents, the resulting transfer of hydroxyls to the anode is decreased by the antiparallel filtrational liquid flow, which leads to an increase in the relaxation time as compared to electroosmosis (without filtration) at the same difference between the pH values in the cathode and anode zones.

In the case where the electroosmotic Q_{el} and filtrational Q_{mass} flows were oppositely directed, the combined flow $Q_{\text{el-mass}}$ (Fig. 5, curve 1) and the voltage across the electrodes (curve 2) decreased gradually with time. After switching off the current (point B), the combined flow $Q_{\text{mass-el}}$ increased over 16 h but did not reach the filtrational flow Q_{mass} , and the residual potential ϕ (curve 3) did not decrease to zero. The mechanism of ion transfer is similar to the above-described mechanism; however, there are differences between them.

Mass transfer caused by the hydrostatic pressure gradient $Q_{\text{mass}} = 3.5 \cdot 10^{-4} \text{ cm}^2/\text{sec}$ substantially hampers migration of cations to the cathode positioned in the left chamber. Because of the decrease in the inflow of metal cations, the electroosmotic flow, voltage, and residual potential were decreased as compared to their values in the case of parallel combined electrofiltrational transfer.

In the absence of an external electric field, solute ions move together with the filtrational flow of liquid. A larger number of cations, as compared to the number of anions, come from the gel. Therefore, the potential difference U_{fl} (potential of flow) arises between the platinum electrodes as a result of the discharge of ions of both signs on them. According to the experiments, the values of U_{fl} do not exceed 1 mV.

It follows from the experiments that electroosmotic dehydration can be applied validly only to gels having a low water permeability, in particular, to peat gels having a high degree of decomposition or mechanical dispersion and gels compacted by an external load.

CONCLUSIONS

The foregoing shows that a pressure gradient in a gel causes a discrete and not continuous transfer of unbound molecules in it, deformation of its skeleton, and partial failure of the water structure. As the temperature and temperature gradients in swollen gels increase, the thermal transfer of moisture in them increases because of the increase in the number and rate of translations of unbound water molecules. In the case where there are concentration gradients of dissolved salts there arises osmotic transfer of water through the gel to the region of higher salt concentration. The transfer of the solvent and the salt and acid solutions in a swollen gel containing absorbed ions is accompanied by ion-exchange processes and causes a change in its structure, porosity, and acidity index pH and in the intensity of migration of particles. The mechanisms of electroosmotic and combined parallel and antiparallel filtrational-electroosmotic mass transfer have been investigated. In the case of electroosmosis, the polar liquid is transferred from the anode to the cathode because of the increase in the concentration of cations carried from the gel in the near-cathode zone. The reasons for the relaxation of the gel to the equilibrium state under the action of a constant electric field have been considered.

NOTATION

S_{mix} , entropy of mixing; n_i , number of moles of the m mixed components; N_i , their mole fractions; R , universal gas constant, J/(mole·K); ΔG , Gibbs potential; ΔH , enthalpy; T , temperature, K; V_0 , molar volume of the liquid, m^3/mole ; E_b , electric field strength at the solution–particle boundary, V/m; x , coordinate, m; i , pressure gradient, cm of $\text{H}_2\text{O}/\text{cm}$; Q_{mass} , flow of filtrational mass transfer, cm^3/sec ; Q_{el} , electroosmotic flow, cm^3/sec ; $Q_{\text{mass}\pm\text{el}}$, combined filtrational and electroosmotic flow, cm^3/sec ; $Q_{\text{mass}\pm\text{th}}$, combined thermal and filtrational flow, cm^3/sec ; F , cross section of the sample, cm^2 ; v , rate of mass transfer, cm/sec ; ∇T , temperature gradient, K/cm; C_2 , volumetric molar concentration of a solute, mole/m^3 ; p , vapor pressure over the moisture absorbed by the gel, Pa; p_s , vapor pressure over the pure water, Pa; p_0 and p_{0s} , pressures of saturated vapors over the solution and the pure solvent, respectively, Pa; a , distance that a liquid molecule is translated, m; τ_0 , average period of thermal vibrations of molecules, sec; δ , porosity, $\delta = 1 - \gamma_0/\rho$; ρ , density of the solid gel ingredients, kg/m^3 ; γ , density of the swollen material, kg/m^3 ; γ_0 , density of the dry gel basis in the volume of the wet stock, kg/m^3 , $\gamma_0 = \gamma/(1 + u)$; u , moisture content, kg of liquid/kg of dry basis; W , energy of binding of water molecules together and to the polar centers of material sorption, kJ/mole; P , hydrostatic pressure, Pa; $k = d(D\gamma_0 u)/dP$, coefficient of filtrational mass transfer, sec; D , diffusion coefficient of liquid molecules, m^2/sec ; H_1 and H_2 , hydrostatic pressures applied to the left and right faces of the sample, cm of H_2O ; l , length of the sample, cm; J , current, A; t , time, sec; α , degree of dissociation of functional groups; u , voltage drop on the electrodes, V; ϕ , residual potential, V; U_{fl} , potential of flow, V; e , electron charge, C. Subscripts: mix, mixing; fl, flow; s, saturation; b, boundary; el, electroosmotic; mass, mass transfer; th, thermal transfer.

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