ELECTROOSMOSIS IN LAYERED POROUS SYSTEMS

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Regularities of electroosmosis in bilayer diaphragms are investigated. Formulas describing the change of rate of the process in comparison with electroosmosis on a homogeneous diaphragm are obtained. The calculation results are confirmed by experimental data.

The practical use of electroosmosis for dewateringand stabilizing soils and for displacing one liquid by another is presently being investigated widely [1-4]. Experimental data obtained with layered soils are given in particular in [4]. However, the results of theoretical investigations as applied to real complex systems are lagging considerably behind practical requirements.

We will investigate below electroosmosis of the liquid in horizontal porous systems consisting of two successively positioned layers with a different nature of the surface or structure of the pore space (Fig. 1). The value of l_i is much greater than $l_{\mathrm{cr}\,i}$ [5].* The external electric field is applied on the entire system. The flow rate of the liquid through the bilayer diaphragm is regarded as being composed of a number of components. We will take at first the case where the layers differ by the nature of the surface, the signs of the ξ-potentials of the layers are the same, and the direction of the flow during electroosmosis, formulated according to the classical scheme on each layer, correspond to the positive direction oz. We will discuss the results of the effect of mass forces in each layer of the double diaphragm separately. The effect of the mass forces arising on applying an external electric field in layer l_1 gives rise to the appearance of pressure differences and flow components similar to that which occurs during inhibited electroosmosis [6]. The electric forces appearing on application of the external electric field in layer l_2 also leads to a flow component. Due to it and the inhibiting effect of layer l_1 (according to our conditions it is located behind the now "active" part of the diaphragm) a pressure drop also appears: the liquid is, so to speak, "absorbed" into layer l_1. The pressure (p) on the end of the diaphragm AB should be greater than at the boundary of the layers CD. Since on the second end EF it is again equal to the atmospheric pressure (a pressure difference is not applied from the outside), a pressure drop obviously also occurs in l_2 which inhibits the flow caused by the effect of the mass forces of l_2. As a result new flow components occur. The total component of the flow due to pressures can be considered as caused by two pressure drops: one in $l_1(\Delta p_1)$ and the second in $l_2(\Delta p_2)$. Since the structure and electric fields in each layer are considered uniform ($l_i > l_{\mathrm{cr}\,i}$), the change of the pressure gradients occurs at the boundary of the layers. The values of Δp_1 and Δp_2 depend on the magnitude of forces of each layer. However, we can say with certainty that

$$\Delta p_1 = -\Delta p_2. \qquad (1)$$

The results obviously only change quantitatively if the ζ-potentials of the layers have different signs or the chemical nature of the layers is the same, but the average radii of the pores differ so much that the effect of the double electric layer is felt on the magnitude of the electrical conductivity of the solution in the pores $\alpha > 1$.

To determine the regularities of the electroosmotic movement in our diaphragms, we will investigate it for the modeled system: a bundle of identical cylindrical horizontal capillaries. The differential equations of motion in one capillary have the form [6]

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*The quantity l_i denotes the general form of notation of the lengths of layers 1 and 2 (see Fig. 1). Such a united form of notation is used further for all pairs of variables or pairs of equation differing only in indices.

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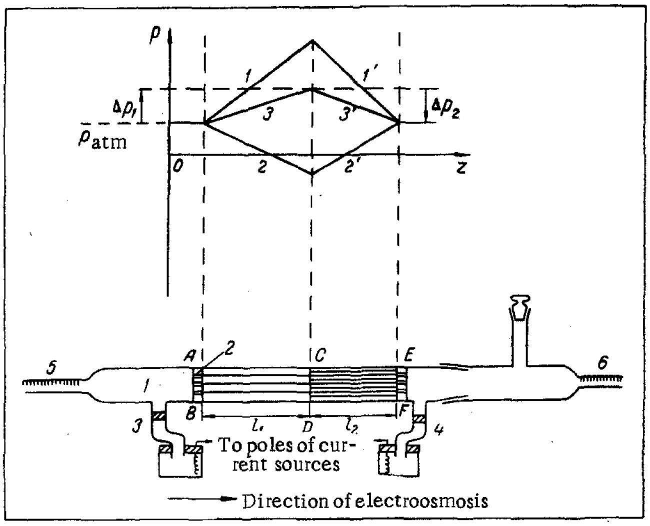

Fig. 1. 1, 1') Pressure drops due to the effect of mass forces of layer l_1; 2, 2') to the effect of mass forces of layer l_2; 3, 3') total pressure drops in diaphragm.

$$\frac{1}{r_i}\cdot\frac{d}{dr_i}\left(\frac{dv_i}{dr_i}r_i\right)-\frac{\varepsilon E_{zi}}{4\pi\eta}\cdot\frac{1}{r_i}\cdot\frac{d}{dr_i}\left(\frac{d\varphi_i}{dr_i}r_i\right)=C_i, \tag{2}$$

$$\frac{1}{\eta}\cdot\frac{dp_i}{dz}=\frac{\Delta p_i}{l_i}=C_i; \tag{3}$$

C_i is a presently unknown constant for layer i. The subscript i of r signifies that the coordinate system is fixed for the given capillary. According to [8, 9], φ_i is determined by the expression

$$\varphi_i=\varphi_{Ri}\frac{I_0(\varkappa r_i)}{I_0(\varkappa R_i)}. \tag{4}$$

The general form of the solution of Eq. (2) with consideration of (4) is

$$v_i=C_i\frac{r_i^2}{4}+C_{i+1}\ln r_i+C_{i+2}+\frac{\varepsilon E_{zi}}{4\pi\eta}\varphi_{Ri}\frac{I_0(\varkappa r_i)}{I_0(\varkappa R_i)}. \tag{5}$$

The constants of integration C_{i+1} and C_{i+2} are determined from the boundary conditions:

$$r_i=0\quad dv_i/dr_i=0;\qquad r_i=R_i\quad v_i=0. \tag{6}$$

Taking into account (1) and (6), we obtain from (5) the expression for v_1 and v_2 with an accuracy to the unknown C_1:

$$v_1=C_1\frac{r_1^2}{4}+C_1\frac{R_1^2}{4}-\frac{\varepsilon E_{z1}}{4\pi\eta}\varphi_{R1}+\frac{\varepsilon E_{z1}}{4\pi\eta}\varphi_{R1}\frac{I_0(\varkappa r_1)}{I_0(\varkappa R_1)}, \tag{7}$$

$$v_2=-C_1\frac{l_1}{l_2}\frac{r_2^2}{4}+C_1\frac{l_1}{l_2}\frac{R_2^2}{4}-\frac{\varepsilon E_{z2}}{4\pi\eta}\varphi_{R2}+\frac{\varepsilon E_{z2}}{4\pi\eta}\varphi_{R2}\frac{I_0(\varkappa r_2)}{I_0(\varkappa R_2)}.$$

We use the thesis that the volume flow velocity in any section of the diaphragm ($q_{do.\,d}$) should be the same. The value of $q_{do.\,o}$ is determined by the expressions:

$$q_{do.\,d}=\frac{SW_1}{\pi R_1^2}\int_0^{R_1}2\pi r_1v_1dr_1=\frac{SW_2}{\pi R_2^2}\int_0^{R_2}2\pi r_2v_2dr_2. \tag{8}$$

The decrease of the flow velocity with an increase of α can be represented as the result of a corresponding decrease of the ζ-potential.

TABLE 1. Characteristics of the Diaphragm and Relative Rates of Electroosmosis on Diaphragms with Layers of Different Structure of the Pore Space

Average diameter of particles on individual layers, $\times 10^6$ m	$l_i \cdot 10^2$, m	$R_{eq}^1 \cdot 10^6$, m	$R_{eq}^2 \cdot 10^6$, m	$\zeta_{1H} \cdot 10^3$, V	$\zeta_{2H} \cdot 10^3$, V	q_{rat1} (exptl.)	q_{rat2} (according to [11])
168/54	$l_1 = 5{,}6$ $l_2 = 1{,}9$	46,6	17,8	—6,2	—6,2	1,1	1,00
168/50	$l_1 = 5{,}4$ $l_2 = 1{,}4$	46,6	13,8	—6,2	—6,2	1,1	1,00
168/36	$l_1 = 5{,}6$ $l_2 = 1{,}4$	46,6	10,1	—6,2	—5,6	0,98	0,94
168/17	$l_1 = 5{,}8$ $l_2 = 1{,}2$	46,6	4,6	—6,2	—4,3	0,75	0,71
152/86	$l_1 = 3{,}5$ $l_2 = 2{,}0$	42,0	23,9	—10,3	—10,3	0,95	1,00
152/63	$l_1 = 3{,}5$ $l_2 = 1{,}5$	42,0	17,4	—10,3	—10,3	1,0	1,00
152/41	$l_1 = 3{,}5$ $l_2 = 1{,}5$	42,0	11,5	—10,3	—9,3	0,87	0,90
152/27	$l_1 = 3{,}5$ $l_2 = 1{,}0$	42,0	7,4	—10,3	—8,5	0,90	0,89
152/10	$l_1 = 3{,}5$ $l_2 = 0{,}8$	42,0	2,8	—10,3	—5,7	0,63	0,56
54/16	$l_1 = 1{,}1$ $l_2 = 0{,}8$	14,9	4,1	—15,5	—9,5	0,59	0,64
54/8	$l_1 = 1{,}1$ $l_2 = 0{,}6$	14,9	2,3	—15,5	—7,5	0,45	0,46

Note. The current in all experiments was (2.5-3) $\times 10^{-3}$ A, and the specific conductivity of the free solution was 9.8-9 $\times 10^{-2}$ $m^{-1}\,\Omega^{-1}$.

Substituting v_1 and v_2 from (7) into (8) and taking the integrals, we find C_1, which enables us to obtain the formulas for the pressure gradients and drops, linear flow velocities, and volume flow rate according to (2), (7), and (8):

$$\left.\frac{dp}{dz}\right|_{l_1} = 2\Bigl\{\frac{W_1}{W_2}\cdot\frac{\varepsilon E_{z1}\varphi_{R1}}{\pi}\Bigl[-1+\frac{2}{\varkappa R_1}\cdot\frac{I_1(\varkappa R_1)}{I_0(\varkappa R_1)}\Bigr]$$

$$-\frac{\varepsilon E_{z2}\varphi_{R2}}{\pi}\Bigl[-1+\frac{2}{\varkappa R_2}\cdot\frac{I_1(\varkappa R_2)}{I_0(\varkappa R_2)}\Bigr]\Bigr\}\Big/\Bigl\{R_1^2\frac{W_1}{W_2}+\frac{l_1}{l_2}R_2^2\Bigr\},$$

$$\Delta p\,|_{l_1} = l_1\left.\frac{dp}{dz}\right|_{l_1} \qquad \left.\frac{dp}{dz}\right|_{l_2} = -\frac{l_1}{l_2}\cdot\left.\frac{dp}{dz}\right|_{l_1},$$

$$v_1 = 2(r_1^2-R_1^2)\Bigl\{\frac{W_1\varepsilon E_{z1}\varphi_{R1}}{W_2 4\pi\eta}\Bigl[-1+\frac{2I_1(\varkappa R_1)}{\varkappa R_1 I_0(\varkappa R_1)}\Bigr]$$

$$-\frac{\varepsilon E_{z2}\varphi_{R2}}{4\pi\eta}\Bigl[-1+\frac{2I_1(\varkappa R_2)}{\varkappa R_2 I_0(\varkappa R_2)}\Bigr]\Bigr\}\Bigl(R_1^2\frac{W_1}{W_2}+\frac{l_1}{l_2}R_2^2\Bigr)^{-1}-\frac{\varepsilon E_{z1}\varphi_{R1}}{4\pi\eta}+\frac{\varepsilon E_{z1}\varphi_{R1}}{4\pi\eta}\cdot\frac{I_0(\varkappa r_1)}{I_0(\varkappa R_1)},$$

$$v_2 = -\frac{2l_1}{l_2}(r_2^2-R_2^2)\Bigl\{-\frac{W_1}{W_2}\cdot\frac{\varepsilon E_{z1}\varphi_{R1}}{4\pi\eta}\Bigl[-1+\frac{2}{\varkappa R_1}\cdot\frac{I_1(\varkappa R_1)}{I_0(\varkappa R_1)}\Bigr]$$

$$-\frac{\varepsilon E_{z2}\varphi_{R2}}{4\pi\eta}\Bigl[-1+\frac{2}{\varkappa R_2}\cdot\frac{I_1(\varkappa R_2)}{I_0(\varkappa R_2)}\Bigr]\Bigr\}\Bigl(R_1^2\frac{W_1}{W_2}+\frac{l_1}{l_2}R_2^2\Bigr)^{-1}-\frac{\varepsilon E_{z2}\varphi_{R2}}{4\pi\eta}+\frac{\varepsilon E_{z2}\varphi_{R2}}{4\pi\eta}\cdot\frac{I_0(\varkappa r_2)}{I_0(\varkappa R_2)},$$

$$q_{\mathrm{do.d}} = W_1 S\Bigl\{\Bigl\{-\frac{W_1}{W_2}\cdot\frac{\varepsilon E_{z1}\varphi_{R1}}{4\pi\eta}\Bigl[-1+\frac{2}{\varkappa R_1}\cdot\frac{I_1(\varkappa R_1)}{I_0(\varkappa R_1)}\Bigr]$$

$$-\frac{\varepsilon E_{z2}\varphi_{R2}}{4\pi\eta}\Bigl[-1+\frac{2}{\varkappa R_2}\cdot\frac{I_1(\varkappa R_2)}{I_0(\varkappa R_2)}\Bigr]\Bigr\}\Bigl(\frac{W_1}{W_2}+\frac{l_1}{l_2}\cdot\frac{R_2^2}{R_1^2}\Bigr)^{-1}-\frac{\varepsilon E_{z1}\varphi_{R1}}{4\pi\eta}\Bigl[1-\frac{2}{\varkappa R_1}\cdot\frac{I_1(\varkappa R_1)}{I_0(\varkappa R_1)}\Bigr]\Bigr\}.$$

TABLE 2.* Characteristics of Diaphragms and Relative Rates on Diaphragms with Layers Differing in the Nature of the Surface

Characteristics of diaphragm	$l_1\cdot10^2$, m	$l_2\cdot10^2$, m	q_{rat1} (exptl.)	q_{rat1} (acc. to [11])	q_{rat2} (exptl.)	q_{rat2} (acc. to [12])
Object No. 1: quartz	6	0	1,00	1,00	3,9	3,9
$\zeta_{1H} = -59.10^{-3}$ V	8	4	0,79	0,73	3,1	2,9
$R_1 = 1.9\cdot10^{-6}$ m	9	6	0,61	0,67	2,4	2,6
Object No. 2: decomposition product of PMS-200	6	6	0,56	0,61	2,2	2,4
$\zeta_{1H} = -15\cdot10^{-3}$ V	4	8	0,41	0,49	1,6	1,9
$R_2 = 1.8\cdot10^{-6}$ m	0	6	0,25	0,25	1,0	1,0
Object No. 1: quartz	6	0	1,00	1,00	2,80	2,80
$\zeta_{1H} = -42\cdot10^{-3}$ V	9	6	0,50	0,56	1,40	1,38
$R_1 = 3.2\cdot10^{-6}$ m	6	6	0,45	0,50	1,27	1,30
Object No. 2: decomposition product of PMS-200	6	9	0,45	0,46	1,27	1,30
$\zeta_{2H} = -15.10^{-3}$ V	4	8	0,40	0,44	1,10	1,23
$R_2 = 1.8\cdot10^{-6}$ m	0	6	0,36	0,36	1,00	1,00
Object No. 1: quartz	6	0	1,00	1,00	1,82	1,82
$\zeta_{1H} = -42\cdot10^{-3}$ V	6	6	0,69	0,61	1,25	1,10
$R_1 = 3.2\cdot10^{-6}$ m	0	6	0,55	0,55	1,00	1,00
Object No. 2: decomposition product of PMS-200						
$\zeta_{2H} = -23\cdot10^{-3}$ V						
$R_2 = 2.5\cdot10^{-6}$ m						

* L. P. Kuzenkov participated in the experiment.

Note. The current in all experiments were $(2.6\text{-}3.5)\times10^{-3}$ A, and the specific conductivity of the free solution was $1.3\times10^{-2}\,\Omega^{-1}\,\mathrm{m}^{-1}$.

In the case of sufficiently wide capillaries ($\varkappa R_i > 5\text{-}10$ [7]) the second terms in all brackets of Eqs. (9) can be neglected, as a result of which the equations become considerably less cumbersome. In addition, under these conditions $\varphi_{R1} = \zeta_1$ and $\varphi_{R2} = \zeta_2$. In the experiments, the results of which are given below, the last condition was met. We need indicate also that the experiments were carried out on powdered diaphrams, the particle size in each fractions varying within narrow limits (the extreme values differed by less than two times). Thus, here $W_1 = W_2 = W$.

If the electrical conductivities of the solutions inside the pores are the same, the last equality permits assuming $E_{z1} = E_{z2}$. In fine-pores systems, where the α are different, $E_{z1} \neq E_{z2}$. However, their relation is determined from the general laws of electrostatics:

$$\frac{E_{z2}}{E_{z1}} = \frac{\alpha_1}{\alpha_2}.$$

Since the value of ζ is associated with ζ_{iH} by the relation $\zeta_i = \alpha_i\zeta_{iH}$, it is easy to see that

$$\frac{\zeta_2 E_{z2}}{\zeta_1 E_{z1}} = \frac{\zeta_{2H}}{\zeta_{1H}}.$$

With consideration of the aforesaid the last Eq. (9) as applied to the systems on which the experiments were conducted has the form

$$q_{\text{do.d}} = \frac{WS\varepsilon E_{z1}\zeta_1}{4\pi\eta}\left[\frac{1-\dfrac{\zeta_{2H}}{\zeta_{1H}}}{1+\dfrac{l_1R_2^2}{l_2R_1^2}} - 1\right]^{*}. \tag{10}$$

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*Using the classical concepts relative to the mechanism of electroosmosis and the usual conditionality of determining the positive direction of the electric field strength, we can easily show that with our method of fixing the coordinate system the sign of the value of $q_{\text{do.d}}$ obtained in a concrete case determined the direction of the flow with respect to the poles of the current source. (A positive value of $q_{\text{do.d}}$ means that the direction of the flow corresponds to the direction of motion of the positive charge in an electric field.)

For the quantity $q_{\mathrm{rat}\,i}$ we have:

$$q_{\mathrm{rat}\,1} = 1 - \frac{1 - \dfrac{\zeta_{2\mathrm{H}}}{\zeta_{1\mathrm{H}}}}{1 + \dfrac{l_1 R_2^2}{l_2 R_1^2}}, \qquad (11)$$

$$q_{\mathrm{rat}\,2} = \frac{\zeta_{1\mathrm{H}}}{\zeta_{2\mathrm{H}}} + \frac{1 - \dfrac{\zeta_{1\mathrm{H}}}{\zeta_{2\mathrm{H}}}}{1 + \dfrac{l_1 R_2^2}{l_2 R_1^2}}. \qquad (12)$$

The values of $q_{\mathrm{rat}\,1}$ and $q_{\mathrm{rat}\,2}$ give an idea about the acceleration or deceleration of motion in a bilayer diaphragm in comparison with electroosmosis in layers isolated from one another. Experiments on measuring $q_{\mathrm{do.d}}$ on double diaphragms were carried out on an instrument, a diagram of which is given in Fig. 1. To obtain the double diaphragms a column of powder of the same chemical nature or the same fraction was formed on a perforated plate 2 soldered into tube 1. Powder of another fraction or another nature was layered on this column. Both layers were located between drains 3 and 4. The measurement of $q_{\mathrm{do.d}}$ was taken by means of graduated capillaries 5 and 6. As the powder we used fractions of polystyrene; polystyrene polymerized with dyes [5]; quartz and the decomposition product of PMS-200 polyorganosiloxane (annealing temperature 600-700°C and duration 72 h). In the first two cases the powder particles were spherical and in the other cases irregular. An aqueous solution of KCl served as the liquid.

From the powder with spherical particles we formed diaphragms whose layers differed only in the structure of the pore space. Calculations of the values of $q_{\mathrm{rat}\,1}$ from the experimental results are given in Table 1 (seventh column). Also given there are the results of calculations made according to Eq. (11) (eighth column), for which $\zeta_{1\mathrm{H}}$ and $\zeta_{1\mathrm{H}}$ were determined in parallel experiments. As the pore radii needed for the calculation we used the quantity $R_{\mathrm{eq}\,i}$, which obviously is somewhat conditional [5]. From the powder of quartz and the decomposition product of PMS-200 we formed bilayer diaphragms with layers differing not only in pore radii (the difference here was much less than in the preceding cases) but also in the values of the ζ-potentials of the layers. The characteristics of the systems and relative rates determined from experiments and calculated by Eqs. (11) and (12) are presented in Table 2. Here the average pore radius was taken for R_i.

As we see from the data in the tables, the agreement between the values of $q_{\mathrm{rat}\,i}$ obtained from the experimental data and calculated by Eqs. (11) and (12) is completely satisfactory (the maximum divergence is about 10%).

Thus it follows from the results obtained that the regularities of electroosmosis in layered diaphragms differ considerably from the classical, corresponding to flow of a liquid in a homogeneous diaphragm. A determination of their specific characteristics will permit taking into account the change of the flow velocities in bilayer diaphragms, which in our opinion is of considerable practical interest.

NOTATION

E_{zi}	is the tangential (axial) component of the electric field;
l_i	is the length of layer;
$l_{\mathrm{cr}\,i}$	is the critical length of layer;
p_i	is the pressure at a given point;
Δp_i	is the pressure drop in layer;
$q_{\mathrm{do.d}}$	is the flow rate (volume flow velocity) of liquid in double diaphragm;
$q_{\mathrm{rat}\,i}$	is the ratio of $q_{\mathrm{do.d}}$ to flow rate during electroosmosis in a homogeneous diaphragm corresponding to layer i;
r_i	is the radial coordinate;
R_i	is the average radius of pores and radius of capillary;
$R_{\mathrm{eq}\,i}$	is the equivalent radius of pores;
S	is the section of diaphragm;
W_i	is the porosity;
v_i	is the linear velocity;

z is the axial coordinate;

I_i is the modified Bessel function of the i-th order;

α is the efficiency;

ε is the dielectric constant of liquid;

η is its viscosity;

φ_i is the component of electric potential of system due to excess ions at a given point;

$\varphi_{R_i} = \varphi_i$ in $r_i = R_i$;

ζ_{iH} is the electrokinetic potential calculated by the Helmholtz–Smoluchowski formula;

ζ_i is the electrokinetic potential calculated with consideration of α;

$\varkappa$ is the reverse thickness of double electric layer. The subscript i denotes that the value refers to layer i (i = 1, 2).

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