LAWS OF ELECTROKINETIC FLOW THROUGH CAPILLARY-POROUS BODY WITH MICROINHOMOGENEOUS SURFACE

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On the basis of experimental data, the applicability of existing formulas for predicting the dependence of the flow rate through powder-mixture diaphragms on the mixture-component ratio is analyzed.

As is known, applying a constant electric field to a capillary-porous body saturated by electrolytes leads to the appearance of a flow known as the electrokinetic (or electroosmotic) flow. The laws of electroosmosia and of flows produced by the action of other forces, for example filtration, are qualitatively different. Since electrokinetic flow is an extremely specific phenomenon, it is of undoubted scientific interest, and offers the possibility of fundamentally new solutions to applied problems.

The present work forms part of a series of investigations into the laws of electrokinetic flow through a porous body with a pore space consisting of sections with different filtration coefficients, different surface types, and different solution concentrations (below, these sections will be referred to as layers) [1-4].

The specific problem here is the investigation of flow through a diaphragm formed from mechanical powder mixtures. This is the limiting version of the considered systems, where the layer has microextension (such systems will be called microheteroporous bodies below). Note that, in principle, it makes no difference to the conclusions given in the present work whether the diaphragm is formed of individual particles or consists of rigidly connected sections.

The laws of flow in microheteroporous systems are particularly complex. The classical formulas (Helmholtz–Smolukhovskii formulas, with or without a correction for surface conductivity [5]) are inapplicable; they are derived for systems with constant parameter values. It is perhaps psssible to note only two formulas given in [1, 6] which may be brought to bear in our problem. In [6], a formula was proposed on the basis of a derivation from qualitative considerations. For the formula for electroosmosis in multilayer diaphragms (henceforward referred to as the multilayer-electroosmosis formula) [1], the problem was solved under seriously constrained conditions: purely sequential arrangement of the layers, each layer of sufficiently great extent, all parameters unchanged by the current. Note that the structural relations between sections in a microheteroporous diaphragms do not correspond, strictly speaking, to the structural differences on which the derivation of the given formula rests: the layers in such a diaphragm are distributed not only sequentially, but also in parallel.

What is meant by "sufficient extent" is that no change in the layer boundaries has any effect on the flow as a whole. The rigidity of the condition depends significantly on the type of boundary effect [7-11]. Thus, in the case of "inactive" diaphragms,* end effects are related to change in the velocity curves in the boundary layers because of mechanical interaction of the fluxes. From general considerations, it is improbable that the region with the transitional cuvve extends over more than hundreds of thousands of microns. However, this assumption is based on approximate calculations relating only to a single cylinder of regular form [1, 7].

In active diaphragms the position is more complex. As well as steady ("mechanical") effects, unsteady effects appear because of the presence of concentration-redistribution sources on the layer boundaries [8-11]. The change in parameters may extent over a large part of the layer, and even be of considerable extent (centimeters). In microheteroporous diaphragms, these sources are sited at microdistances; in addition, pronounced polarization of the intrinsic particle field may in principle appear here [12].

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*"Inactive" ("active") diaphragms are such that not one (at least one) of the parameters changes under the action of an electric field.

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TABLE 1. Characteristic Properties of Individual Components Appearing in Powder Pairs Forming Mixed Diaphragms of Given Composition

System No.	Component	Component No.	Electrolyte and solution pH	$\varkappa_0 \cdot 10^6$, $\Omega^{-1} \cdot m^{-1}$	$\zeta \cdot 10^3$, V	α	$K_f \cdot 10^9$, $N^{-1} \cdot sec^{-1}$	S (specific) 10^{-3}, m^2/kg
1	Quartz	1	KCl; 6,0	7	—51	1,0	4,3	0,25*
	Phosphorite	2			—22	1,0	2,5	1,3*
2	Quartz	1	KCl	7	—73	1,0	3,8	0,3*
	Al_2O_3	2			+7	1,0	1,5	48*
3	Quartz	1	HCl; 4,5	0,16	—82	1,8	0,2	3 †
	Al_2O_3	2			+83	2,45	0,01	2,7* 10,5 †

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* Determined from argon absorption.

† Determined by Deryagin method.

The literature includes no secure estimates of the minimal layer thicknesses limiting the applicability of the multilayer-electroosmosis formula; this question may only be illuminated by experiment. From general considerations, it is quite impossible to expect that the formula will completely represent the features of the electroosmotic behavior of any mixed diaphragms, but it will very probably be acceptable as a first approximation.

Although the Reshetnikov formula and the multilayer-electroosmosis formula have a common form, they differ significantly in the physical meaning of the constant characterizing the dispersion of the components. The common form of the two equations is*

$$q_{\text{mix}} = \frac{X + \frac{\alpha_1}{\zeta_1}\frac{\zeta_2}{\alpha_2}(1 - X)K}{X + (1 - X)K}\, q_1, \tag{1}$$

where q_1 is the velocity through a homogeneous diaphragm of component 1, defined by the expression $\varepsilon I \zeta_1 / 4\pi \varkappa_0 \alpha_1 \eta$; K is a constant whose physical meaning differs in the Reshetnikov and multilayer-electroosmosis equations: $K = S_2/S_1$ in the first (hereafter referred to as K_R) and $K = K_{f1}/K_{f2}$ in the second (hereafter referred to as K_M).

The investigation centers on three pairs of powders. The parameter values of layers obtained in working with diaphragms consisting entirely of the given element are given in Table 1.† The basic requirement is choosing the pairs is a strong difference in the electrosurface characteristics of the components. In the first pair, the ζ potentials are of the same sign and significantly different in size; the diaphragms are inactive. In the two other pairs the ζ potentials are of different sign; one pair has inactive diaphragms and the other active diaphragms. In the latter case, the conditions were limitingly rigorous; as well as the activity of the "layers" and the difference in signs of the ζ potentials, those potentials were of large absolute magnitude (almost of the maximum known magnitude). Strong opposed (oppositely directed) flows around the surface of two neighboring particles led to strong oppositely directed (opposed) flows in the volume of the same pore. The distance at which change in direction of the linear velocities occurred was a few microns. Obviously, careful attention must be paid here to the flow laminar conditions.

The preparation of the experimental samples, the equipment and procedure for velocity measurement, the procedure of the electrokinetic experiments, and the measurements of the individual parameters were the same

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* The common form of the formulas has been changed from that given in the original works. The original Reshetnikov formula has ζ_{mix} on the left, and ζ_2/ζ_1 rather than $\zeta_2\alpha_1/\zeta_1\alpha_2$ on the left, all the ζ being quantities calculated by substituting the observed velocities into the Helmholtz–Smolukhovskii formula, which requires correction for the physical meaning of the actual ζ. They have been replaced here by parameters equal in value but different in physical meaning. In the multilayer-electroosmosis formula, the layer-thickness ratio has been replaced by the ratio of their volumes; it is taken into account that only the total volume of layers of a given component is important.

† The specific surfaces were measured, at our request, at the Institute of Refractory Materials, Academy of Sciences of the USSR, in the physicotechnical-research laboratory, by the argon-absorption method and by the Deryagin method [16, 17]. The difference in the surfaces obviously arises because the surface of all the pores is determined in the first case and only that of the through pores in the second.

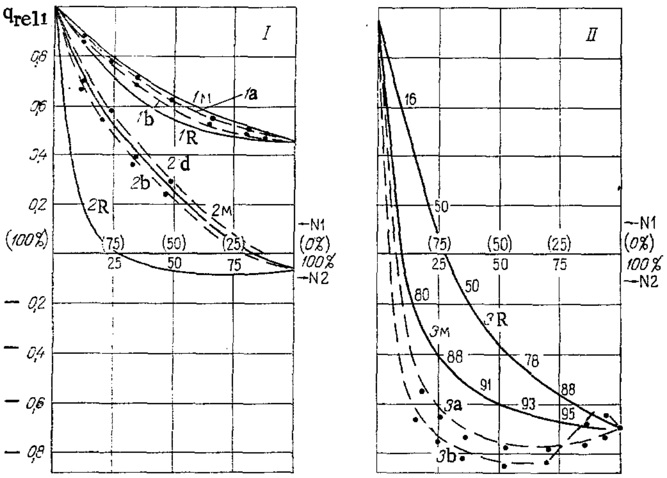

Fig. 1. Dependence of relative velocity of electrokinetic flow on amount (vol. %) of component 1 (2) in mixed inactive (I) and active (II) diaphragms. The numbering of all the curves (1, 2, 3) corresponds to the numbering of the systems in Table 1. The continuous curves are calculated from the formulas; curves numbered with the suffix M correspond to $q_{rel\,1M}$, and those with the suffix R to $q_{rel\,1R}$. The dashed curves and the points correspond to experiment; curves numbered with the suffixes a and b correspond to results obtained when working with an alternating field and those with the suffixes c and d to constant-field results. The two-figure numbers on curves 3M and 3R indicate the accuracy of estimating $q_{rel\,1}$ using $q_{rel\,1M}$ and $q_{rel\,1R}$ (as a percentage of the change in velocity observed in experiments with an alternating).

as those usually employed [13, 14]. Note, however, that either an alternating electric field with a frequency of 0.054 Hz or a constant field, acting for no more than 5 minutes, was applied to the system. This was associated with an attempt to reduce the role of unsteady effects [15]. However, quantitative calculations of the resolving time proved impossible. After 5 minutes no change in velocity was observed but, in view of the small extent of the layers, it is not possible to assert that the changes occurred so rapidly that the transition of the whole layer from one state to another was simply imperceptible.

The results are shown in Fig. 1 in the form of dependences of the relative velocity on the composition of the diaphragm. The relative velocity $q_{rel\,1}$ is the ratio of velocities in the mixed diaphragm and a homogeneous diaphragm formed of component 1. In Fig. 1, both experimental relative velocity values,* $q_{rel\,1e}$ (with the use of both fields), and values calculated by the two formulas, $q_{rel\,1R}$ and $q_{rel\,1M}$† are shown. The plus (minus) sign means that the flow through the diaphragm is in the same direction as (opposite direction to) the flow through the diaphragm of component 1.

Consider first of all the results obtained with inactive diaphragms (Fig. 1, I). Comparison of $q_{rel\,1e}$ values obtained with constant alternating fields indicates that they depend practically on the character of the field. From a comparison of $q_{rel\,1e} \sim q_{rel\,1R} \sim q_{rel\,1M}$, it follows that, where the ζ potentials of the components are of the same sign, all the velocities corresponding to a single composition are practically equal; but, where the ζ potentials are of different sign, $q_{rel\,1R}$ differs strongly from $q_{rel\,1e}$, whereas $q_{rel\,1M}$ is practically equal to $q_{rel\,1e}$.

According to theoretical conceptions regarding multilayer electroosmosis, the relative flow velocity in mixed diaphragms should not depend on the form of diaphragm (which would be the case in working with the same number of components but not intermingled). To verify this conclusion, experiments were conducted on a series of diaphragms made of mixtures of the same composition but with a change in shape of the diaphragm: 1) cylinder; 2) truncated cone (cross sections differing by a factor of 9); 3, 4) two- and three-layer diaphragms

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*Obtained by direct substitution of the observed velocities when working with mixed and homogeneous diaphragms.
†Obtained by substituting into the formula the component parameters values shown in Table 1 and the variations X.

of a few centimeters, arranged next to one another, with a change of 5 and 3 times in the cross section on passing from layer to layer. The experimental results obtained entirely confirmed the hypothesis.

Concluding the discussion of work with inactive diaphragms, it may be deduced that, if the different layer sections are no larger than in the second of the systems investigated here, the multilayer-electroomosis formula will correctly predict their electroosmotic behavior. The Reshetnikov formula gives markedly worse results.

From the curves shown in Fig. 1, II, constructed from experimental results with active diaphragms, it follows that the experimental velocities, generally speaking, differ from those calculated by the two formulas. However, the discrepancy is incomparably less when the multilayer-electroosmosis formula is used. Close to the individual sections of each calculated curve, figures are shown indicating the relation between the value calculated from the given formula and the experimental value (in percent) for a quantity measured from $q_{\mathrm{rel}\,1e} = 1$ to the observed value when an alternating field is used.* It seems logical to measure from $q_{\mathrm{rel}\,1e}$, since all the results here correlate precisely with what would be the case for a homogeneous diaphragm of powder 1. It follows from these figures that the error in predicting $q_{\mathrm{rel}\,1}$ using calculations from the multilayer-electroosmosis formula is no more than 10% (20%) for all diaphragms containing more than 20% (10%) of finely disperse Al_2O_3 powder determining the direction of the total transfer. The Reshetnikov formula gives velocity from the actual values (for the 10-20% fine fraction, the error reaches 80-50%).

From a practical viewpoint, the prediction of the flow direction is important for prognosis. Here also, matters are incomparably better when the formula for $q_{\mathrm{rel}\,1M}$ is used.

Concluding the consideration of results in working with active diaphragms, one further line of comparison of $q_{\mathrm{rel}\,1e}$ and $q_{\mathrm{rel}\,1M}$ may be examined. It is evident from Fig. 1, II, that $q_{\mathrm{rel}\,1M}$ always lie above $q_{\mathrm{rel}\,1e}$. This means that the role of Al_2O_3 is greater than would be expected from the additivity law. Taking into account that the ζ potentials of the components have different signs, and also that Al_2O_3-powder particles are considerably smaller than the quartz particles, this situation may be qualitatively explained in that the fine particles coat the surface of the quartz, reducing the effective role of the quartz in creating the total flux. This explanation agrees with data in [18] in connection with the superposition of affects in mixed systems.

Thus, although the complex systems studied in the present work differ significantly in the character of the deviation of their structure from those for which the "multilayer-electroosmosis formula" was derived, the results of calculations using this formula are in satisfactory agreement, in quantitative terms, with the behavior of all the investigated diaphragms. Taking into account the very rigorous condition on the choice of powder pairs in the present work (especially in the case of active systems), the agreement obtained allows the conclusion that the multilayer-electroosmosis formula may be used to predict electrokinetic behavior to be extended to a very large number of real complex capillary-porous bodies. This may be taken to include all microheteroporous systems consisting of sections extending over a few microns, the parameters of which differ no more severely than those of the active mixed diaphragms investigated here. It should also be emphasized that the conclusion cannot, in principle, be extrapolated to systems with homogeneous sections of smaller extent (because of the impossibility of estimating the boundary condition).

NOTATION

I, current strength; K, constant in Eq. (1); K_M, constant in multilayer-electroosmosis formula; K_R, constant in Reshetnikov formula; K_e, constant in Eq. (1) calculated from experimental data; K_{fi}, filtration coefficient; q_1, bulk velocity through homogeneous diaphragm of component 1; q_{mix}, (bulk) electroosmosis velocity through mixed diaphragm; $q_{\mathrm{rel}\,1}$, ratio of electroosmosis velocities through mixed diaphragm and homogeneous diaphragm of component 1 (q_{mix}/q_1); $q_{\mathrm{rel}\,1M}$, relative velocity calculated from multilayer-electroosmosis formula; $q_{\mathrm{rel}\,1R}$, relative velocity calculated from Reshetnikov formula; $q_{\mathrm{rel}\,1e}$, relative velocity calculated from experimental data using Eq. (1); S_i, specific surface; X, relative quantity of component 1 (vol. % of total quantity of both components); α_i, efficiency factor; ε, dielectric permittivity of liquid; η, liquid viscosity; ζ_1, electrokinetic potential; x_0, specific electroconduction of free solution. Subscripts: 1, 2, parameters for homogeneous diaphragm of components 1 and 2, respectively, or simply for component 1 or 2.

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*The choice of values obtained using an alternating rather than a constant field is not fundamental, since the values are close.

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