Cell theory of the electroosmosis in the concentrated diaphragms consisting of spherical particles of colloid dispersity with the account of the insoluble boundary layer influence

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The electroosmotic transfer (ratio of velocity of liquid to electric current density) and conductivity of disperse system were calculated as functions of volume fraction of disperse particles. The considered model of electric double layer (EDL) was generalized by taking into account the reducing dissolving ability of liquid near the surface (non-dissolving boundary layer). The problem was solved for limiting case of large degree of EDL overlapping in interparticle space. The obtained results explain the main features of experimental data.

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I. PREMISES FOR THE PROBLEM SOLUTION AND THE MODEL CHARACTERISTICS

The achievements in the quantitative theory of the suspension kinetic properties concern almost exclusively diluted systems when the consideration of a single disperse particle in a infinite disperse medium volume can be in the theory base. In the concentrated systems (pastes, diaphragms being from colloid particles) the picture of the phenomena is becoming complicated substantially under the influence of the interaction between equilibrium and polarization fields that strongly impedes the theory construction. However, just in the concentrated systems with the particles of the colloid dispersity the quite interesting influence on the kinetic properties in anomalous fluid layers near the surface, inasmuch as in the concentrated systems these layers occupy substantial volume part of the threshold space.

Just in such systems the authors [1-3] systematically were investigating the electroosmosis as a function of the disperse phase concentration and had found simple but enough general regularities: such as the linear dependence of the electroosmotic transfer \( P_e \) a reverse value of the particle concentration, the part of the segment being cut off by the straight line \( P_e(C^{-1}) \) on the abscissa with the fluid boundary layer thickness, other peculiarities. For the explanation of these regularities the model of the near wall layer of the fluid in which it combines the non-dissolving volume properties with the hydrodynamic mobility was proposed in the work [4]. The calculations in the work [4] were based on the simplest geometric model representing the porous space of the suspension by plane capillaries. The model of the plane capillary, however, for suspension porous space is too rough, all the more, the question is the effects substantially depending on the geometry interface (in particular the dependence of \( P_e \) on the volume particle fraction). Therefore, the question arised is it possible to explain the experiment in the model more realistically than plane capillaries taking into consideration the particle surface curvature by the model of the hydrodynamically mobile non-dissolving near wall layer.

The possibility to receive the answer to this question has appeared in connection with the development [5,6] of the procedure for the use of the cell model widely applied while solving purely hydrodynamic tasks to the electrokinetic problems.

II. STATEMENT OF A TASK

In the cell model the consideration of a suspension is the consideration of one of its typical structural unit - a radius of a particle “belonging” to it in the fluid volume. And the main simplification consists in that the boundary of this volume is considered to be a sphere (instead of corresponding polyhedron). The fraction of the volume being occupied by a particle in the cell corresponds to the volume particle fraction in the suspension. Having designated the cell radius by \( c \) we obtain:

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\[ \alpha = \frac{a^3}{c^3}. \]  

Introducing the idea about non-dissolving boundary layer we shall designate the radius of the dissolving and non-dissolving layer in the cell by \( b \). Then the thickness \( h \) of the non-dissolving boundary layer will be equal:

\[ h = b - a, \]

and the volume fraction of the non-dissolving water (see Fig. [1])

\[ \alpha_1 = \frac{(b^3 - a^3)}{c^3}. \]

The presence of the non-dissolving layer means that the diffuse shell of the double electric layer is completely in the dissolving water. Namely, the volume force is applied to it from the electric field side. We’ll restrict our consideration about high degree of overlapping of diffuse double layer of neighbor particles, when Debye length \( R_D \) is much larger that thickness of dissolving layer: \( R_D/(c \times b - h) \ll 1 \). It corresponds to the supposition that the volume charge density and also the volume force are constant in all points of the dissolving layer (homogeneous approximation). Then for the calculation of the electroosmosis rate of the 1-1 valent binary electrolyte the following equation system must be solved:

\[
- \eta \, \text{rot} \, \text{rot} \, \vec{v} - \text{grad} \, (p + RT \gamma^+ \mu^+ + RT \gamma^- \mu^-) = 0, \tag{4}
\]

\[
d \vec{v} = 0, \tag{5}
\]

\[
d \text{grad} \mu^\pm = 0, \tag{6}
\]

where \( \eta \) is the fluid viscosity, \( p \) is the pressure, \( \nu \) is the fluid rate, is dimensionless (in the \( RT \) units) electrochemical ion potentials, \( C \) are their concentrations. In this case \( \gamma^\pm = C - C_o \), \( C_o \) is of the concentration of the solution being equilibrium with the suspension:

\[ c^\pm = \frac{G^2}{2} + \sqrt{\frac{G^2}{4} + C_o^2}, \tag{7} \]

\[ \rho = F \left( C^+ - C^- \right) \equiv -FG, \tag{8} \]

where \( F \) is the Faraday constant.

The particle charge \( Q \) is expressed through \( G \):

\[ Q = -\frac{4\pi}{3} (C^3 - b^3)FG. \tag{9} \]

In the non-dissolving layer the volume force does not act on the fluid because on the definition the ions do not penetrate there. For this region of equation system (4) - (6) is simplified at the expense of all members containing \( \mu \). (4) - (6) system must be solved jointly with the edge conditions:

\[ \nu_r|_{r=a} = 0, \tag{10} \]

\[ \nu_\theta|_{r=a} = 0, \tag{11} \]

\[ \nu_r|_{r=b^-} = \nu_r|_{r=b^+}, \tag{12} \]

\[ \nu_\theta|_{r=b^-} = \nu_\theta|_{r=b^+}, \tag{13} \]

\[ P|_{r=b^-} = P|_{r=b^+}, \tag{14} \]

\[ \Pi_\nu|_{r=b^-} = \Pi_\nu|_{r=b^+}, \tag{15} \]
rot $\nu|_{r=c} = 0$, \hspace{1cm} (16)

$$(-D^{\pm} \frac{\partial \mu}{\partial r} + \nu_r)|_{r=b+0} = 0.$$ \hspace{1cm} (17)

Here $\Pi$ is the tangent component of the tensor of the viscous stresses (during its calculation shall take the same viscosity for both the dissolving and non-dissolving layers) the symbols $b \pm a$ designate the limits of the corresponding values while the radius tends to $b$ both from the right and from the left respectively. $D^{\pm}$ is the ion diffusion coefficients. Condition (16) is the cell edge condition for the Cuveabara model [7].

Besides, the conditions characterizing the electroosmosis process must be given:

$$\frac{F}{\cos \theta}(-D^+ C^+ \frac{\partial \mu^+}{\partial r} + D^- C^- \frac{\partial \mu^-}{\partial r} + \nu_r(C^+ - C^-))|_{r=c} = I_E,$$ \hspace{1cm} (18)

$$\mu^- + \mu^+|_{r=c} = 0,$$ \hspace{1cm} (19)

$$\int_{r=a} r^2 \Pi ds + RT \int_{b<r<c} (C^+ - C^-) \text{grad}(\mu^+ - \mu^-) d\nu = 0,$$ \hspace{1cm} (20)

where $I_E$ is electric current, $\Pi$ is the tensor of the viscous stresses. Condition (19) means the absence of the concentration difference in the suspension. Condition (20) means the compensation of the viscous force acting a particle by sum of the volume electrical forces acting the charged fluid. The absence of the difference in pressure on the diaphragm made from particles.

The volume rate $I_v$ of the fluid in the cell model is expressed by the formula

$$I_v = \frac{\nu_r}{\cos \theta}|_{r=c},$$ \hspace{1cm} (21)

and the average electric field $E$ is equal

$$E = \frac{RT \cos \theta (\mu^+ - \mu^-)}{F_c|_{r=c}}.$$ \hspace{1cm} (22)

Having determined these values we have found the electroosmotic transfer $P_e$ and electroconductivity $K$:

$$P_e = \frac{I_v}{I_E},$$ \hspace{1cm} (23)

$$K_\Sigma = \frac{I_E}{E}.$$ \hspace{1cm} (24)

III. PROBLEM SOLUTION

The edge problem (4) - (20) is reduced to 12 linear algebraic equations of the following by substitution of the general solutions:

$$\mu^\pm = \cos \theta (A_1 \pm r + A_2^\pm r^{-2}),$$ \hspace{1cm} (25)

$$\nu_r = \cos \theta \left(B_1 + \frac{2B_2}{r^3} + \frac{B_3 r^2}{10} + \frac{B_4}{r}\right),$$ \hspace{1cm} (26)

$$\nu_\theta = -\sin \theta \left(B_1 + \frac{B_2}{r^3} + \frac{B_3 r^2}{5} + \frac{B_4}{2r}\right),$$ \hspace{1cm} (27)

$$p = \eta \cos \theta \left(B_3 r + \frac{B_4}{r^2}\right).$$ \hspace{1cm} (28)
The solution for the rate at $b \leq r \leq c$ formally coincides with (27) if one considers the instead the pressure.

$$S = p + RT\gamma^+\mu^+ + RT\gamma^-\mu^-.$$  

The calculation of the integrals included in condition (20) using (25) - (28) shows that (20) is equal to the following

$$B_4 - \frac{a^2RT}{3\eta}(-\gamma^+A_2^+ + \gamma^-A_2^-)(\frac{1}{a} - \frac{b^3}{a^3}) = 0.$$  

Rest edge conditions are transformed into the linear equations in trivial way.

The analytical expressions obtained for $P_v$ and $K_V$ from the solution of these equations are quite awkward and they are inconvenient. Therefore, the solution analysis will be based on the numerical investigation of the most typical situations.

While concretizing the parameters of equations (4) - (20) we gave their values characteristic for the systems being studied in the experiments on the electroosmosis on the diaphragms based on the synthetic diamond with the particles of 150 nm size in the HCl solutions with the 0.01 - 1.0 mmole/l concentration. The viscosity was 1.0 mPa.c. The diffusion coefficients were $D^+ = 8.86 \cdot 10^{-5}$ cm$^2$/c, $D^- = 1.94 \cdot 10^{-5}$ cm$^2$/c. The dependencies of the electroosmositic transfer $P_v$ on the particle charge, on the volume fraction and the non-dissolving boundary layer thickness calculated using the mentioned values of the system characteristics are shown in Figs. 2-4.

IV. THE CALCULATION RESULT DISCUSSION

The main circumstance while interpreting the dependencies in Figs. 2-4 is that the local conductivity $K$ and the charge density $\rho$ in the dissolving fluid of the threshold space in the homogeneous approximation has the dependence character depicted in Figures 3 and 4.

If the average field strength applied to the suspension is not changed the electroosmosis rate is proportional to the particle charge and the volume charge density ($I_vQ_P$). The fluid in the porous space is charged, therefore, the flow gives birth to the convection component of the electric current $I_v(Q) = I_v(Q)/I_E$. On the other hand, the migration component of the electroconduction associated with the ion movement through the fluid is proportional to the local conductivity. Thus, at small charges the sum current will be determined mainly by the electromigration component and must slowly grow with the charge increase (Fig. 2, region 1). At great particle charges the sum is determined by the convection component and is proportional to the charge square (Fig. 2, region 2).

With the account of the mentioned statement it is not difficult to explain the maxima on the dependencies $P_v(Q) = I_v(Q)/I_E(Q)$ in Fig. 5: region 1 corresponds to the ascending branch, region 2 corresponds to the descending branch in Fig. 4. On appearing of the non-dissolving layer the volume charge moves away from the surface. In this case, inasmuch as the particle charge does not change, the sum volume force remained as previous one, only the region of its application also moved away from the surface, i.e., to there where the flow is developing easily. Therefore, also the electroosmosis rate and the convection current grows and the latter increases more substantially, inasmuch as it is determined by the movement only in the region of the dissolving volume where the local rate is high, then as the flows in the non-dissolving volume being retarded by the surface make the contributions in the integral electroosmosis rate. Therefore, at small charges (region 1 in Fig. 2) when the current is determined by the electromigration component and does not increase with the growth in the non-dissolving volume; the electroosmotic transfer is growing with the average electroosmosis rate. At great charges (region 2, Fig. 2) when the current is determined by the convection component and is growing with the non-dissolving volume more rapidly than the electroosmosis rate does the electroosmotic transfer drops (Fig. 3). The increase in the electroosmotic transfer at simultaneous sharp increase of the electroconductivity observed by the authors [8] in the diamond diaphragms during the destruction of the non-dissolving boundary layer under the action of the saccharose solution being introduced in the diaphragm corresponds to this. As to the dependence of the electroosmotic transfer on the reverse value of the volume fraction as it is seen from Fig. 4 the linear dependencies $P_v(A_1-1)$ are obtained in wide interval of the volume fraction values including even at the relatively its small values when the porous space cannot be considered completely in the homogeneous approximation.

Thus, the calculations of the electroosmotic transfer by the cell model based on the ideas about the near wall layer as about the non-dissolving and hydrodynamically mobile layer show the complete correspondence of the qualitative regularities obtained by the authors. This allows to hope for the receiving a quantitative information about the near wall layer while comparing in details the calculations obtained with the experimental data.
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FIG. 1. Structural elements in the cell model of a disperse system. $a$-radius of a particle; $h$-thickness of the non-dissolving layer; $b$-radius of the non-dissolving layer in the cell; $c$-cell radius; 1-particle surface charge; 2-external boundary of the non-dissolving layer; 3-external boundary of a diffuse layer.
FIG. 2. Dependencies of the electroosmotic transfer $P (cm^3/K)$ and diaphragm electroconductivity $K, (1/ohmcm)$ on particles charge $Q$. 
FIG. 3. Dependencies of the electroosmotic transfer $P_e$ and diaphragm electroconductivity $K$ on the thickness of the non-dissolving boundary layer $h(m^{-10})$. 
FIG. 4. Dependencies of the electroosmotic transfer $P_e$ and diaphragm electroconductivity $K$ on the reciprocal volume particle fraction (different values of the non-dissolving boundary layer thickness $h, m^{-1}$).
FIG. 5. Dependence of local conductivity $K$ in the dissolving fluid on particles charge $Q$ (homogeneous approximation).
FIG. 6. Dependence of charge density $p$ in the dissolving fluid on particles charge $Q$ (homogeneous approximation).
FIG. 7. Dependencies of convection $I_{cc}$ and migration $I_{em}$ components of the electric current and the sum current $I_e$ on particles charge $Q$. 
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