J. Appl. Maths Mechs Vol. 57, No. 3, pp. 577–581, 1993
Printed in Great Britain.

0021–8928/93 $24.00+.00

ELECTRO-OSMOSIS ON MODIFIED (MOSAIC) SOLID SURFACES†

A. G. PETROV and V. YE. SMORODIN

Moscow

(*Received* 2 *January* 1992)

A theory of electro-osmosis on energetically (electrically) inhomogeneous (neutral as a whole) dielectric substrates is developed. An exact formulation of the problem of the electric flow of a wetting film of electrolyte along a mosaic (electrically heterogeneous) surface of a solid is given. The electric field strength and potential distribution in the system are found for steady-state conditions. General expressions are obtained for the disjoining and hydrostatic pressure in the film, the hydrodynamic velocity field and the equation of the film profile. Criteria for the transition from a continuous to a mosaic structure are established.

THE MECHANISM of electro-osmosis, that is, the flow of the solution of an electrolyte under the action of an external electric field in a heterogeneous "electrolyte–solid" system (the latter is most often a capillary-porous medium [1]) was described for the first time by Helmholtz. Later, Smoluchowski showed that, for sufficiently large pores, the mean rate of transport is independent of the radius of the capillary. More recently, the development of the theory of electro-osmosis was associated with the description of the structure of electrical double layer (EDL) of the ions and the scaling effects of the "disjoining pressure" Π (according to B. V. Deryagin) taking account of the dependence of the permittivity of the dielectric on the electric field strength, the finite nature of the dimensions of the ions, etc.

It is believed at the present time that the main problem which is hindering further development of the theory of electro-osmosis and the EDL (or, more widely, electrokinetic phenomena) is the lack of reliable empirical and theoretical data on the dependence of the permittivity ε and the shear viscosity η on the thickness of the layer h, which reveal anomalies [3]. The obscurity surrounding the meaning of one of the basic concepts of the classical Helmholtz–Smoluchowski theory of the electrokinetic phenomena: the electrokinetic potential ζ, and its relationship to the interphase potential Ψ_d and theoretical models of the EDL, are also associated with this. Not one of the existing theoretical models can completely explain the experimental data.

A constructive solution of the above-mentioned problems has recently been proposed by one of us based on taking account of the energetic inhomogeneity of the "mosaic character" of the surface of a solid (of colloidal dimensions), which has been ignored in all of the previous theories as well as the fact that the topological structure of fluid layers depends on their thickness [4–9].

The aim of this paper is to give a systematic description of an electrodynamic theory of electro-osmosis on "mosaic" surfaces taking account of the structure of the cohesive EDL.

---

†*Prikl. Mat. Mekh.* Vol. 57, No. 3, pp. 172–175, 1993.

1. THE CHARGE DISTRIBUTION AND EQUATION FOR THE POTENTIAL IN A SYMMETRIC BINARY ELECTROLYTE

According to Boltzmann's law, the charge density distribution in a symmetric binary electrolyte is given by the expression [3]

$$\rho = -2Zen\,\mathrm{sh}[Ze\psi/(kT)] \tag{1.1}$$

where Z is the number of electrons in the negatively charged ion which determines its charge, e is the electron charge, n is the number of ions with a charge of one sign per unit volume, T is the temperature on the Kelvin scale, k is Boltzmann's constant and ψ is the electric field potential. The potential distribution in an electrolyte obeys Gauss' law

$$\Delta\psi = -4\pi\rho/\varepsilon \tag{1.2}$$

where ε is the permittivity of the electrolyte.

2. BOUNDARY CONDITIONS

Consider a thin layer of electrolyte, placed between a solid substrate (the characteristics of which we shall denote by the subscript 0) and an air medium (the characteristics of which are denoted by the subscript 1). The conditions on the boundary with the air can be written in the following form

$$\varepsilon_1\partial\psi_1/\partial n - \varepsilon\partial\psi/\partial n = -4\pi\sigma_1, \quad \psi_1 - \psi = 0 \tag{2.1}$$

where σ_1 is the surface charge density. In an aqueous electrolyte, the permittivity ε is greater than the permittivity in air by two orders of magnitude and the first boundary condition (3.1) can therefore be simplified

$$\partial\psi/\partial n = 0 \tag{2.2}$$

On the solid substrate, the boundary condition can be written in the form $\partial\psi/\partial z = 4\pi\sigma/\varepsilon$, $z = 0$ since, in view of the thinness of the electrolyte layer, the quantity $\varepsilon\partial\psi/\partial z - \varepsilon\psi/h$ is considerably greater than $\varepsilon_0\partial\psi_0/\partial z$.

The charge on the solid substrate σ can be substantial in a number of cases and it must then be taken into account.

3. LINEARIZATION AND SOLUTION OF THE LINEAR BOUNDARY-VALUE PROBLEM FOR THE POTENTIAL. THE DISJOINING PRESSURE

Under the condition that $|Ze\psi/(kT)| \ll 1$, expression (1.1) can be linearized

$$\begin{gathered}\rho \approx -2n\psi(Ze)^2/(kT) = -\varepsilon\kappa^2\psi/(4\pi)\\ \kappa^2 = 8\pi n(Ze)^2/(\varepsilon kT)\end{gathered} \tag{3.1}$$

From (3.1), (1.2), (2.2) and (2.3), we obtain the following linear boundary-value problem

$$\begin{gathered}d^2\psi/dz^2 = \kappa^2\psi, \quad 0 \leqslant z \leqslant h(x,y)\\ d\psi/dz = 4\pi\sigma/\varepsilon, \quad z = 0; \quad d\psi/dz = 0, z = h(x,y)\end{gathered} \tag{3.2}$$

where z is a Cartesian coordinate which is perpendicular to the surface of the substrate, $z = 0$ is the equation of the surface of the substrate $z = h(x, y)$ is the equation of the free surface, and κ is the inverse Debye radius.

Let us assume that the change in the potential across the layer is much greater than the change along the layer

$$|\partial\psi/\partial x| + |\partial\psi/\partial y| \ll |\partial\psi/\partial z|$$

The solution of problem (3.2) has the form

$$\psi = \psi_h \operatorname{ch}[\kappa(z-h)], \quad \psi_h = -4\pi\sigma/(\varepsilon\kappa \operatorname{sh}(\kappa h)) \tag{3.3}$$

where ψ_h is the value of the potential on the free surface. The components of the electric field vector and the disjoining pressure [3] are determined from this

$$\Pi_e(h) = -\int_0^{\psi(h)} \rho(\psi)d\psi = \frac{2\pi\sigma^2}{\varepsilon \operatorname{sh}^2(\kappa h)} \tag{3.4}$$

for a fixed surface charge. Here, account has been taken of the fact that, by virtue of the condition κl, $l/h \gg 1$, the term $\varepsilon E^2(h)/(8\pi)$ may be neglected.

4. ELECTRO-OSMOTIC FLOW

The force $\rho E = -\rho\nabla\psi$ acting on unit volume of the electrolyte, gives rise to an electro-osmotic flow. It can be described by the equations for the slow flow of a viscous incompressible fluid in a thin layer

$$-\nabla p - \rho\nabla\psi + \partial\tau/\partial z = 0, \quad \partial h/\partial t + \partial(hv_x)/\partial x + \partial(hv_y)/\partial y = 0 \tag{4.1}$$

where $\tau = (\eta\partial v_x/\partial z, \eta\partial v_y/\partial z, 0)$ is the tangential stress vector.

The solution must satisfy the sticking condition on the solid substrate, the condition that the tangential stress on the free boundary is equal to zero and, also, the Laplace condition

$$\begin{gathered} z = 0: v_x = 0, \quad v_y = 0 \\ z = h: \partial v_x/\partial z = 0, \quad \partial v_y/\partial z = 0, \quad p = p_a - \alpha\nabla^2 h \end{gathered} \tag{4.2}$$

where p_a is atmospheric pressure and α is the surface tension of the film on the free boundary (we assume that it is constant).

On integrating the first equation of (4.1) in the projection on the z axis and satisfying condition (4.2) on the free surface, we find

$$p + \int_0^{\psi(h(x,y))} \rho(\psi)d\psi = F(x,y); \quad F(x,y) = p_a - \alpha\nabla^2 h - \Pi_e \tag{4.3}$$

Hence, the first equation of (4.1) in the projection on the x and y axes takes the form

$$\eta\partial^2 v_x/\partial z^2 = \partial F(x,y)/\partial x; \quad \eta\partial^2 v_y/\partial z^2 = \partial F(x,y)/\partial y \tag{4.4}$$

On integrating Eq. (4.4) with respect to z while taking account of the boundary conditions (4.2) we obtain

$$v = (z^2 - 2hz)\nabla(F(x,y)/(2\eta))$$

The velocity averaged over the thickness is given by the expressions

$$\bar{\upsilon}_x = \frac{h^2}{3\eta}\frac{\partial}{\partial x}(\alpha\nabla^2 h + \Pi_e), \quad \upsilon_y = \frac{h^2}{3\eta}\frac{\partial}{\partial y}(\alpha\nabla^2 h + \Pi_e) \tag{4.5}$$

and, when these are substituted into the second equation of (4.1) and account is taken of (4.5), we obtain the equation for the height of the film

$$\frac{\partial h}{\partial T} + \frac{1}{3\eta}\left(\frac{\partial}{\partial x}\left(h^3\frac{\partial}{\partial x}\right) + \frac{\partial}{\partial y}\left(h^3\frac{\partial}{\partial y}\right)\right)(\alpha\nabla^2 h + \Pi_e) = 0 \tag{4.6}$$

5. EQUILIBRIUM AND STABILITY OF THE FILM

It follows from relationships (4.5), that the equation of the profile of the equilibrium film has the form

$$\alpha\nabla^2 h + \Pi_e = \text{const} \tag{5.1}$$

Let us consider the equilibrium of a film of electrolyte on a solid substrate, on the surface of which there is a discrete charge distribution. We will assume that the charges on the substrate are arranged in circles of radius a which is small compared with the dimensions of the cell R $(a \ll R)$.

Let us consider the cell $0 \leqslant r \leqslant R$ and find the solution of the equilibrium equation (5.1), which is symmetric with respect to the angle of the film

$$\frac{d}{dr}\left(r\frac{dh}{dr}\right) + \frac{2\pi\sigma^2 r}{\alpha\varepsilon\,\mathrm{sh}^2(\kappa h)} = Cr \tag{5.2}$$

under the condition on the boundary $r = R$ of the cell and the condition that the volume of the cell $\pi R^2 h$ is specified

$$r = R\colon\ \frac{dh}{dr} = 0; \quad R^2\bar{h} = 2\int_0^R rh(r)dr \tag{5.3}$$

where $\bar{h}$ is the mean thickness of the film; $\sigma \neq 0$ when $0 \leqslant r \leqslant a$ and $\sigma = 0$ when $r > a$.

On integrating Eq. (5.2) from 0 to $r > a$ and satisfying conditions (5.3), we obtain

$$h = \bar{h} - B\left(\ln\frac{r}{R} + \frac{3}{4} - \frac{r^2}{2R^2}\right), \quad B = \frac{2\pi}{\alpha\varepsilon}\int_0^a \frac{r'\sigma^2 dr'}{\mathrm{sh}^2(\kappa h(r'))} \tag{5.4}$$

It is obvious that the film will be continuous and unbroken when $h(R) \leqslant 0$. Otherwise, rupture of the film occurs. The condition for the surface to have a mosaic form

$$h(R) = \bar{h} - \tfrac{1}{4}B = 0 \tag{5.5}$$

follows from this. When $a \ll R$, $h(r')$ in the expression for B (5.4) in the integrand can be replaced by $h(a)$ and, then

$$\kappa B = \frac{\pi\kappa}{\alpha\varepsilon}\left(\frac{\sigma a}{\mathrm{sh}(\kappa h(a))}\right)^2, \quad \kappa h(a) = \kappa\bar{h} + \kappa B\left(\ln\frac{R}{a} - \frac{3}{4}\right)$$

Instead of B, let us substitute the quantity $4h$ which is equal to it in accordance with (5.5). The condition for the film to have a mosaic form is then reduced to the following

$$2\sqrt{\kappa\bar{h}}\,\mathrm{sh}\left(\kappa\bar{h}\left(4\ln\frac{R}{a}-2\right)\right)\leqslant\sqrt{\frac{\pi\kappa}{\alpha\varepsilon}}\sigma a$$

Using this relation, it is possible in the case of an actual set of physical parameters of the system to determine the type of structure of a film EDL or its stability. For example, let the system have the parameters $R/a \approx 10^3$, $\varepsilon = 80$, $\alpha = 0.1$ J/m^2, $\sigma = 10^{-3}$ K/m^2, and $\kappa = 10^{-7}$ m. A thickness of the film EDL of $\bar{h} = 10^{-8}$ m then turns out to be critical. The destabilizing factors are: a reduction in the thickness of the film, an increase in the surface charges or the dimensions of the "centre", and the concentration of the electrolyte. Using relationship (5.5), it is possible numerically to obtain different characteristic curves which separate "mosaic" and continuous structures (for example, in the $(\bar{h}, \sigma)$ plane etc.).

REFERENCES

1. TIKHOMOLOVA K. P., *Electro-osmosis.* Khimiya, Leningrad, 1989.
2. DUKHIN S. S., *Electrical Conductivity and Electrokinetic Properties of Disperse Systems.* Naukova Dumka, Kiev, 1975.
3. DERYAGIN, B. V., CHURAYEV N. V. and MULLER V. M., *Surface Forces.* Nauka, Moscow, 1975.
4. SMORODIN V. Ye,. Effective viscosity of wetting films on heterogeneous surfaces. *Dokl. Akad. Nauk SSSR* **313,** 5, 1173–1177, 1990.
5. SMORODIN V. Ye. and DERYAGUIN B. V., On the factor on nonuniformity of the surface of solids in the interface phenomena. *J. Colloid Interface Sci.* **142,** 1, 272–277, 1991.
6. SMORODIN V. Ye. On the topological structure and physical properties of films on energetically inhomogeneous surfaces. *Poverkhnost* **6,** 85–91, 1991.
7. SMORODIN V. Ye., On the theory of the electrical double layer on mosaic (modified) substrates. *Dokl. Akad. Nauk SSSR* **312,** 6, 1415–1418, 1990.
8. SMORODIN V. Ye., Filtration and electro-osmosis in heterophilic disperse media. *Dokl. Akad. Nauk SSSR* **318,** 2, 381–384, 1991.
9. SMORODIN V. Ye., On the theory of modified partition membranes. *Kolloid. Zh.* **52,** 2, 390–395, 1990.

Translated by E.L.S.