

Determination of the Electrokinetic Potential of Porous Glass by the Streaming Potential Method in a Flat Capillary

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The streaming potential method is one of the main experimental methods that makes it possible to calculate the electrokinetic potential from the values measured for a capillary-porous system. In the case when the liquid flow occurs in a capillary whose walls are not porous (ion-permeable), and the radius of the capillary (or the half-width of a flat capillary) is much larger than the thickness of the diffuse layer δ

($\delta = [(\epsilon\epsilon_0 RT)/F^2 \sum_i z_i^2 C_i]^{1/2}$, where ϵ and ϵ_0 are the permittivities of the medium and vacuum, respectively, R is the gas constant, and T is temperature, z_i and C_i are the charges and molar concentrations of ions that are part of the electrolyte), the electrokinetic potential (ζ) can be calculated from the values of the streaming potential (E_s) by using the well-known Helmholtz–Smoluchowski equation [1, 2]:

$$\zeta = \eta \kappa E_s / \epsilon \epsilon_0 \Delta P, \quad (1)$$

where η is the fluid viscosity, κ is the specific electrical conductivity of the solution in the capillary, ϵ and ϵ_0 are the relative permittivity of the medium and the permittivity of the vacuum, respectively, and ΔP is the pressure difference at the ends of the capillary.

The streaming potentials were measured in a SurPASS 3 adjustable gap cell for flat samples. The plane-parallel capillary in which the equilibrium solution flowed was formed from two plates of 8V-NT (3 M HCl) MIP porous glass (PG) obtained by leaching a monolithic sodium borosilicate glass with 3 M hydrochloric acid [3] with dimensions of $20 \times 10 \times 1$ (length, width, thickness) mm. Before the measurements, the wet plates were brought into equilibrium with the electrolyte solution of the given concentration (10^{-1} to 10^{-3} M NaCl solutions with pH 5.5 ± 0.1) and fixed in the cell with adhesive tape. In the assembled cell, the plates formed a flat capillary 20 mm long and 10 mm wide. The gap between the plates (capillary height h) specified by the micrometric screw of the cell was 100 ± 2 μm . At such a height of the capillary, the

effect of the ions of the electrical double layer (EDL) on the electrical conductivity of the solution in the capillary (surface conductivity) can be neglected, since the maximum thickness of the diffuse layer does not exceed 10 nm; i.e., we can assume that the specific electrical conductivity of the solution in capillary κ is practically equal to the specific electrical conductivity of a bulk solution in equilibrium with the capillary κ_V .

Since PG, brought into equilibrium with a sodium chloride solution, is filled with electrolyte ions, it is a conductor, and this must be taken into account when analyzing the results of the measurements of the streaming potentials. The effect of the structure and electrical conductivity of the porous plates, which make up the walls of a plane-parallel capillary, was taken into consideration using the approach developed in [4, 5]. The capillary formed in the measuring cell actually consists of three parallel conductors (capillary walls and the solution layer separating them) of the same width b ; then, assuming that the walls of the capillary are identical, its conductivity L (Ohm^{-1}) can be written in the following form:

$$L = \frac{S_{\text{sol}}}{l} \kappa_V + \frac{2S_{\text{PG}}}{l} \kappa_{\text{PG}}, \quad (2)$$

where l is the length of the capillary, $S_{\text{sol}} = hb$ is the cross-sectional area of the solution layer between the plates, $S_{\text{PG}} = h_{\text{PG}}b$ is the cross-sectional area of the PG plate, and κ_{PG} is the specific electrical conductivity of PG.

We assume that the pore space of the PG is N cylindrical pores of the same radius r located at the same angle to the end surfaces of the plates and the pore length is Kl . Then the value of K in the cylindrical pore model is the tortuosity coefficient, which reflects the elongation of the electric current bullet (or liquid) along the plate compared to its geometric length. The number of pores N can be related to the bulk porosity (the ratio of the pore volume to the plate volume equal to lbh_{PG}/W), since the volume of one pore is $\pi r^2 kl$:

$$N = \frac{Wbh_{PG}}{\pi r^2 K}. \quad (3)$$

It can also be shown [6] that in the considered model $W\beta = K^2$, where β is the coefficient of the structural resistance of the porous plate, which reflects the contribution of the nonconductive skeleton to the electrical resistance of the PG. The specific electrical conductivity of PG κ_{PG} can be expressed as follows:

$$\kappa_{PG} = \kappa_V \alpha / \beta, \quad (4)$$

where $\kappa = \kappa_V \alpha$, κ is the specific electrical conductivity of the solution in pores, and α is the efficiency coefficient [3, 7]. Then the conductivity of the porous capillary wall ($1/R_{PG}$), which is a parallel connection of N identical conductors, taking into account Eqs. (3) and (4), takes the form

$$1/R_{PG} = N/R_l = N \kappa \pi r^2 / Kl = bh_{PG} \kappa_V \alpha / l\beta. \quad (5)$$

For the conductivity of the capillary as a whole, we obtain

$$L = \frac{bh}{l} \kappa_V + \frac{2bh_{PG}\alpha}{l\beta} \kappa_V = \frac{b}{l} \kappa_V \left(h + 2\alpha \frac{h_{PG}}{\beta} \right). \quad (6)$$

If we assume that the streaming current I_s passes only through the central (solution) part of the capillary [4], then, taking into account the conductivity of its walls, the Helmholtz–Smoluchowski equation is transformed to the following form:

$$\begin{aligned} \zeta_e &= \frac{\eta \kappa_V E_s}{\varepsilon \varepsilon_0 P} \left(1 + \frac{2h_{PG} \kappa_{PG}}{h \kappa_V} \right) \\ &= \frac{\eta \kappa_V E_s}{\varepsilon \varepsilon_0 \Delta P} \left(1 + \frac{2h_{PG} \alpha}{h \beta} \right) \equiv \frac{\eta \kappa_V E_s}{\varepsilon \varepsilon_0 \Delta P} (1 + B\alpha), \end{aligned} \quad (7)$$

where ζ_e is the electrokinetic potential of the porous plate surface and $B \equiv 2h_{PG}/h\beta$. At the zero electrical conductivity of the walls of the capillary, i.e., when β tends to infinity (or parameter B tends to zero), which means the transition from a porous body to a continuous one, Eq. (7) reduces to Eq. (1) when the specific electrical conductivities of the bulk solution and the solution in the capillary are equal ($\kappa_V = \kappa$).

We now assume that the solution's flow through a plane-parallel capillary with porous walls is considered taking into account the passage of the streaming current not only through the central part of the solution but also through the pore space of the capillary walls [5]. The streaming current in the central part of the capillary ($I_{s,h}$) and along both porous walls ($I_{s,2PG}$) can be written as follows:

$$I_{s,h} = -\varepsilon \varepsilon_0 b h \zeta_e \Delta P / l \eta, \quad (8)$$

$$\begin{aligned} I_{s,2PG} &= -2N \varepsilon \varepsilon_0 \pi r^2 \zeta_i \Delta P / Kl \eta \\ &= -2\varepsilon \varepsilon_0 \zeta_i b h_{PG} \Delta P / l \eta \beta, \end{aligned} \quad (9)$$

where ζ_i is the effective electrokinetic potential of the surface of the pore channels [5]. We assume that we

are measuring the streaming potential on the most porous wall of a flat capillary by the usual method: the liquid flows through the pores under the action of external pressure. Then this effective electrokinetic potential corresponds to value ζ , which we would calculate using the Helmholtz–Smoluchowski equation (1), which does not take into account the overlapping of the EDL in thin pores, i.e., without taking into account the effect of the EDL's overlap on the measured value of the streaming potential.

Using Eqs. (6), (8), and (9), we obtain an expression for the streaming potential:

$$E_s = \frac{-(I_{s,h} + I_{s,2PG})}{L} = \frac{\varepsilon \varepsilon_0 \Delta P [\zeta_e h + 2\zeta_i (h_{PG}/\beta)]}{\eta \kappa_V [h + 2\alpha (h_{PG}/\beta)]}. \quad (10)$$

Using parameter B , we obtain an expression for calculating the electrokinetic potential of the porous surface of a plane-parallel capillary:

$$\zeta_e = \frac{\eta \kappa_V E_s}{\varepsilon \varepsilon_0 \Delta P} (1 + B\alpha) - B\zeta_i. \quad (11)$$

Analyzing Eq. (11) we see that at $B \rightarrow 0$ (the nonporous walls of a plane-parallel capillary), it, like Eq. (7), reduces to the usual Helmholtz–Smoluchowski equation (1).

Measurements of the parameters of equilibrium sodium chloride solutions, the electrokinetic characteristics of a plane-parallel capillary, and the values of the electrokinetic potentials ζ_{AP} calculated using the usual classical Helmholtz–Smoluchowski equation (each value is the average of 5–12 results obtained in a specific series of measurements on the SurPASS 3 setup) are given in Table 1. The correlation coefficients of the obtained results (linearity of dependences $E_s - P$) were more than 0.99. The temperature interval in which the measurements were carried out corresponded to $24 \pm 1^\circ\text{C}$. The same table shows the values of the structural resistance coefficients, efficiency coefficients, and electrokinetic potentials ζ_i found for PG membranes 8V-NT MIP obtained from the same glass at the same time and under the same conditions as the porous plates from which the capillary was formed for measurements using the SurPASS 3 setup [3]. A comparison of the values of the electrokinetic potentials found for a plane-parallel capillary with microporous walls according to various equations is shown in Fig. 1. It can be seen that the $|\zeta_{AP}|$ values, found without taking into account the contribution of the porous conducting capillary walls to the measured values of the streaming potentials (dependence 1), decrease with dilution, which contradicts the theoretical concepts of the EDL structure. Note that the same character of the dependence of the electrokinetic potential on the concentration of an indifferent electrolyte is also observed for the ζ values found for PG membranes without the effect of the EDL's overlap in the capillaries and surface conductivity on the streaming potentials [8, 9]. Accounting for the conductivity

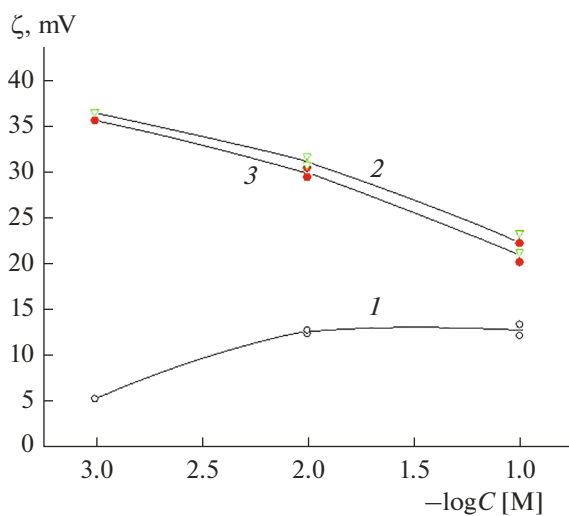
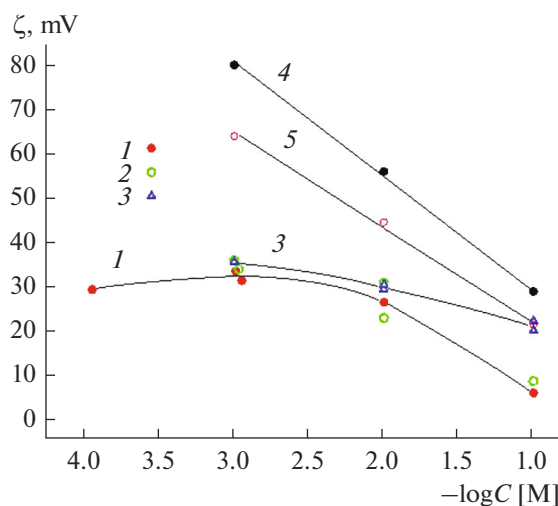
Table 1. Experimental results obtained for a plane-parallel capillary and 8V-NT (3 M HCl) MIP microporous membrane in NaCl solutions (the bulk porosity of PG samples W was 0.24)

C, M	pH	$\kappa_p, \text{Ohm}^{-1}\text{m}^{-1}$	$\eta \times 10^4, \text{Pa s}$	ε	$-E_s/P \times 10^8, \text{W/Pa}$	$-\zeta_{AP}, \text{mV}$	β from ζ_i	α	$-\zeta_i, \text{mV}$
0.1	5.61	9.210×10^{-1}	9.16	78.80	1.06	12.2	26.68	1.0	1.54
0.1	5.60	9.620×10^{-1}	9.17	78.82	1.01	13.4	26.68	1.0	1.54
0.01	5.44	1.132×10^{-1}	8.95	78.44	8.49	12.4	26.42	1.96	1.71
0.01	5.45	1.214×10^{-1}	8.37	78.20	8.37	12.8	26.42	1.96	1.71
0.001	5.43	1.247×10^{-2}	9.30	79.03	31.34	5.3	24.24	7.16	1.07
0.001	5.45	1.314×10^{-2}	9.06	78.67	31.10	5.3	24.24	7.16	1.07

of the porous walls of a plane-parallel capillary (curve 2) leads to the type of dependence $\zeta_e - \log C$ usually observed for microporous glasses. We also note that taking into account the streaming current along the porous walls of the capillary (dependence 3) has an insignificant effect on the values of the electrokinetic potential ζ_e , since the streaming currents in the nanopores of the walls and the values of the electrokinetic potentials ζ_i are small (Table 1). This is due to the high degree of the EDL's overlap in 8V-NT (3 M HCl) MIP nanopores with the average radius of 2.3 nm [3] over the entire studied concentration range of NaCl solutions.

A comparison of the results of determining the electrokinetic potentials for various silica materials is shown in Fig. 2. It can be seen that, for 8V-NT (3 M HCl) MIP at $C \leq 10^{-2}$ M concentrations of the NaCl solutions (dependence 3), the ζ_e values are close both to the values of the electrokinetic potentials found for

8V-NT (3 M HCl) MIP membranes (dependence 1) and the values of the electrokinetic potentials found for porous particles of 8V-NT (3 M HCl) MIP by microelectrophoresis, taking into account that the particle is porous [10]. Dependences 4 and 5 were obtained for the plane-parallel capillaries formed from various samples of quartz glass with a grade 14 polish; and the capillary heights were 50 [12] and 60 [11] μm . Higher $|\zeta|$ -potentials values for quartz glass that has been in contact with an electrolyte for a short time are usually related to the virtual absence of an ion-transmitting gel layer on the surface. For microporous glasses, the presence of gel layers on the surface of the pore channels is determined by the fact that the pores contain secondary silica, whose presence reduces the values of the electrokinetically mobile charge and, conse-

**Fig. 1.** Dependences of the electrokinetic potential of the surface of 8V-NT (3 M HCl) MIP plates in NaCl solutions: (1) ζ_{AP} ; (2) ζ_e calculated by Eq. (7); (3) ζ_e calculated by Eq. (11).**Fig. 2.** Electrokinetic potentials of silicate materials in NaCl solutions in the neutral pH region: (1) 8V-NT membrane (3 M HCl) MIP, streaming potential method [3]; (2) particles of 8V-NT (3 M HCl) MIP, by the microelectrophoresis method [9] and this study; (3) ζ_e values for 8V-NT (3 M HCl) MIP plates calculated by Eq. (10); (4) plane-parallel capillary made of quartz glass, streaming potential method [11]; (5) plane-parallel capillary made of quartz glass, streaming potential method [12].

quently, the $|\zeta|$ values. In addition, we should take into account the probability of a decrease in the absolute value of the surface charge of the microporous material due to the effect of the EDL overlap [13], which will also lead to a decrease in $|\zeta|$ in dilute solutions. In a 0.1 M NaCl solution, it turned out that the electrokinetic potential of the porous surface of a plane-parallel capillary approaches the values found for a continuous surface. To verify the observed regularities, further studies of the concentration dependences of the electrokinetic potential at a fixed displacement from the isoelectric point (the pH value at which the ζ value for the given surface is zero) are required.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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