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The influence of surface charge on the ionic conductivity of the electrolyte in a nanochannel

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The flow of ion current in a nanochannel formed by a glass nanopipette close to a flat polymer surface at distances commensurate with or less than the diameter of its aperture (~ 100 nm) was studied. The gap between the pipette and the plane was controlled using the feedback loop of a scanning ion conductance microscope. An increase in ionic conductivity was detected as the nanopipette approached the surface. The axially symmetric pipette–plane system was considered as an adaptive T-shaped nanochannel. The dependence of the T-channel conductivity on the aperture size, temperature, and ion concentration was studied. It has been shown that the effect of increasing conductivity is due to the surface charge.

Keywords: nanopipette, scanning ion conductance microscope, nanochannel, peak effect, surface charge.

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Studying the features of electric charge transfer in sharp-pointed and narrow nanoscale channels filled with liquid electrolyte is important for the development of micro- and nanofluidics [1–2], nanoionics [3] and new approaches to DNA analysis [4]. Modern methods of DNA sequencing are based on the use of artificial solid-state and natural organic pores of small size [5], however, their creation still requires solving a number of problems caused by the high cost and complexity of manufacturing technologies, overgrowth and contamination of pores, etc. An alternative method for creating artificial nanochannels and nanopores for DNA sequencing could be precision electromechanical control of ultra-small gaps in adaptive channels. Since nanopore sequencing uses the effect of nucleotides on ionic conductivity, it is of interest to study the conductivity of adaptive nanochannels, including accounting of the surface charge that is known to arise on glass or polymer walls.

In this paper, we studied the conductivity of glass nanopipettes (NP) filled with liquid electrolyte with aperture diameters ~ 100 nm (Figure 1), formed by the thermal drawing method. Such probes are used to measure ionic currents flowing through ion channels in cell membranes [6], as well as to visualize the surface of biological objects using scanning ion conductance microscopy (SICM) [7], nucleic acid lithography [8], etc. The aperture diameter (~ 100 nm) and wall thickness (~ 30 nm) of NP were determined from the images (Figure 2, *a*), obtained on scanning electron microscope (SEM) and their cross sections (Figure 2, *b*), made using Image J program.

We studied the flow of ion current through NP close to flat surface of polymer (ethyl vinyl acetate melt) at distances commensurate with the diameter of NP aperture (Figure 1). The ion current was measured using Ag/AgCl electrodes and current–voltage converter.

To control the gap size *h*, a tracking system (TS) of the scanning ion conductivity microscope (SCIM) [9] was used. To initially set the gap *h*, using an inertial propulsion device based on a piezo actuator, a step-by-step rough approach of NP to the polymer surface was performed with the TS turned on until the ion current corresponding to the current $\sim 0.9I_s$ was achieved, where I_s — saturation current flowing through NP located far from the surface. After this, the feedback loop was broken and the dependence $I(z)$ was measured by reverse smooth change of the gap *h* using the same piezo actuator.

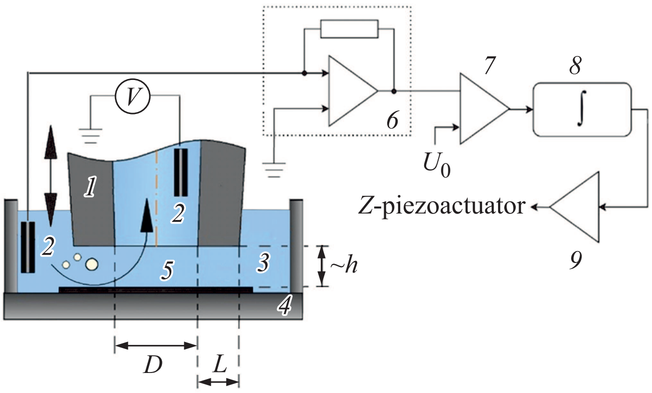

Figure 1. Experimental scheme: *1* — nanopipette, *2* — Ag/AgCl electrodes, *3* — liquid electrolyte, *4* — glass sample bottle, *5* — polymer, *6* — current-voltage converter, *7* — differential amplifier, *8* — integrator, *9* — high-voltage piezo actuator control amplifier. *D* — aperture diameter, *L* — NP wall thickness, *h* — height of the gap between the NP end and the polymer surface.

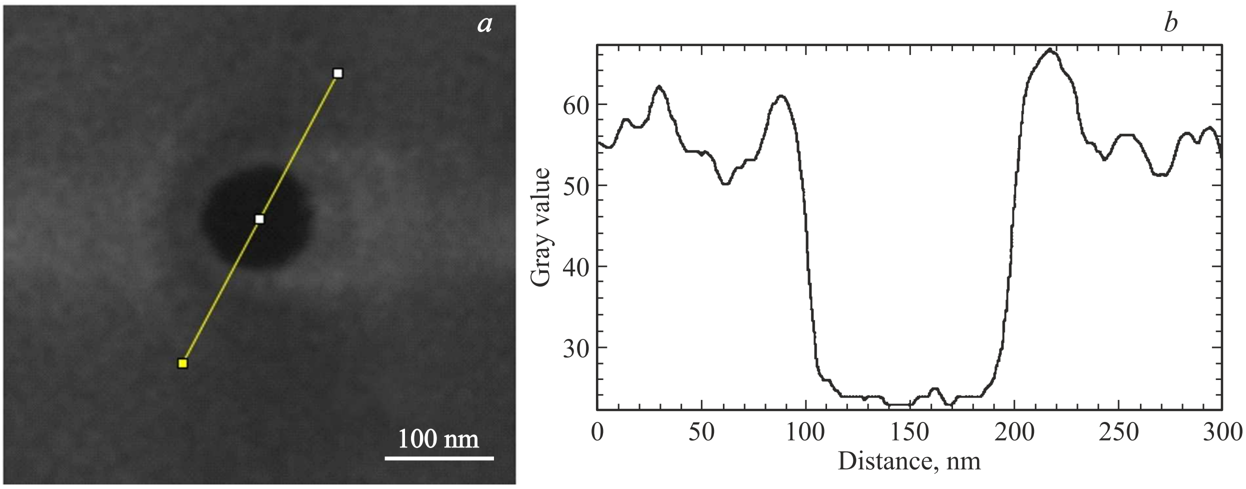

Figure 2. SEM image of the top of NP (a) and its cross section (b).

We considered NP with a finite wall thickness close to a plane as 3D adaptive nanochannel with axial symmetry, having the shape of T-shaped intersection (T-channel) in cross-section.

In this paper, current-distance curves $I(z)$ were measured at different concentrations of NaCl solution. Generally speaking, when NP approaches a flat surface at distances smaller than the size of its aperture, a smooth blocking of the ion flow through the aperture should occur, as well as a decrease in T-channel conductivity. This conductivity behavior actually occurs at a positive potential across NP. However, when approaching small distances ($h \sim 100$ nm) and at negative potential on NP in a certain range of values h T-channel conductivity increases, and the current flowing through NP aperture turns out to be higher than the saturation current [10]. With further NP approach to the plane, T-channel conductivity decreases (Figure 3, a, b). This nontrivial behavior of the T-channel conductivity vs. its size h will be called as „peak effect“. With bias voltage increasing and buffer concentration decreasing, an increase in the peak effect was observed. Heating the electrolyte by 10°C and higher also led to the appearance of the „peak effect“ if it was absent at room temperature ($\sim 20°$C). In T-channels with large aperture ($D > 100$ nm) or at a high concentration of NaCl solution (more than ~ 1800 mM/l) there was no „peak effect“. At different concentrations of ions in NP and electrolyte (17 mM/l in NP and 154 mM/l in the sample bottle), the increase in the ion current reached $(400-500)$% relative to the saturation current (Figure 3, c), however, this measurement mode had low stability and was observed at large values of $h \sim 500$ nm.

It is known that a electrical double layer (EDL) and a diffuse layer of ions with a characteristic decay length of the electrokinetic potential (Debye length) shall form near the walls of a solid at the interface with a liquid electrolyte. Typically, the features of ion kinetics in nanochannels and nanopores, the sizes of which are commensurate with the Debye length, [11] are associated with the overlap of diffuse layers from opposite walls.

Since the Debye length increases with decrease in ion concentration and temperature increasing [12], the appearance of „peak effect“ with concentration decreasing of the salt solution (Figure 3, a) and temperature increasing, at first glance, can be associated with an increase in the Debye length. However, this does not agree with the fact that in our experiments there is no overlap of diffuse layers, because when the ion concentration in the electrolyte is more than ~ 20 mM/l, the Debye length is less than ~ 1 nm, which is much smaller than the aperture diameter ~ 100 nm.

To clarify the nature of the „peak effect“ ion kinetics in the T-channel was simulated by the finite element method using the Comsol Multiphysics 5.6 software package. The distribution of the electrical induction vector and the ionic current density were calculated in the system of Poisson and Nernst-Planck equations, taking into account the bulk charge in the electrolyte and the surface charge on the walls. It was found that at D and $h \lesssim 100$ nm, in a certain range of values h, increase in the conductivity of the T-channel occurs due to the features of the electric field configuration at the edges of the aperture, provided that a negative potential is applied to Ag/AgCl electrode in the pipette relative to the electrode in the sample bottle, and there is a negative surface charge on the channel walls in the range $(0.02-0.1)$ C/m^2, the value of which is associated with an electric field. In the absence of the surface charge or positive potential on the pipette, there is no increase in conductivity, and the conductivity of the T-channel gradually decreases.

Note that the increasing branch in dependence $I(z)$ at negative potential on the electrode in NP was also observed in [12]; however, the authors do not discuss the decreasing branch, apparently suggesting that the peak on the dependence $I(z)$ is due to a simple decrease in the

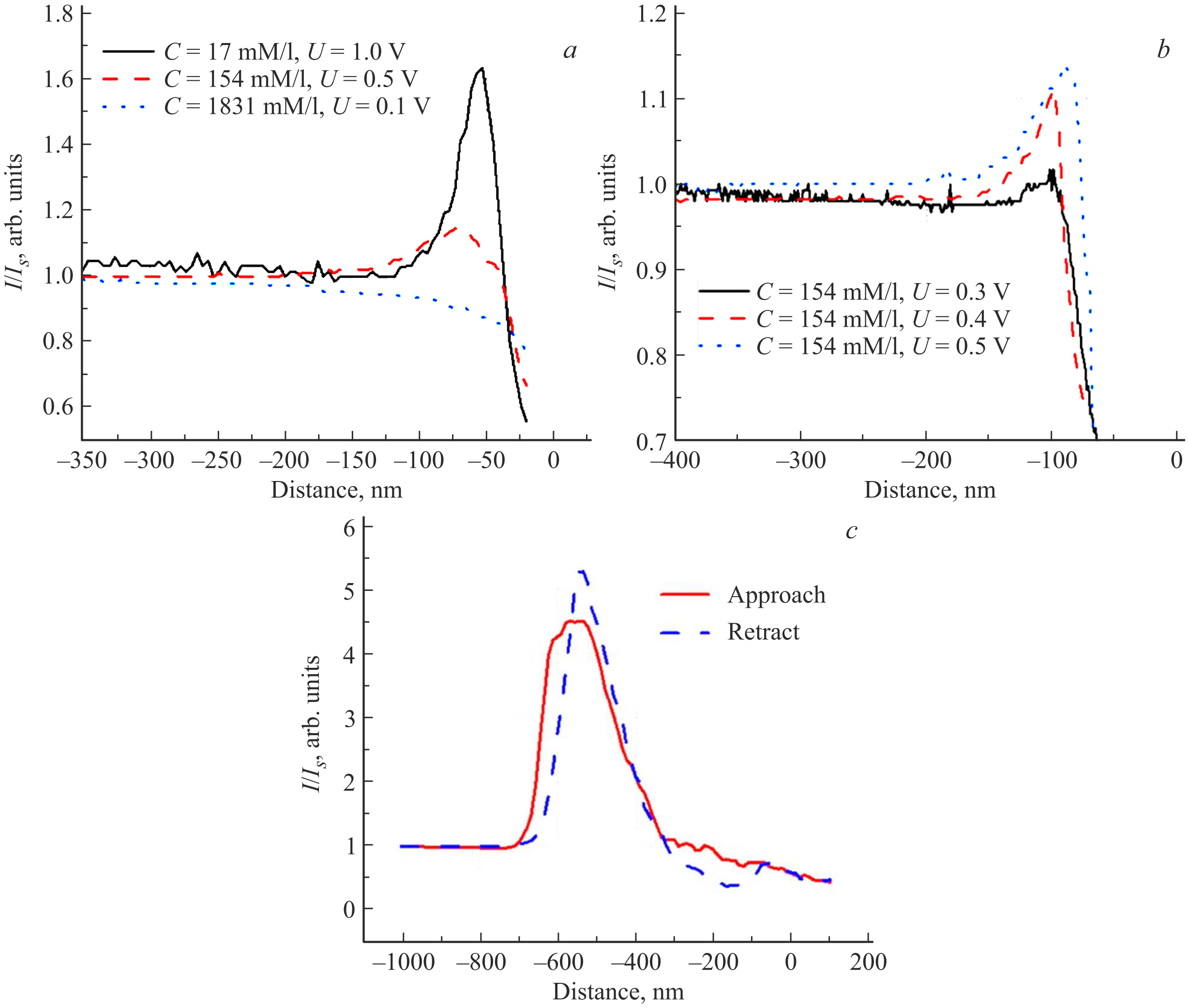

Figure 3. Experimental dependences $I(z)$ with changes in electrolyte concentrations (a) and voltage applied to bias electrode (b) for the retract curves. Experimental dependence $I(z)$ at different ion concentrations in NP (17 mM/l) and in the sample bottle (154 mM/l) on the approach and retract curves (c). The ion current is normalized to the saturation current.

conductivity of the nanochannel associated with the purely geometric block of the ion flow through the aperture by a flat surface, which occurs with decrease h. However, our modeling showed that the decrease in the T-channel conductivity at small values of h cannot be explained by a purely geometric block of the ion flow with a flat surface, since the increase in the ion current that occurs when NP approaches at negative potential on the electrode with a negatively charged surface, exceeds in a certain range h the decrease in current due to the purely geometric block of the aperture.

To explain the decreasing branch in the dependence $I(z)$, in addition to the purely geometric screening of NP aperture by flat surface, one should also take into account the dependence of the surface charge on the electric field at the surface, the increase in viscosity with decrease in h and thermal heating of the electrolyte under the influence of flowing current.

As a conclusion, note that the „peak effect“ can be used to determine the local charge of a surface or to determine the pH of solution. Precise changes in the geometry of the T-channel under the control of the tracking system, in principle, make it possible to reduce the gap h to ~ 1 nm, which opens up certain prospects for the charged molecules detection or for DNA sequencing.

Conflict of interest

The authors declare that they have no conflict of interest.

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