Determination of electrokinetic potential of porous glasses by methods of streaming potential, electroosmosis and electrophoresis

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Complex research of structural and electrokinetic characteristics of nano- and the ultraporous glasses prepared from sodium borosilicate (SBG) glass DV1-Sh in KCl background solutions of various concentrations in a wide pH range has been performed. It is shown that for ultraporous membranes with the sizes of porous channels r in the range $10-70$ nm appreciable electroosmotic flows and a good agreement of electrokinetic potential values determined by three different methods are observed. It is established that for nanoporous ($r < 10$ nm) glass membranes change of electroosmotic flow velocity with time is due to the development of concentration polarization.

Keywords: electrokinetic potential, electroosmotic flow.

1. Introduction

It is known that nanostructured porous glasses (PG) with controllable nanometric range parameters of structure and adjustable adsorptive and optical properties find a variety of applications [1−3]. In particular, suitability of PGs for their application as functional membrane elements in microfluidic chip (MFC) systems for the biochemical analysis [4] is revealed. Depending on the pore size and the secondary silica contents PGs can be used as electroosmotic pumps or as sensory elements with indicated complexes being introduced. In this connection definition of electroosmotic flows and electrokinetic potential values depending on pore space structure of membranes from PGs, which is defined by composition, thermal treatment of initial alkali borosilicate (ABS) glasses and conditions of obtaining of PG [5], are actual.

2. Objects and techniques

Porous high-silica glasses were prepared from industrial sodium borosilicate (SBG) glass DV1-Sh with bithermal treatment (650 °C, 530 °C) and two-frame structure by leaching in 3 M solution of hydrochloric acid (DV1-Sh (3 M HCl)). Afterwards, some of the samples were treated by a 0.5 M KOH solution for 10 hours (DV1-Sh (3 M HCl + 10-KOH)).

For the samples obtained the following electrokinetic characteristics were determined:

– Specific membrane conductivity κ_M by difference method [6]; κ_M values were used for calculating the efficiency coefficient α ($\alpha = \kappa_M \beta / \kappa_V$, where κ_V is the specific conductivity of bulk solution, β is the structural resistance coefficient, which characterize the contribution of the non-conducting skeleton to the membrane conductivity).

– Counterion transport numbers n_+ by method of membrane potential in a flowing cell [7].

– Electrokinetic potential ζ by methods of electroosmosis, streaming potential and ultramicroelectrophoresis; ζ – potential values of membranes were calculated from experimental data using Helmholtz−Smoluchowski's equations:

$$\zeta^0 = \frac{\eta \kappa_V E_S}{\varepsilon \varepsilon_0 P} \quad - \quad \text{method of streaming potential} \tag{1}$$

$$\zeta^0 = \frac{\eta \kappa_V Q}{\varepsilon \varepsilon_0 I} \quad - \quad \text{method of electroosmosis} \tag{2}$$

(where E_S is the streaming potential, P is the applied pressure, η is the fluid viscosity, $Q = V/t$ is the volume velocity of a liquid, I is the current strength) and taking into account both electrical double layers overlapping [8], and real specific conductivity of pore solution [9]:

$$\zeta_\alpha^* = \frac{(\eta \kappa_V \alpha E_S [Q]) / (\varepsilon \varepsilon_0 P [I])}{f(kr_\beta, \zeta_\alpha^*, \beta^*)} \tag{3}$$

where β^* is the parameter, including electrolyte properties, k is Debay's parameter.

After measurements of electroosmotic flow and streaming potential some of the membranes were washed with HCl, then watered, dried up and powdered. The ζ-potential value was also determinated for powders by method of ultramicro-electrophoresis.

The values of ζ-potential were calculated from electrophoretic data using Smoluchowski's equation:

$$\zeta^S = \frac{\eta}{\varepsilon\varepsilon_0} U_{ef} \qquad (4)$$

(where U_{ef} is the electrophoretic mobility) and also taking into account conductivity of PG particles (Henry's equation) [10]:

$$\zeta = \frac{\eta}{\varepsilon\varepsilon_0} U_{ef}\left(1 + \frac{\kappa_M}{2\kappa_V}\right) = \zeta^S\left(1 + \frac{\alpha}{2\beta}\right) \qquad (5)$$

For porous glasses under investigation structural parameters were also determined: BET surface area S_0 (by thermal desorption of nitrogen with chromatographic registration), volume porosity W, structural resistance coefficient β, liquid filtration coefficient G. Measurements of G values were carried out in the range of pressure $0.3-0.5$ atm in a 0.1 M electrolyte solution to avoid the influence of electroviscous effect. Values of the mean pore radius were calculated by the equations

$$r_{S_0} = \frac{2W}{(1-W)\rho S_0} \qquad (6)$$

$$r_\beta = \sqrt{8G\eta d_M \beta} \qquad (7)$$

where ρ is the glass density, d_M is the membrane thickness.

Measurements of colloidal-chemical characteristics of porous glasses were carried out in KCl background solutions with concentration of $10^{-4}-10^{-1}$ M in the pH range 2–7. All solutions were prepared on bidistilled water with specific conductivity $\sim 2\times 10^{-6}\ \Omega^{-1}\text{cm}^{-1}$.

3. Experimental results and discussions

3.1. Structural parameters of porous glasses

Investigation of the porous glasses obtained began with studying their structural characteristics in 0.1 M KCl solutions. It is worth noting that the obtained membranes DV1-Sh (3 M HCl) and DV1-Sh (3 M HCl + 10-KOH) after a sufficiently long-term storage in air were put to contact with a 0.1 M KCl solution at once, and PG DV1-Sh* (3 M HCl) and DV1-Sh* (3 M HCl + 10-KOH) (parallel samples) were previously placed for 2 days in a 0.1 M HCl solution.

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T a b l e 1. Structural parameters of porous glasses under investigation. R_{init} – initial parameter values, R_{fin} – final parameter values (parameter values at the end of experiment).

Membrane	W_{init}	W_{fin}	β_{init}	β_{fin}	$G_{init}\times10^{12}$ [cm^{2}s/g]	$r_{\beta\,init}$ [nm]	$G_{fin}\times10^{12}$ [cm^{2}s/g]	$r_{\beta\,fin}$ [nm]	$S_{0\,fin}$ [m^2/g]	$r_{S0\,fin}$ [nm]
DV1-Sh* (3 M HCl)	0.25 / 0.24*	0.31 / 0.29*	7.27 / 8.20*	6.03 / 6.89*	–	–	7.71*	9.2*	37	11
DV1-Sh (3 M HCl + 10-KOH)	–	0.44	3.53	3.47	909	71.6	935	71.6	10	70.9
DV1-Sh* (3 M HCl + 10-KOH)	0.42	0.42	4.06	3.64	638	61.4	669	61.7	–	–

It can be seen from the data of Tab. 1 that for PGs, leached in HCl, the porosity value increases and β value decreases during the contact of the membranes with electrolyte solutions, owing to dissolution and removal of secondary silica from pore space.

The additional alkaline treatment of PGs for 10 hours leads to an increase in the size of pore channels and also to a volume porosity growth, which causes a decrease in the specific surface area and in the structural resistance coefficients.

Note that the structural parameters of ultraporous membranes remain practically constant during experimental time.

3.2. Specific conductivity of porous glasses

The measurements of efficiency coefficients show (Fig. 1**a**) that for all the porous glasses investigated α values decrease with increasing KCl solution concentration in accordance with decreasing contribution of the EDL ions into specific conductivity of pore solution. A comparison of values α at C = const ($C < 0.1$ M) shows that efficiency coefficients increase with the mean pore radius diminishing (in accordance with the theoretical conceptions), therefore the additional alkaline treatment of PGs results in essential (especially in the diluted solutions) α values decreasing.

It is necessary to pay attention to that fact that for membranes DV1-Sh (3 M HCl) and DV1-Sh (3 M HCl + 10-KOH) (not exposed before measurements to 0.1 M HCl treatment) a decrease of efficiency coefficient values after electroosmotic measurements (Fig. 1**a**, curves 1, 2 and 4, 5) is observed, whereas for PG DV1-Sh* (3 M HCl) and DV1-Sh* (3 M HCl + 10-KOH) no appreciable change of α values has occurred. It should be noticed that α–log C dependence for PG DV1-Sh (3 M HCl + 10-KOH) coincides with that for membrane DV1-Sh* (3 M HCl + 10-KOH) (Fig. 1**a**, curve 5) and earlier obtained data for PG DV1-Sh (3 M HCl + 3.5-KOH) [11].

The analysis of changes of α values for membrane DV1-Sh (3 M HCl) shows that both before and after electroosmotic measurements α values (at C = const) are greater than that for the parallel sample. We should notice that initial α values for glass DV1-Sh (3 M HCl) (Fig. 1**a**, curve 1) are incredibly high. Such electrokinetic behavior of nanoporous membranes is apparently connected with changes in the internal
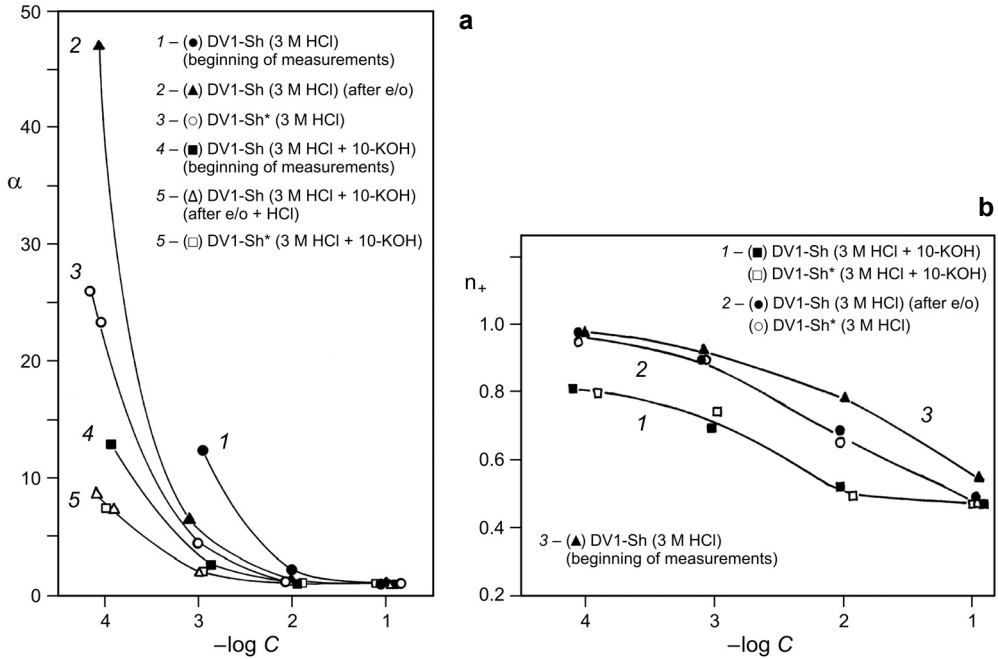
Fig. 1. Transport characteristics of the membranes investigated: efficiency coefficient (**a**) and counterion transport numbers (**b**) *vs*. concentration of KCl solutions.

structure of liquate channels, and first of all with the changing of globule packing of secondary silica. And this difference is most likely connected with the fact that in HCl solution secondary silica swells and is structured practically at a zero charge of a surface, and in a salt solution at considerable negative surface charge. Let us notice that the difference between measured parameters of membranes DV1-Sh (3 M HCl) and DV1-Sh* (3 M HCl) during contact with KCl solutions considerably decreases, but does not disappear.

3.3. Counterion transport numbers in membranes

The results of counterion (K^+) transport numbers measurement show (Fig. 1**b**) that an increase in salt level and in pore size leads to a monotonic decrease in the n_+ values. These tendencies are in accordance with decreasing contribution of the EDL ions to the membrane transport. In the most diluted solution membranes, leached in HCl solution, possess practically ideal selectivity ($n_+ = 0.94 - 0.98$).

Let us notice that for PG DV1-Sh (3 M HCl) n_+ value after electroosmotic measurements decreases (at $C < 10^{-3}$ M) and becomes equal to n_+ for PG DV1-Sh* (3 M HCl). This is in accordance with the results of membrane specific conductivity measurements. In the case of membranes DV1-Sh* (3 M HCl + 10-KOH) and DV1-Sh (3 M HCl + 10-KOH) no essential differences in counterion transport number values were observed.

3.4. Electrokinetic potential

3.4.1. Method of streaming potential

The analysis of ζ_α^* concentration dependences for membranes DV1-Sh (3 M HCl) and DV1-Sh (3 M HCl + 10-KOH) (Fig. 2a) has shown that the absolute values of electrokinetic potentials were greater before than after electroosmotic measurements. It should be noticed that the angular coefficient of dependences $\zeta_\alpha^* - \log C$ differs, too.
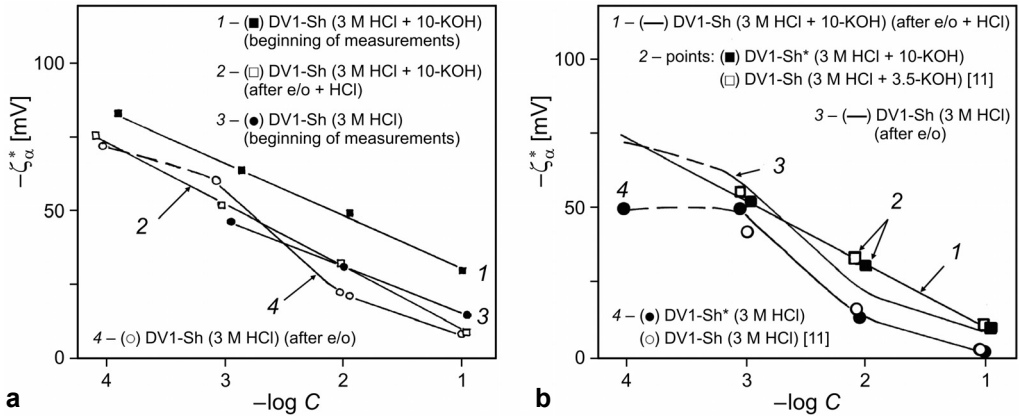

Fig. 2. Electrokinetic potential ζ_α^* of the membranes investigated *vs.* concentration of KCl solutions.

It is seen (Fig. 2b) that for membrane DV1-Sh (3 M HCl + 10-KOH) after treatment of 0.1 M HCl, $|\zeta_\alpha^*|$ values coincide with those for membranes DV1-Sh* (3 M HCl + 10-KOH) and DV1-Sh (3 M HCl + 3.5-KOH) [11] (line 1 and points 2). For PG DV1-Sh (3 M HCl) (after electroosmotic measurements) $|\zeta_\alpha^*|$ values remain higher than for membranes DV1-Sh* (3 M HCl) and DV1-Sh (3 M HCl) [11] (curves 3 and 4), whereas values of electrokinetic potentials for those PGs are similar. It is worthwhile to notice that the laws obtained in the case of electrokinetic potential, completely agree with the results of measurement of specific conductivity of the membranes investigated (see Section 3.2). From Fig. 2 it is also seen that for the membranes investigated absolute ζ-potential values increase with pore sizes, which can be connected with a decrease of an ion-permeable layer thickness on the surface of pore channels.

3.4.2. Method of ultramicroelectrophoresis

The dependences of electrophoretic mobility of particles of PGs being investigated on pH on the background of 10^{-2} M and 10^{-3} M KCl are presented in Fig. 3a. A growth of particle mobility with an increase in the mean pore radius and with a decrease in concentration of background electrolyte is observed. The analysis of $U_{ef} - pH$
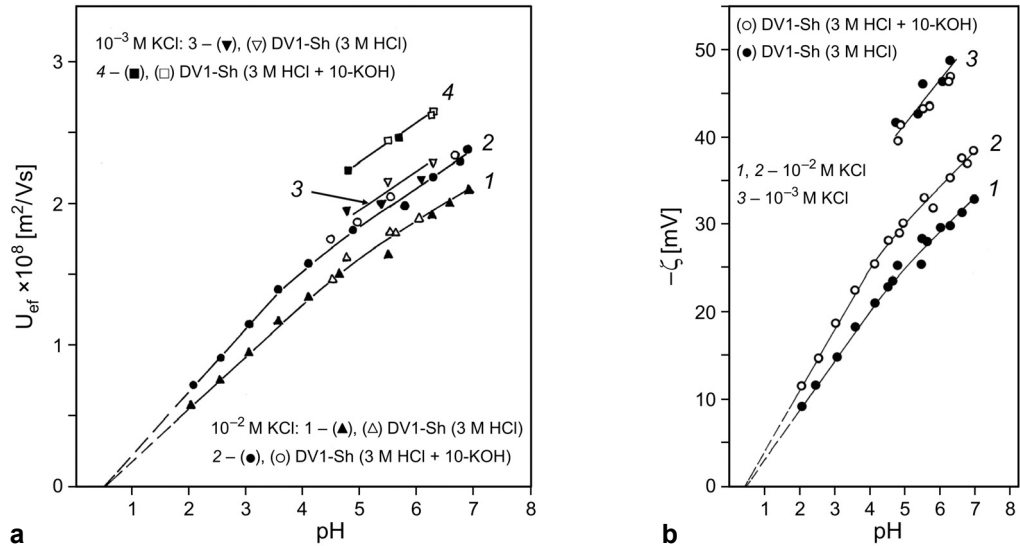
Fig. 3. Electrophoretic mobility (**a**) and electrokinetic potential (**b**) of PG particles *vs.* pH on the background of KCl solutions.

dependences allows us to conclude that the isoelectric point (IET) lies close to $pH_{IET} = 0.5$ that is similar to IET position in HCl solutions [9].

The comparison of ζ-potential values, calculated taking into account own conductivity of particles, has shown (Fig. 3**b**) that values of electrokinetic potentials on the background of 10^{-3} M KCl are similar. On the background of 10^{-2} M KCl usual ratio of ζ values is observed – the transition from nanoporous to ultraporous glasses leads to an increase in $|\zeta|$ value. However, it should be noticed that this difference does not exceed 5 mV in neutral pH range.

3.4.3. Method of electroosmosis – Comparison of the results obtained with the data of other methods

The determination of ζ values by a method of electroosmosis on nanoporous glasses was very difficult because of the electroosmotic flow velocity changing with time. This was due to the presence of secondary silica in the PG pore space, and was also connected with the concentration polarization increasing with time, owing to the essential difference in counterion transport numbers between bulk and pore solutions.

The results of electroosmotic flow measurements and calculated electrokinetic potentials for the ultraporous membranes are presented in Fig. 4 and Tab. 2. It is seen that for ultraporous glasses the ζ values measured by the three methods are in a good agreement. Note that in the diluted solution for glasses with pore radius close to 10 nm is not enough to take into account only own conductivity of particles (method of
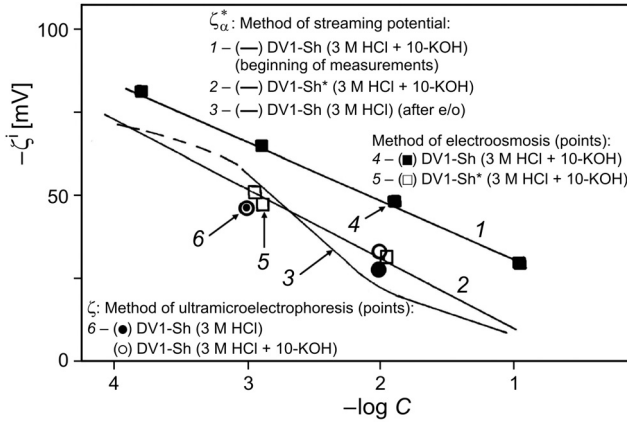
Fig. 4. Electrokinetic potential ζ^i determined by various methods *vs*. concentration of KCl solutions.

T a b l e 2. Results of volume velocity measurements and calculations of electrokinetic potential values.

C [M]	κ_V [Ω^{-1}cm^{-1}]	α	I [mA]	V/It [cm^3/As]	$-\zeta^0$ [mV]	$-\zeta_\alpha^*$ [mV]
V1-Sh* (3 M HCl + 10-KOH)						
0.98×10^{-2}	1.246×10^{-3}	1.10	8.8	0.151	27.0	32.7
1.15×10^{-3}	1.518×10^{-4}	1.84	1.2	0.965	20.0	52.1
1.29×10^{-3}	1.705×10^{-4}	1.85	1.25	0.772	18.4	47.9
DV1-Sh (3 M HCl + 10-KOH)						
1.05×10^{-1}	1.760×10^{-2}	1.00	30	0.017	27.7	28.5
1.08×10^{-2}	1.326×10^{-3}	1.00	10.4	0.247	45.9	49.8
1.54×10^{-3}	1.635×10^{-4}	2.55	1.25	0.899	20.6	65.5
1.55×10^{-4}	2.075×10^{-5}	7.11	0.2	2.042	5.91	81.9

ultramicroelectrophoresis) for calculation of correct ζ-potential values, but it is also required that polarization phenomena in a electric double layer should be considered.

4. Conclusions

It is established that for ultraporous membranes with the pore sizes ranging from 10 to 70 nm appreciable electroosmotic flows are observed. The constancy of structural parameters and velocity of electroosmosis in time for those membranes testifies to the possibility of using them for creation of electroosmotic pumps.

It is shown that for ultraporous membranes, a good agreement of the electrokinetic potentials found by means of three independent methods is observed. This enables us to calculate the electroosmotic flow values from the electrokinetic potential values determined by the method of streaming potential, which is one of the most exact methods of experimental definition of the ζ-potential value since application of

the external electromoving force calling by-effects (heating, polarization) is not required. For nanoporous glass membranes a change of electroosmotic flow velocity with time owing to the development of concentration polarizations is observed.

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