Diffusion charateristics and electrical conductivity of the porous glass menbranes

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The diffusion characteristics and electrical conductivity of the high silica porous glass (PG) membranes manufactured from the phase-separated alkali borosilicate glasses were investigated. The study of the diffusion coefficient values of the electrolyte solutions through the PG membranes (D_{PG}) was carried out at 20 – 50 ^{0}C by porous diaphragm method. It was shown that D_{PG} values are lower in comparison with ones in the free solution and are independent of pore dimension (radius r) ranging between 1 to 12 nm. Such events may be conditioned by an influence of such factors as the structural resistance of PG skeleton as well the electric double layer on the walls of the thin pores.

Introduction

At the leaching of the two-phase alkali borosilicate (ABS) glasses with interconnected structure by acid solutions alkali borates are dissolved and moved off from the glass [1]. As a result the porous glasses (PGs) are produced. The PGs are widely used in optics as new types of heterogeneous laser media for preparation of the solid – liquid laser elements or as effective adsorbents ensured to solve different ecology problems. The advantages of PGs are conditioned by their high thermal, chemical and microbiological stability in association with the controlled parameters of the porous structure.

During the leaching of the phase-separated ABS glasses so-called secondary silica of the chemical unstable phase forms the silica gel precipitates inside the pore volume. Irregular distribution of such precipitates is responsible for a macro inhomogeneous structure of the PGs [2]. Add treatment of the PGs by the alkali solutions causes the dissolution of the secondary silica and its removal from the glass. To the total disposal of the secondary silica the values of porosity (W) and a pore radius (r) of the PGs are increased up to values, which are determined by a composition of the ABS glass and by a regime of its thermal treatment[3].

The layered-and-inhomogeneous structure of PGs creates the add diffusion impediments for the transfer processes inside the thin-porous PGs that results in a decrease of the D_{PG} values at the decrease of the pore radius r. Influence of the pore structure on the D_{PG} value can be described by a structural resistance coefficient β, which takes into consideration a decrease of cross section area of the PG's membrane open to diffusion at the expense of non-conductive skeleton [4]:

$$D_{PG} \sim D_0 / \beta, \qquad (1)$$

where D_0 is a coefficient of the electrolyte diffusion in a free solution. Besides consideration must be given to the mass transfer impediments associated with existence of the electric double layer (EDL) on the walls of the PG's pores. Influence of the EDL would be reflected by changes in the mobility of ions as well the cation transport numbers in the PG membrane in comparison with free solution [4]. Such EDL influence so much the greater, the smaller are the value of W and r.

The aim of our work was the study of an interrelation between diffusion and electrochemical characteristics of the PG's membranes and their porous structure parameters depending on such factors as a composition of initial ABS glass, a regime of its thermal treatment as well a leaching conditions.

Experimental

The objects of the investigation were the PG samples in a form of polished disc (thickness L = 2 mm, and diameter d = 10 and 35 mm), obtained by leaching of the phase-separated ABS glass of composition (by analysis, mol. %): 6.8 Na_2O, 20.9 B_2O_3, 72.0 SiO_2, 0.3 Al_2O_3 (glass 8B), and 3.7 Na_2O, 4.0 K_2O, 32.3 B_2O_3, 60.0 SiO_2 (glass NK-1). In the Table 1 the thermal treatment regimes of the initial ABS glasses and the parameters of the chemical unstable phase of the phase-separated glasses are shown. The structure parameters of phase-separated glasses were determined by transmission electron microscopy [5] and according with immiscibility diagram of the R_2O-B_2O_3-SiO_2 system (R = Na, K)[1]. The conditions of the two-phase glass leaching and the characteristics of the PG's porous structure obtained by BET and mercury porosity metric methods by Boris I. Venzel' are given in the Table 2. Both the micro porous PG samples (i.e. PGs produced by acid leaching only) and the macro porous samples that didn't possess of so-called second silica (i.e. micro PGs treated in alkali solution in addition) were used.

The compositions of the PG samples were the following (by analysis, mol. %): (0.1-0.2) R_2O, (3-6) B_2O_3, (94-97) SiO_2, ≤ 0.1 Al_2O_3.

The study of the diffusion of HCl solutions through the PG membranes was carried out at 20 – 50 ^{0}C by methods based on the porous diaphragm method and ion metric technique[6]. The values of a diffusion coefficient were calculated according to the equations:

$$\text{at } C_{t=0} = C_1 \qquad D_{PG} = L^2/6\, t_{lag}, \qquad (2)$$

$$\text{at } C_{t=0} = C_2 \qquad D_{PG} = -\,(L^2/3\, t_{lag}), \qquad (3)$$

where D_{PG} is a diffusion coefficient of the electrolyte (HCl or HNO_3 solution) through PG membrane (sm^2/s), t_{lag} is a lagging of an equilibration time (s), $C_{t=0}$, C_1, C_2 are the HCl concentration inside a PG membrane (gram-ion/cm^3) at the follow conditions consequently: in the initial state (at t =0), membrane isn't saturated by diffusate, membrane is saturated by diffusate. The t_{lag} value was graphically determined from the kinetics dependencies of a quantity of the diffused HCl as a t-Axis section intercepted by straight line of which considered dependencies were approximated at $t \rightarrow \infty$.

The structural resistance coefficients β were calculated from membrane conductivity values κ_M measured in 0.1 M HCl solution, i.e. in a system for which the contribution of EDL ions to membrane conductivity can be neglected [7]:

$$\beta = \kappa_M/\kappa_V, \qquad (4)$$

where κ_V is the conductivity of free solution ($S\cdot sm^{-1}$). The pore tortuosity factor χ reflecting the increase a real diffusion path in comparison with the PG membrane thickness L was determined to a first approximation from the values of W and β:

$$\chi = (\beta\cdot W)^{1/2}\ , \qquad (5)$$

Results and Discussion

Pore structure parameters of the micro PGs are conditioned by a composition of the unstable phase of the phase-separated ABS glasses [8]. Namely, the greater SiO_2 quantity in an unstable phase the smaller a value of mean pore radius r and porosity W of the PG samples (Tabs 1, 2).

Table 1. Compositions of the initial glasses, regime of their thermal treatment and the parameters of the phase-separated glass structure.

Initial glass	Time of the thermal treatment at 550 °C, hrs	Chemical unstable phase parameters					
		Relative volume, %	Diameter of the liquation channels, nm	Composition, mol %			
				Na_2O	K_2O	B_2O_3	SiO_2
8B	144	50 -55	25 - 40	15.0	-	39.2	45.8
NK-1	24	~ 50	~ 20	~ 15		~59	~26

Table 2. Pore structure characteristics of the porous glasses.

Two-phase glass	Porous glass number	Leaching conditions C_{HCl}, M/T, ^{0}C	Mean pore radius *r*, Å	Volume porosity *W*, sm^3/sm^3	Specific surface area *SA*, m^2/g
8B	I	0.1 / 50	1.1	0.30	362
	II	3.0 / 50	3.3	0.28	102
	III	3.0 / 100	3.5	0.27	113
	IV	0.1 / 50 (+ KOH)	12.0	0.53	60
NK-1	V	3.0 / 100	7.0 and 10.0	0.42	88

A presence of the second silica in the PG samples causes the β as well χ values of the PGs (r < 10 nm) to rise in comparison with the PGs with r ≥ 10 nm (Table 3).

Table 3. The values of the porous glass structural resistance coefficient β, pore tortuosity factor χ and diffusion coefficient D_{PG} of the HCl solutions through the porous glass membranes ($L = 2$ mm) at 26°C.

Mean pore radius **r**, nm	Structural resistance coefficient β	Pore tortuosity factor χ	Diffusion coefficient $D_{PG} \cdot 10^6$, sm^2/s		
			$D_{PG} = f(t_{lag})$ *)	$D_{PG} = f(t_{lag})$ **)	$D_{PG} = D_0/\beta$
1.1	14.7	2.1	1.9±0.4	2.4± 0.5	2.1
3.3	14.4	2.0	2.5±0.5	2.6± 0.5	2.1
3.5	16.0	2.1	1.9±0.5	2.0± 0.4	1.9
7.0 and 10.0	5.3	1.5	2.2±0.4	5.2± 0.4	5.7
12.0	4.3	1.5	3.2±0.6	6.8± 0.4	7.1

Equal β values for PGI and PGII obtained by phase-separated glass leaching at 50 ^{0}C, but at the different acid concentration, have engaged our attention because these PGs possess different pore dimensions. It should be noted that, of all PGs, glasses obtained at 50 ^{0}C are the most homogeneous [2]. This fact is apparently related to the following event that can be described in the context of glass leaching model [8]. At this temperature the boron containing micro crystals, which are formed as intermediates within the leached layer of two-phase glass, occur in the largest amount and have the highest degree of hydration. This would decrease the degree of surface hydration of colloidal second silica particles and, therefore, promote the subsequent formation of more homogeneous silica gel precipitates.

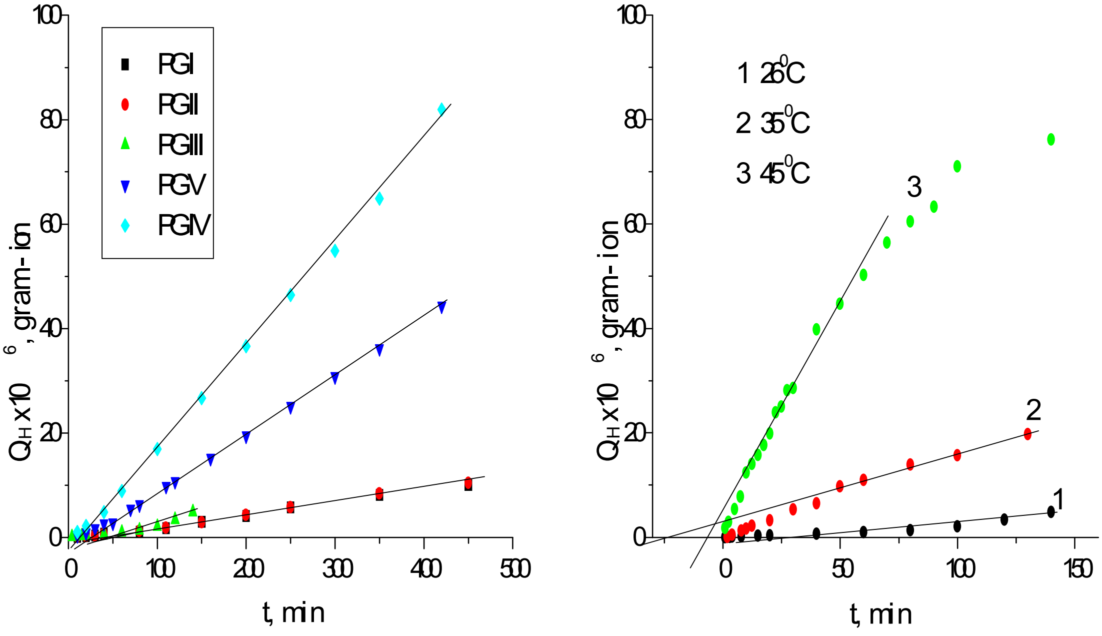
a) b)

Figure 1. Dependencies of the quantity HCl (in conversion to quantity Q_H of H$^+$ - ions) diffused through studied PG membranes at (a) 26 ^{0}C, as well (b) through PGIII membrane at 35 ^{0}C and 45 ^{0}C.

Fig. 1, a, b show the dependencies of the quantity HCl (in conversion to quantity Q_H of H$^+$ - ions) diffused through studied PG membranes. Results of the D_{PG} calculations by equations (2, 3) are given in Table 3. Before investigation PG membrane was washed out with water $^{*)}$ or it was equilibrated with 0.1 M HCl during 1 day at 25 ^{0}C $^{**)}$. It is shown that values of the diffusion coefficient for used electrolytes in thin porous membranes are smaller on the order of magnitude than that in the free solution (~ $3 \cdot 10^{-5}$ sm^2/s). The D_{PG} values for the electrolytes in PG membranes which aren't in equilibrium with a diffusate $(D_{PG})^{*)}$ are nearly independent of r ranging between 1 and 12 nm what is conditioned by an influence of the EDL on the walls of the thin pores. This is in agreement to data [9] which show that in dilute solutions ion transport number $n_{\pm}$ of the 1 – charged ions in PG membranes at r = (2.4 – 13) nm are virtually equal. When the contribution of ions of the EDL to the properties of the liquid in the pores of weakly charged PG membranes is negligible, the decreasing of the D_{PG} values (as compared with free solutions) is mainly caused by influence of the structure factors: $(D_{PG})^{**)} \sim D_0 / \beta$ (Table 3).

Figs 1,b and 2 demonstrate an influence of the leaching solution temperature on the diffusion rate of the HCl in the PG membranes. According to these data the apparent energy of activation of the diffusion process through a PG membrane E (~ 30 Kcal/mol) is much more then in a free solution.

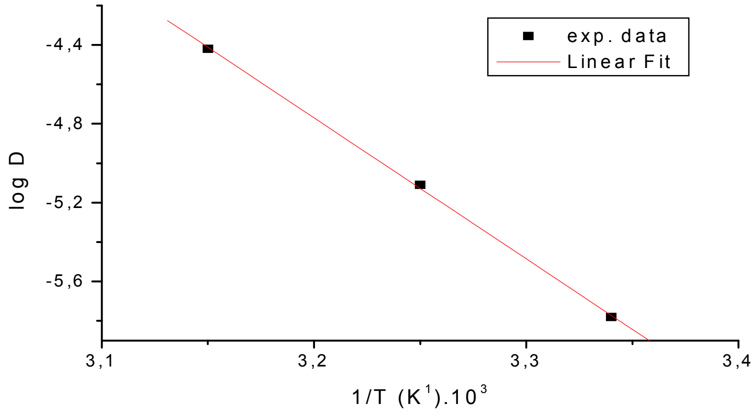

Figure 2. Half-logarithmic relationship of the diffusion coefficients of the HCl passed through porous membrane PG III from a reciprocal solution temperature.

Conclusion

The diffusion characteristics and the structure parameters of the porous glass membranes were investigated by porous diaphragm and electrical conductivity methods.

Derived results suggest that during the acid leaching of the two-phase alkali borosilicate glasses a rate of the mass transfer of the interchanged substances through the leached porous layer influenced by as the structure factors due to presence of a non-conductive silica skeleton as the electrochemical properties of the inner pore surface especially in a case of the dilute solutions.

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