
PHYSICOCHEMICAL STUDIES
OF TECHNOLOGIES

Comparative Characterization of the Diffusion Mobility of Aqueous Calcium Salt Solutions in Porous-Glass Membranes

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Received February 12, 2013

Abstract—Diffusion coefficients of calcium acetate, nitrate, and chloride, which characterize the transport of their aqueous solutions across porous-glass membranes with predominant pore radii of 4.5–70 nm, were determined. A decrease in the membrane pore radii is accompanied in all cases by an exponential fall of the diffusion mobility. The noticeable difference between the anion mobilities, which favors salt separation, grows with increasing radii of transport channels. In a membrane with a pore radius of 4.5 nm, the salt diffusion mobility series is changed.

DOI: 10.1134/S1070427213050010

The possibility of successfully solving a number of problems associated with concentration and separation of solution components is governed by the development and application of membranes with nanometer transport channels. The important properties of membranes include, together with their spatial structure, the composition and structure of their surface, mechanical strength, chemical stability, and radiation hardness. These requirements are fully satisfied by porous-glass (PG) membranes obtained as plates pierced by through channels by successive acid and alkaline treatments of liquated glasses of the sodium borosilicate system [1–4]. Depending on the synthesis conditions, PG membranes may have channels with radii in the range from several to hundreds of nanometers [1–4]. The structure and properties of the hydroxylated surface of PG membranes are similar to those of the well studied varieties of amorphous silica: silica gels and aerosols.

To design and perform membrane filtration processes, it is necessary to determine how the diffusion coefficients depend on the radius of transport channels and chemical nature and concentrations of solutes. On the whole, it has been reliably established [2, 3, 5–8] that the diffusion rate of electrolytes in PG membranes is noticeably lower than that in free solutions. It has

been shown [5–8] that the limitation of the mass transfer of aqueous salt solutions is reliably represented by an exponential dependence of diffusion coefficients D on the radius r_p of transport channels in PG:

$$D = D_0 \exp(-K_p/r_p), \quad (1)$$

where D_0 (at $r_p \rightarrow \infty$) approaches the value for a bulk solution, and the dimensional parameter K_p characterizes the size of the water layer structured by the silica surface. The exclusion (or weak involvement) of the near-wall water in the transport of electrolytes, reflected by the numerical value of K_p , is clearly manifested in studies of the concentration and temperature dependences of the mass transfer [5–8]. It has also been found [5–8] that the salt diffusion rate in PG membranes strongly depends on the ability of cations to disintegrate the boundary layer of water, determined by their charge and tendency to undergo hydration. In this context, it seems necessary to determine the nature and extent of the influence exerted by the type of anions on the rate of the diffusion transport of salts. In the present study, this problem is considered for the example of diffusion of aqueous solutions of calcium chloride, nitrate, and acetate in a set of PG membranes with pore radii of 4.5 to 70 nm.

EXPERIMENTAL

Silica PG membranes were fabricated in the form of disks 25 mm in diameter and 1–3 mm thick by the procedure described in [4] by successive acid-alkaline treatments of liquated slabs of DV-1M glass of composition (mol %) $7\text{Na}_2\text{O}\cdot 23\text{B}_2\text{O}_3\cdot 70\text{SiO}_2$. The porous structure parameters of the membranes (Table 1), specified by synthesis conditions, have been determined previously [4, 5]. In a diffusion study, the membranes were fixed between two cells, one of which (receiver) was charged with twice-distilled water, and the other (feeder), with an aqueous salt solution. The transport dynamics was judged from the data on the amount of Ca^{2+} ions that passed into the receiving cell, obtained by EDTA titration at pH 9–10, with Eriochrome black as indicator [9]. The experiments were carried out under thermostating at $T = 25^\circ\text{C}$ and permanent solution agitation. Within the range 10–20 mm, the fluid level in the feeding cell had no effect on the diffusion rate, which indicates that there is no manifestation of the hydrostatic and osmotic pressures. A steady flow of salts across the membranes was attained with a certain delay whose duration depended on the solution concentration and porous-structure parameters r_p and δ .

The diffusion rate was found from linear time dependences of the amount of transferred salts, $dQ/d\tau$, and represented in accordance with the Fick's first law as

$$dQ/d\tau = DS\delta\Delta c/h, \quad (2)$$

where D is the diffusion coefficient; $S\delta$, free cross-section of a membrane {geometric area with correction for the porosity γ (Table 1)}; and $\Delta c/h$, gradient of the solution concentrations at the inlet and outlet of a membrane with thickness h .

Because the solution concentration in the receiving cell, c_{out} , is substantially lower in all experiments than that at the membrane inlet, c_{in} , the gradient was taken to be

$$\Delta c/h = (c_{\text{in}} - c_{\text{out}})/h \cong c_{\text{in}}/h. \quad (3)$$

The diffusion coefficients of the three salts were found in a wide range of solution concentrations and PG membrane channel radii by substituting experimental values of $dQ/d\tau$ in Eq. (2).

The selected "dimensional" $D-r_p$ dependences,

Table 1. Porous-structure parameters of PG membranes

Pore radius r_p , nm	Porosity δ , cm^3/cm^3	Thickness h , mm	Area S , cm^2
4.5	0.313	0.1	2.985
7.5	0.320	0.2	3.140
10	0.320	0.1	3.460
19	0.389	0.15	3.298
30	0.480	0.1	3.140
40	0.436	0.1	2.835
70	0.569	0.2	2.820

shown in Fig. 1 for the three salts, are similar and reflect the substantial decrease in the diffusion mobility in membranes with narrow channels. In the case of comparatively high comparable concentrations, the diffusion coefficients of calcium chloride are, on the whole, larger than those of the nitrate and, the more so, acetate, in agreement with the anion mobility series in aqueous solutions [10]. It is important to note that a

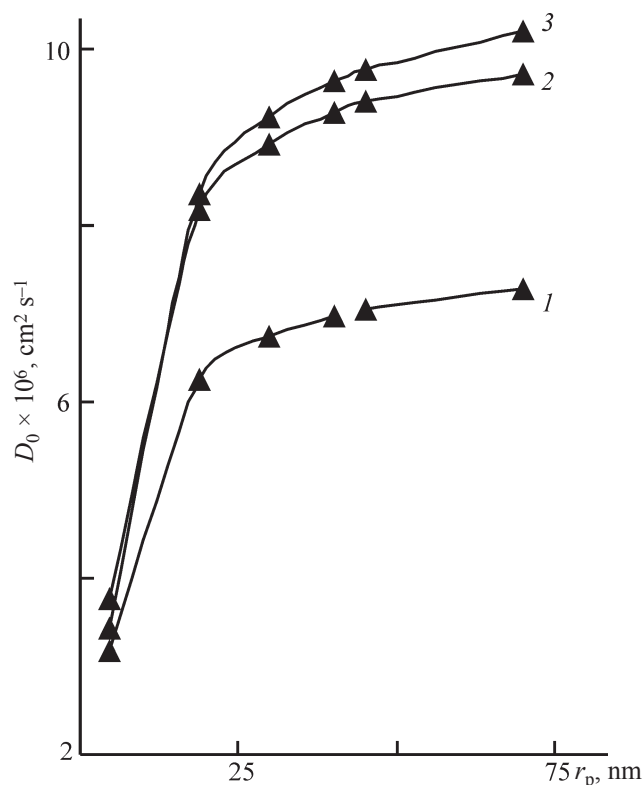


Fig. 1. Dependence of the diffusion coefficient D on the pore radius r_p of PG membranes for solutions with (1) 0.44 M $\text{Ca}(\text{CH}_3\text{COO})_2$, (2) 0.46 M $\text{Ca}(\text{NO}_3)_2$, and (3) 0.50 M CaCl_2 .

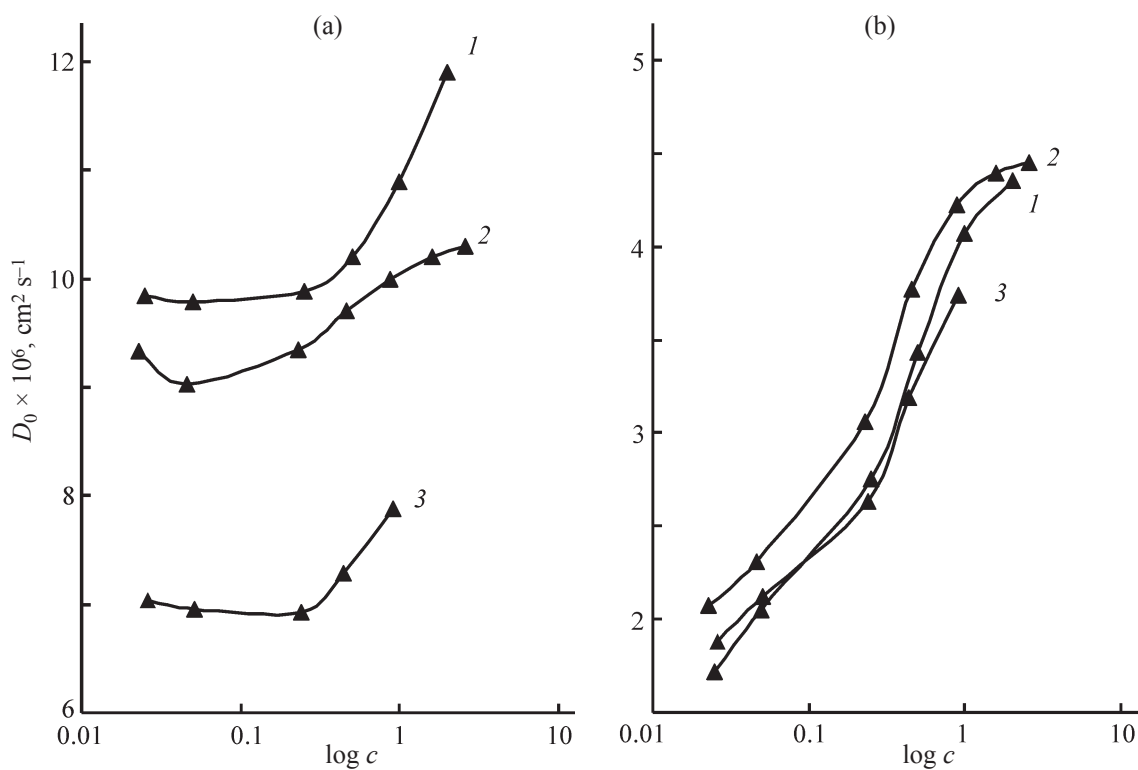
Table 2. Equation (2) parameters characterizing the diffusion of aqueous salt solutions with concentration c in PG membranes

Ca(CH ₃ COO) ₂			Ca(NO ₃) ₂			CaCl ₂		
c , M	K_p , nm	$D_0 \times 10^6$, cm ² s ⁻¹	c , M	K_p , nm	$D_0 \times 10^6$, cm ² s ⁻¹	c , M	K_p , nm	$D_0 \times 10^6$, cm ² s ⁻¹
0.026	6.35	7.7	0.023	7.30	10.3	0.025	8.39	11.1
0.051	5.69	7.5	0.046	6.55	9.9	0.05	7.52	10.9
0.24	4.66	7.4	0.23	5.36	10.1	0.25	6.16	10.8
0.44	3.97	7.7	0.46	4.58	10.4	0.5	5.24	11.0
0.91	3.59	8.3	0.88	4.13	10.6	1.0	4.75	11.7
–	–	–	1.6	4.05	10.8	2.0	4.65	12.7

decrease in the radius of transport channels results in that the values of D become markedly closer. At the same time, in widely porous membranes, a noticeable difference between the anion mobilities is reached on the background of a general acceleration of the mass transfer, which favors the salt separation.

A comparative analysis of the concentration dependences of D in large- and small-radius channels (Fig. 2) reveals additional specific features of the mass transfer.

For example, the decrease in the salt mobility in the series CaCl₂ > Ca(NO₃)₂ > Ca(CH₃COO)₂, strictly observed in the whole concentration range for membranes with channel radii $r_p = 19\text{--}70$ nm (Fig. 2a), is not observed for GS with $r_p = 4.5$ nm (Fig. 2b). In narrow channels, the mobility is the highest for calcium nitrate, with the diffusion coefficients of CaCl₂ and Ca(CH₃COO)₂ becoming closer to each other and, for dilute solutions, the diffusion rate of calcium acetate being even higher

**Fig. 2.** Dependence of the diffusion coefficient D on the concentration c of solutions of (1) CaCl₂, (2) Ca(NO₃)₂, and (3) Ca(CH₃COO)₂ in membranes with pore radii of (a) 70 and (b) 4.5 nm

than that of the chloride. Noteworthy is the change in the run of the D - $\log c$ dependences. As the concentration is lowered in the case of membranes with $r_p = 19$ – 70 nm, gradually sloping portions with weakly pronounced dips are formed (Fig. 2a), in agreement with the known specific features of the diffusion in free solutions [10]. For GS with a channel radius of 4.5 nm, this feature is not observed (Fig. 2b). In this case, an increase in the solution concentration from 0.025 to 2.6 M causes a significant (approximately twofold) rise in the diffusion coefficient, whereas for the membrane with a pore radius of 70 nm, this rise is, on average, only 15%.

The full correspondence of the experimental results to the exponential dependence (1), their linearization in the coordinates $\ln D$ - r_p , and processing by the least-squares method lead to an estimate of the parameters D_0 and K_p (Table 2). The values of D_0 regularly vary with increasing concentration and grow in the order $\text{Ca}(\text{CH}_3\text{COO})_2 < \text{Ca}(\text{NO}_3)_2 < \text{CaCl}_2$. In turn, the dimensional parameter K_p varies within the range of values of 3.6–8.4 nm, comparable with the pore radius of membranes for which the strongest restriction of the salt mobility and change of series is observed. Accordingly, the presence of a near-wall layer of water becomes increasingly less noticeable as the radius of through channels grows, and properties of pore solutions gradually approach those of bulk solutions. Also remarkable is the substantial decrease in K_p with increasing concentration (Table 2), which reflects the active disintegrating effect of electrolytes on the structure of near-wall water. In this case, the values of K_p for the same solution concentrations noticeably decrease in the order $\text{CaCl}_2 > \text{Ca}(\text{NO}_3)_2 > \text{Ca}(\text{CH}_3\text{COO})_2$. This indicates that the acetate ion having high affinity for water the most strongly disintegrates its near-wall layer. With decreasing polarizing capacity of anions, the extent of the boundary layer of water noticeably grows, reaching the largest values for CaCl_2 . Thus, the diffusion rate of aqueous solutions of salts and the possibility of their separation in PG membranes strongly depend on the nature of anions.

The results obtained agree with the concept [11, 12] that the transport of electrolyte solutions in hydrophilic membranes is largely controlled by the specific structure and properties of near-wall water layers. This determines the observed specific features of the diffusion in PG membranes with narrow transport channels and, in particular, the strong effect of the solution concentration

and the changing salt mobility series and shape of D - c dependences.

CONCLUSIONS

(1) The diffusion coefficients of aqueous solutions of calcium acetate, nitrate, and chloride in porous-glass membranes exponentially depend on the radii of transport channels.

(2) The effect of the silica surface of pores on the diffusion mobility of salts becomes weaker with increasing solution concentration and polarizing capacity of anions.

(3) The noticeable difference in the anion mobilities, which favor salt separation, grows with increasing radius of transport channels of the membranes.

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