

RESEARCH ARTICLE

Diffusion transport of $\text{Ca}(\text{NO}_3)_2$ aqueous solution in porous glass membranes

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Abstract: Diffusion coefficients of $\text{Ca}(\text{NO}_3)_2$ in its passage through the set of porous glass membranes at 20–70°C were determined and discussed in terms of the structuring of the water boundary layers near the silica surface.

Keywords: porous glass membranes, calcium nitrate diffusion, dependence on pore radii

1 Introduction

It is almost evident that the diffusion coefficients D of substances in the fine-pore hydrophilic membranes are lower than those in their aqueous solutions and, the smaller the cross-section of membrane channels, the stronger the influence of their surface on the diffusion mobility. However, in a quantitative plane, this statement is to be verified only by performing experiments with membranes of the same chemical nature but with different closely controlled structural parameters. Such experiments can be realized using porous glass (PG) membranes prepared by consequent acid and alkaline etching of liquated sodium borosilicate glass.^[1–3] Special convenience of PG for the purpose of revealing dimensional features of the diffusion is that it is suited for the production in the form of thin plates/membranes with through channels of controlled radius, which may be varied over a wide range.^[3,4]

The quantitative dimensional peculiarities of aqueous salts solutions diffusion transport through the set of PG membranes with varied pore radius (r_p) have been studied only in our works.^[3,5,6] The base of the results interpretation and numerical simulation was proposed in the form of the equation:

$$D = D_\infty \exp(-K_s/r_p) \quad (1)$$

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where D_∞ is the diffusion coefficient in bulk solution, and K_s (nm) is the dimension parameter characterizing the extent to which the silica surface affects the structure and properties of a particular solution.

In this communication, one specified example of such experiments and discussion of the results is proposed.

2 Experimental

The PG membranes were prepared in the form of thin (1 mm) disks/plates 25 mm in diameter. To obtain desired parameters of the membranes porous structure (Table 1), DV-1M glass of composition (mol %) $7\text{Na}_2\text{O} \cdot 23\text{B}_2\text{O}_3 \cdot 70\text{SiO}_2$ was subjected to special thermal treatment and subsequent acid and base etching under controlled conditions.^[3,4]

Table 1. Pore radius and porosity of the PGs under study

No	1	2	3	4	5	6	7
r_p (nm)	4.5	7.5	19.0	30.0	40.0	45.0	70.0
δ (%)	31	32	39	48	44	42	57

In the diffusion studies membranes were fixed between two cells: the receiving cell full of twice distilled water and the feeding cell full of aqueous $\text{Ca}(\text{NO}_3)_2$ 0.5M solution. The diffusion dynamics was judged from data of continuous analysis of the salt amount in the receiving cell by EDTA titration. In the experiments, the system was thermostatically controlled in the range 20–70°C and solutions in both cells were continuously stirred.

3 Results and discussion

In all cases, the time dependencies of the salt amount (Q) passed through the membranes became linear within

1 h as shown by typical results in Figure 1. The concentration gradient was taken equal to

$$c/h = (c_{in} - c_{out})/h \sim c_{in}/h \quad (2)$$

where $h = 1$ mm is the thickness of the membrane, and c_{in} is the inlet solution concentration, which far exceeds the current solution concentration in the receiving cell c_{out} . In the calculations of the diffusion coefficients D , the stationary flux through a membrane was expressed, in accordance with the first Fick's law, as

$$dQ/d\tau = D \cdot s \cdot c_{in} \quad (3)$$

where the free cross-section of the membrane (s) was taken equal to its geometrical area corrected for the known porosity δ (Table 1).

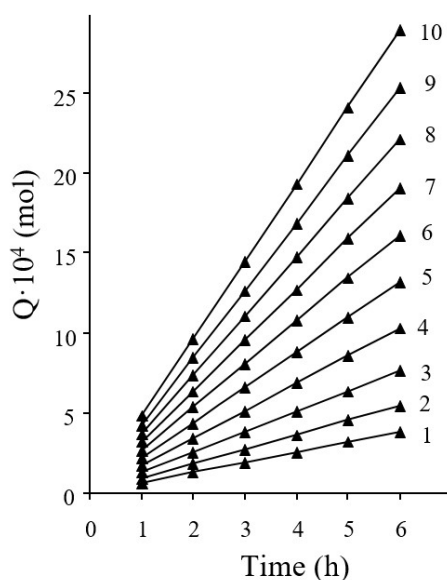


Figure 1. The dynamics of $\text{Ca}(\text{NO}_3)_2$ amount transported through the membrane with pore radius of 4.5 nm at the temperature ($^{\circ}\text{C}$): 25 (1), 30 (2), 35 (3), 40 (4), 45 (5), 50 (6), 55 (7), 60 (8), 65 (9), 70 (10)

Selected results demonstrating the steady state of the process and the general, on the whole, type and extent of the influence exerted by temperature on the rate of the diffusion transport of $\text{Ca}(\text{NO}_3)_2$ are shown in Figure 1 in case of PG with a pore radius $r_p = 4.5$ nm. The temperature dependencies of the diffusion coefficient D in a set of membranes, calculated using these and similar data, are shown in Figure 2(a).

The most pronounced decrease in the salt mobility, which characterizes the hindrance to diffusion in the near-boundary layer of the pore solution, is observed in pores with small radius and is reliably recorded at moderate experimental temperature. The rigidity of the network of hydrogen bonds in the near-wall wa-

ter, imposed by the silica surface^[7,8] diminishes, on the whole, the mobility of pore solution components. As for the increase in the diffusion coefficients with temperature, it is accompanied by their progressive convergence to become virtually coinciding, with $D = (29.5 \pm 0.5) \cdot 10^{-6} \text{ m}^2/\text{s}$ at $\sim 70^{\circ}\text{C}$.

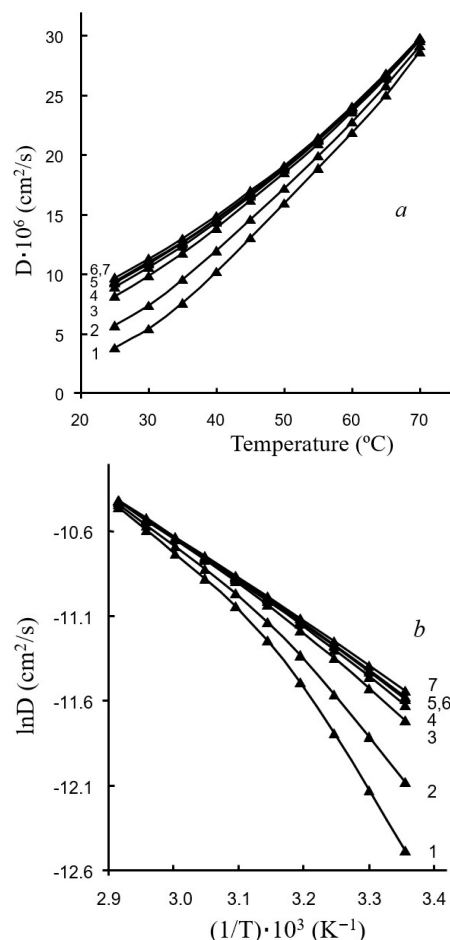


Figure 2. (a) Dependencies of the diffusion coefficient D of $\text{Ca}(\text{NO}_3)_2$ in PG membranes on temperature and (b) the same dependencies plotted in the Arrhenius coordinates. Membrane channel radius r_p (nm): 4.5(1), 7.5(2), 19(3), 30(4), 40(5), 45(6) and 70(7)

The dependencies (Figure 2(a)) characterize the activation of the thermal mobility of the pore solution, which overcomes the structuring effect of the membrane channel walls. The disintegration of the boundary layers of the solution is, thus, complete as a temperature of approximately 70°C is reached. Thus near this temperature, the properties of water in narrow pores of silica cease to be different from those of the bulk liquid.^[7,8]

It should be noted that the $D(T)$ dependencies are not almost linear in the Arrhenius equation coordinates (Figure 2(b)). This is a reflection of the pronounced structural and energetic inhomogeneity of the pore solution, preserved up to a temperature of 70°C , at which the

properties of the solution in the membranes are completely equalized, irrespective of the size of transport channels. Nevertheless, the run of the $\ln D(1/T)$ dependencies clearly demonstrates that the energy expenditure substantially increases in the course of a gradual thermal disintegration of the near-wall layers of the solution. This can be additionally confirmed by estimating the conditional activation energies E^* of the diffusion, with the gently and steeply sloping portions of the $\ln D(1/T)$ dependencies approximated by straight lines. The results presented in Figure 3 clearly demonstrate both a significant rise in E^* in the range of disintegration of the near-wall layers of the solution and a general enhancement of the hindrance to diffusion in small-radius pores.

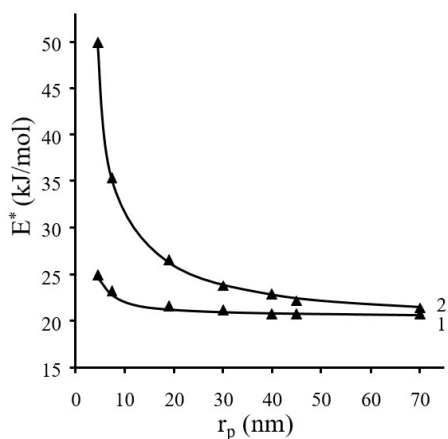


Figure 3. Activation energy E^* of diffusion vs. the membrane channel radius r_p on (1) gently and (2) steeply sloping portions of the $\ln D(1/T)$ dependencies

The dependencies of the diffusion coefficient of $\text{Ca}(\text{NO}_3)_2$ on the pore radius of PG membranes are completely described by Equation (1) which is confirmed by the clearly pronounced linearity of their plots in the $\ln D(1/r_p)$ coordinates in the entire temperature range $25 \div 70^\circ\text{C}$ (Figure 4).

The asymptotics of Equation (1) reflects the physically justified conditions: $D \rightarrow D_\infty$ at $r_p \rightarrow \infty$ and $D \rightarrow 0$ at $r_p \rightarrow 0$ and shows that the rule $D = 0.368 D_\infty$ is satisfied at $r_p = K_s$, i.e., the long-range-action parameter of the surface is numerically equal to the pore radius of the glass membrane in which the diffusion coefficient of the solute is approximately 2.7 times smaller than its value in a free solution.

Processing of the isotherms (Figure 4) gives values of K_s and D_∞ (Table 2). The values D_∞ characterize the influence of temperature on diffusion of $\text{Ca}(\text{NO}_3)_2$ in bulk solution which finds confirmation in a strictly linear relationship $\ln D_\infty(1/T)$ shown in Figure 5. Activation energy in this case $E^* = 20$ kJ/mol is close to its value in case of diffusion in membrane with pore radius 70 nm

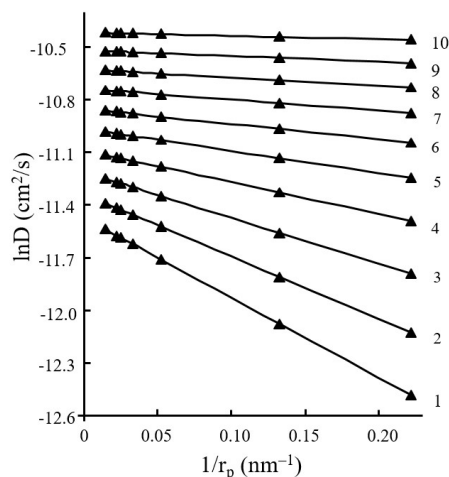


Figure 4. Dependencies of the diffusion coefficient of

(Figure 3). In turn, the numerical value of K_s , characterizing the effective thickness of the boundary layer of a solution, demonstrates its considerable length at 25°C ($K_s = 4.6$ nm) and near total destruction ($K_s = 0.2$ nm) when temperature reaches 70°C .

Table 2. Change of Equation (1) parameters with temperature

$T/^\circ\text{C}$	K_s (nm)	$D_\infty \cdot 10^6$ (cm^2/s)
25	4.6	10.4
30	3.6	11.9
35	2.6	13.5
40	1.8	15.3
45	1.3	17.3
50	0.9	19.4
55	0.6	21.7
60	0.5	24.3
65	0.3	27
70	0.1	30

Thus, the maximum hindrance of $\text{Ca}(\text{NO}_3)_2$ diffusion at 25°C in PG with pore radius of 4.5 nm (Figure 2-4) is due to the full overlapping of boundary layers. It may also be noted confidently predicted growth of K_s at temperature below 25°C (Table 2), reflecting the increase in the proportion of layer structured by silica surface in the overall content of the pore solution.

4 Conclusion

Our study of transport of aqueous solution of $\text{Ca}(\text{NO}_3)_2$ across porous glass membranes revealed a substantial decrease in the diffusion coefficient (D) of

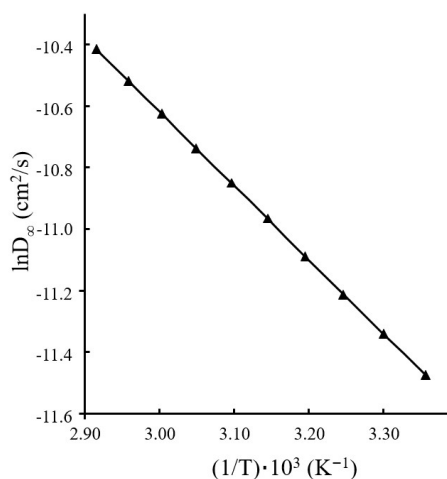


Figure 5. Temperature dependence of the diffusion coefficient of $\text{Ca}(\text{NO}_3)_2$ in aqueous solution

salt with pore radius (r_p) decreasing from 70 to 4.5 nm. The general run of the $D(r_p)$ dependences is consistent with the concept that there exists a near-wall layer of the pore solution, with limited diffusion mobility. The structuring influence of the silica surface on the diffusion mobility of aqueous electrolyte solution was shown to extend over an average boundary layer thickness of about 70 nm.

The activation of the thermal mobility of $\text{Ca}(\text{NO}_3)_2$ solution in PG membranes on raising the temperature of the experiment to 70°C leads to total disintegration of the boundary layer, with the structuring effect of the surface on the diffusion transport of the salt eliminated.

The exponential dependence (1) entirely fits experimental data.

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References

- [1] Enke D, Janowski F and Schwieger W. Porous glasses in the 21st century – a short review. *Microporous and Mesoporous Materials*, 2003, **60**(1): 19-30.
<https://doi.org/10.1134/S1087659615010186>
- [2] Kreisberg VA and Antropova TV. Changing the relation between micro- and mesoporosity in porous glass: the effect of different factors. *Microporous and Mesoporous Materials*, 2014, **190**(5): 128-138.
<https://doi.org/10.1016/j.micromeso.2014.02.002>
- [3] Pak VN, Gavronskaya YY and Burkat TM. *Porous glass and nanostructured materials*. N.Y.: Nova Sci. Publishers, 2015: 134.
- [4] Lyubavin MV, Burkat TM and Pak VN. Fabrication of silica membranes with controlled pore structure. *Inorganic Materials*, 2008, **44**(2): 203-206.
<https://doi.org/10.1134/S0020168508020222>
- [5] Pak VN, Nepomnyashchii AB and Stromova ES. Diffusion transport of aqueous solutions of alkali metal chlorides in porous glass membranes. *Russian Journal of Physical Chemistry (A)*, 2007, **81**(3): 475-478.
<https://doi.org/10.1134/S0036024407030326>
- [6] Akuzhaeva GS, Gavronskaya YY and Pak VN. Dimensional and concentration dependencies of diffusion of aqueous alkaline-earth metal nitrate solutions in porous-glass membranes. *Russian Journal of Applied Chemistry*, 2012, **85**(6): 862-866.
<https://doi.org/10.1134/S1070427212060043>
- [7] Derjaguin BV. Modern state of the investigation of long-range surface forces. *Langmuir*, 1987, **3**(5): 601-606.
<https://doi.org/10.1021/la00077a001>
- [8] Churaev NV, Sobolev VD and Starov VM. Disjoining pressure of thin nonfreezing interlayers. *Journal of Colloid and Interface Science*, 2002, **247**(1): 79-84.
<https://doi.org/10.1006/jcis.2001.8098>