Diffusion Phenomena in Gels

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The formulation and solution of fundamental problems of the study of transport phenomena in micro-and nano-porous gels are considered. To study the diffusion in the gels the optical methods are used. This method allows a real-time visualization of the introduced impurities spreading in gels. It is found that the decomposition of the spectrum of the reflected radiation in the optical range allows one to get more information not only about the nature of the diffusion distribution of the considered impurities, but also on the state of the gel itself. Investigated gels are of different lifetimes, whereby a strong influence of these parameters on the rate of diffusion is identified. Relaxation processes must also be taken into account in mass-transfer models describing diffusion in gels. The time-dependent model of diffusion laws is of particular interest. Its application to the modeling of mass transfer processes will bring further understanding of cause and effect relationship of relaxation and diffusion processes.

1. Introduction

Gel is a specific two-phase system. One phase represents a relatively sparse spatial network of polymer molecules which are bonded at the intersections of intermolecular bonds. The second phase is a liquid (in some cases - the water), which occupies the space between the polymer molecules. This fluid does not have any chemical bond with the polymer molecules, i.e. does not form chemical compounds with them.

All these features create interesting applications of gels in industries and technologies. Gels are widely used in production of polymers, catalysts, sorbents, membrane filters, service wellbore fluids, cosmetic and pharmacy compositions (Kajiwara and Osada, 2000). Presently, the promising application of gels is the use in regenerative medicine for growth of different biological issues, including stem cells in vitro (Westrin and Axelsson, 1991). The gel capillary network can be used for transport of nutrients to separate cells with culture broth and for removal of cell metabolism. One of variants of problem solution is creation of artificial hydrogel matrix with complicated spatial system of microchannels: this task assumes formulation and solving of fundamental problems for study of micro- and nano-porous systems in hydrogel matrix (Amsden, 1998).

The peculiarity of mass transfer of gels is diffusion movement in microchannels of complex shape and structure, skirting macromolecules dispersed phase, the interaction with which strongly affects the rate of transfer (Fang et al., 2008). Gel structure is spatially and temporary heterogeneous. For this reason, the appearence of stagnitiion areas on the microscale is possible where the diffusion transfer occurs with a time delay. Thus, diffusion at the micro level is always three-dimensional, and the velocity is locally unstady and it is not isotropic in space (Pokusaev et al., 2013). This particularity of mass transfer is important for unsteady processes when diffusive relaxation processes are not completed. In this case, the mass transfer at the microscale is not described by a simple one-dimensional diffusion equation with constant coefficient.

The transfer processes in gels have such features as unsteady and anisotropy: they are determined the nature, structure, and behavior of transfer medium (Kazenin et al., 2011). For this type of systems the critical aspect is the effect of solute size in comparison with inner scales of microchannels within the transfer medium (Ozturk et al., 2010). For characterization of the unsteady mass transfer in the gel on the macro scale, one uses the effective diffusion coefficients, which differ from the real diffusion coefficients of the matter in fluid (Lauffer, 1961).

There are many publications relating to the study of the diffusion in gels, either by experimental measurements of diffusion coefficients for gels of different chemical compositions (see, for example, research of Muhr and Blanshard, 1982), or by different degrees of validity for the relation the calculation of the diffusion coefficients (critical analysis of some of them is given, for example, in Amsden, 1998). In recent years, a growing understanding of the mass transfer in microstructure environments cannot be described by Fick's law, even when using the effective diffusion coefficients (Neuman and Tartakovsky, 2009).

The goal of this paper was experimental study of diffusion in gels with optical methods. That is why we studied optical properties of initial solutions and the produced gels with different density and lifetime. One of objectives was experimental prove of relation between the solute transfer rate and the local-time state of the gel, since the gel is a medium with time-varying properties. At last, optical methods can be used for measuring the gel structure anisotropy through visualization of distribution of solute diffusion transfer, and this can offer physical explanation of this phenomenon.

2. Methods and objects

The study of transfer process in microsystems is often based on optical methods. For example, the optical methods are instrumental for study of physical-chemical mechanisms of interfacial convection during laser heating (Karlov et al., 2013), and for study of microflows in the brim meniscus of wetting (Karlov et al., 2002). Optical tools help in visualization of transfer process in real time mode and useful for understanding the physical and chemical features of the process. They are useful for obtaining of direct data on macrokinetic transfer coefficients; in some cases these coefficients can be related to parameters describing the intrinsic structure of the transport medium. The importance of the use of imaging techniques in modern science confirmed the award of the Nobel Prize in Chemistry in 2014 for his work on the development of such methods.

Optical techniques are commonly used to determine impurity transfer coefficients in a steady homogeneous medium (see, for example, research of Leel et al., 2004) and in gels (Helseth, 2011). Determining of diffusion coefficients was based on measuring of distribution of solute concentration over the distance, that is, we tracked down the movement of iso-concentration planes. This method is known as a method of moving boundaries, and the calculation of diffusion coefficient is based on the velocity of transport of a constant-concentration solute inside a gel matrix (Malkin and Chalykh, 1979). Wherein the magnitude of the transfer coefficient can be influenced by convection, surface effects, etc., the presence of which cannot be identified by this method.

The optical method was used for estimating of the diffusion coefficient for a solute in a gel. This choice of optical methods was supported by high accuracy of methods, contactless nature, and informative value of tools. The experimental diagram is shown in Figure 1. The setup is a microscope with an illumination system equipped with a device for placement and movement of a cell comprising a gel sample. The setup has an option of placing an additional (external to the cell) box with immersion liquids for ameliorating the effect of cell wall curvature. The microscope's digital camera is focused on the boundary of transport substance (solute) traveling in the gel volume. The setup was designed for recoding a flat front of the moving boundary of the transport substance or a spherical front from a point source. The latter version was needed for estimating the properties of diffusion anisotropy in gels.

To estimate the order of the diffusion coefficient, the following formula was applied:

$$D = x^2/(4t) , \tag{1}$$

where D is the diffusion coefficient, x is the iso-concentration plane displacement velocity, t is time. Eq(1) follows from the expression for the self-similar variable of the diffusion equation.

For study of diffusion process in a plain diffusion layer, we used gels on the basis of silicates. Gels of different density were produced. The stock solution of sodium silicate was diluted with distilled water to the different levels of density. The gel-generating mixture was prepared by adding of hydrochloric acid to the salt solution and the mixture pH was adjusted to the range 3.5 – 4.5. The density of silicate aquatic solution was controlled by refractometry method. Since the gel structure might be time-variable, we used both fresh and "aged" gels (with lifetime more than 24 h) for study of aging on transfer processes.
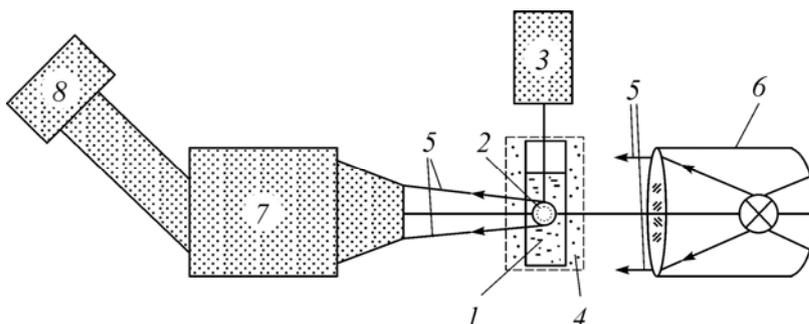
Figure 1: Experimental setup diagram: 1 — cell with gel sample, 2 — moving boundary of the marker substance, 3 — system for marker feeding, 4 — the additional cell with immersion fluid, 5 — light beams, 6 — illumination system, 7 — microscope, 8 — digital camera

The study of gel microstructure influence on diffusion in a plain layer was used a water solution of potassium permanganate $KMnO_4$, which is a "true" solution, being a mixture at molecular level. This substance is gel-inert additives, that is, diffusion of this solute does not change gel properties.

3. Results and discussion

The dependency of refractive index on gel density brings a conclusion about a difference of reflection and transmission spectra for gel samples at different densities, and this phenomenon can be a foundation for developing a spectral method for analysis of gel structure.

The regular visual observation for the condition of diffusive front is good for qualitative study only. A more accurate approach is an experiment on measuring the relative transmittance (or absorbance) of white light passing through the gel and the diffusing substance. Meanwhile the substances of the studied system have different spectral absorption characteristics, so the data on light absorbance at different wavelength of light are very informative. The data on $KMnO_4$ in the sodium silicate gel are plotted in Figure 2, where we have shown the dynamics of light transmittance for a diffusive component in different points of the gel sample. These spectral studies demonstrated that measurement of diffusion in gel with a moving boundary method for different wavelengths of probing light gave different values for diffusion coefficient for the same component; this can be indication of selective interaction between the component and structures of the silica gel. Therefore, the data for transmittance spectra for silica gel samples might be used for study and control of sorption features of the gel matrix (when the multiphase and multicomponent filtration flows take place).

As it was mentioned above, the gel is not a steady structure. Processes of recondensation with variation and thickening of the structured mesh occur in the gel; that is, the medium of diffusion changes with time (they call this process as "gel aging"). Therefore it is meaningless to tell about transfer coefficients in gels beyond the time limits. This fact was confirmed in experiments: we measured the diffusion coefficient for $KMnO_4$ in silicate gels with different densities and different lifetime (a fresh gel and one-day aged gel). Gels of different density were produced. The stock solution of sodium silicate was diluted with distilled water to the levels of density 1.04, 1.068, and 1.09 g/cm^3. The density of silicate aquatic solution was controlled by refractometry method through measuring the refractive index with the Abbe refractometer. The results are plotted in Figure 3. As it is shown below, this minor difference in the initial density of sodium silicate solution produces differences in properties of final gels (optical and diffusion-related properties). This graph shows that the diffusion coefficient decreases with the gel density (this is predictable due to condensing of gel mesh) and with gel lifetime. When relaxation processes take place, the structured mesh also changes and becomes denser.

It is experimentally found that there are two characteristic stages in time for unsteady mass transfer in the gel that is rendered in Figure 4. For the experiments an "old" gel designed with an open surface more than a day is used. It is assumed that by this time it all relaxation processes are fully completed. Part of the dispersion liquid evaporated, whereby the microscopically in homogeneous multiphase structure is formed along the inside boundary. A part of the gel away from its borders remains in liquid-phase. In the border areas of the gel liquid evaporated, resulting in a formation of air microchannels.

There is a fractal stage at the initial stage of unsteady mass transfer in a diffusing substance across the border of the dried gel (object 3 in Figure 4). This stage lasts during the first minute from the starting of the process. Concentration front has a pronounced fractal structure. Then the diffusion step begins (object 4 in Figure 4), when the fractal boundary starts to blur. Far from the boundary of the gel, we observed the interaction between processes of fractal and diffusion mass transfer (object 5 in Figure 4).
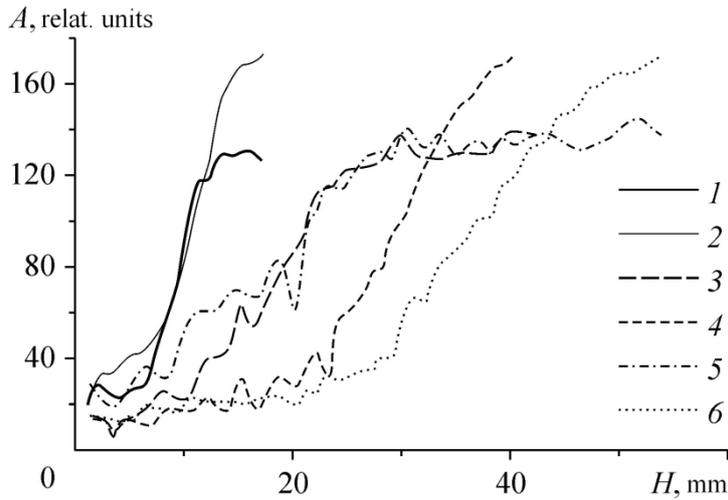
A, relat. units

Figure 2: Spectral-revealed curves of solute front movement in the gel. The abscissa axis plots the distance from the initial solute front while diffusion into the gel (gel is on the right, and solvent is on the left), mm; the ordinate axis is the relative transmittance intensity of light at given wavelength A (the complete transparency corresponds to number 256, the complete absorbance stands for 0). Position of diffusion front: 1, 2 - initial, 3, 4 - intermediate, 5, 6 - final. Wavelengths: 1, 3, 5 - red light (650±2 nm), 2, 4, 6 - green light (530±2 nm).

Probable mechanism of the fractal surface formation at the initial stage of mass transfer in the gel is the movement of colored liquid on the dried capillaries under the influence of the Laplace pressure. The movement of colored liquid in each capillary is stops, when the transferred substance merges with the gelling liquid (water). Compare to the structural channels formed by dispersion phase, this is macroinhomogeneity a part of which filled by the water. Thus, the diffusion process goes not only toward the gelled fluid from the fractal surface, but also within the already colored volume filling macroinhomogeneity by diffusing substance.

Let us consider the process of diffusion in gel with the evolving structure. We assume that recondensation in gel produces temporary local stagnation zones without any mass transfer to the ambient zones; the solute concentration there becomes frozen for a time. This is a typical time of gel relaxation τ, which describes the duration of gel restructuring processes.

For this kind of diffusion model, a 1D nonstationary diffusion equation for gel can be written in the following form:

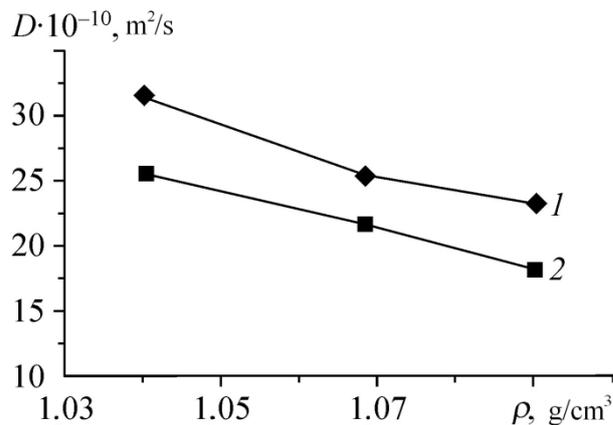$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - K(C - C|_{t-\tau}),$$ (2)

$D \cdot 10^{-10}$, m^2/s

Figure 3: Dependency of diffusion coefficient (D×10^{-10} m^2/s) in sodium silicate gel on its density (ρ, g/cm^3) while gel aging: 1 — fresh gel, 2 — old gel.
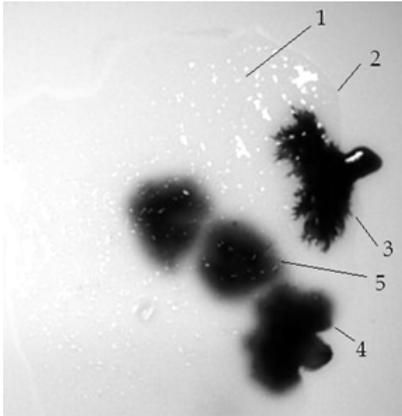
Figure 4: Various stages of water diffusion in the gel KMnO₄ solution: 1 - the thin layer of gel; 2 – the border of the gel; 3 – the initial (fractal) stage of droplets diffusion in the gel; 4 - diffusion stage; 5 – interection of fractal and diffusion stages for drops inside the gel.

where C is the transfer substance concentration, t is the current time, x is the longitudinal coordinate, and D is the diffusion coefficient of the transfer substance in the liquid phase of gel. Averaged over volume and time τ, the transfer coefficient between the typical and dense structured mesh zones K depends on the gel density (and this produces dependency on the current time of diffusion process t), on the volumetric fraction of gel with dense structure, diffusion coefficient D, and the scale of developed dense structures. The value of K, the same way as τ, is a characteristic of the intrinsic structure of gel. Note here that the concentration in the last term of Eq(2) is taken at moment of $t-\tau$, i.e., since the formation of a stagnant zone which has been decomposed till this moment and released out the accumulated solute.

If we assume the relaxation time to be a small parameter (this is not a compulsory condition for gels), we can decompose $C|_{t-\tau}$ into a series in t and keep only two main terms of the series, and then we obtain:

$$C|_{t-\tau} = C(t) - \tau \frac{\partial C}{\partial t} + \cdots,$$ (3)

Substitution of Eq(3) in Eq(2) gives us an equation

$$\frac{\partial C}{\partial t} = D_{ef} \frac{\partial^2 C}{\partial x^2},$$ (4)

where

$$D_{ef} = \frac{D}{1 + K\tau}.$$ (5)

This relation for diffusion coefficient in gels was developed by Lauffer (1961) from phenomenological ideas. The Eq(5) for diffusion coefficient in gels is included into a single complex of values $K\tau$, which describes the intrinsic structure of gel and can be calculated from direct experimental data. Thus, the optical-spectral study of diffusion in gels gives information about dynamics of gel intrinsic structure.

We should note that Eq(5) was obtained for small relaxation times τ, but when this condition is not fulfilled, the reverse problem of diffusion on the basis of Eq(2) should be considered. For this situation the parameters K and τ are the functions of current time t, so time interpolation of these parameters can be done with exponential laws. As the gel aging process continues, the transfer coefficient decreases. We should emphasize that this type of time dynamics is inherent for diffusion processes in true solutions, but for diffusion of nanoparticles in gels the time evolution of coefficients might be more complicated.

The physical meaning of the time delay in the present model of mass transfer is associated with the inertial properties of the system that responds to the impact is not instantaneously, but rather with a time lag.

Experimental measurements show that the rate of mass transfer in the gel is less than for diffusion in a homogeneous fluid (water). The probable reason for this is the heterogeneity of the microstructure of the transfer medium. The rapid transfer of unsteady diffusion material in the direction opposite to the gradient of

the initial concentration occurs along the longitudinal channels. Slow unsteady three-dimensional diffusion of internal filling of the dead space with clean water occurs under the influence of small local concentration gradients. The model relates the effective diffusion coefficient with the real diffusion coefficient for fluid.

The dependence of the mass transfer rate in gels on the geometry of the diffusion zone is experimentally detected. On this basis, it can be assumed that in the gels the convective mechanism taking place due to various physical and chemical mechanisms. However, due to the high resistance the velocity of the gelled fluid is much lower than in a pure fluid.

4. Conclusions

Spectral studies show that the measurement of gel diffusion method, by the technique of the moving boundary for different wavelengths of the probing radiation, gives different values of the diffusion coefficient. This indicates the selective interaction of the diffusible component with microstructural elements of silica gel.

Visualization of unsteady filling in the horizontal thin layer of "old" (dried) gel by colored substances allows one to find a fractal structure of the original concentration front. The reason for its occurrence is the movement of colored liquid on thin dry microchannels due to capillary forces due to Laplace pressure. There is a possibility of forming in gel at the initial moment of a mass transfer of inhomogeneous volume zones with different concentrations of the substance.

Based on the analysis of the experimental data, a new model of non-stationary diffusion with a time delay in micro-inhomogeneous medium is presented. The model takes into account the heterogeneity of the gel structure related to the existence of local stagnant zones. In these zones, the diffusing material for some time is not communicating with the environment and therefore its concentration is kept constant. Here the characteristic time delay is taken into account. This time delay characterizes the duration of the internal transitional processes of mass transfer. The effective value for the diffusion coefficient in gels is obtained by comprising a single set of parameters characterizing the processes micro transfer in a structured environment.

Acknowledgements

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