The Diffusion Properties of the Hydrogels

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Abstract—**Mass-transfer properties of silicate and agarose hydrogels with different dispersed phase concentrations were investigated. Performed measurements allowed to determine the temporal and spatial dynamics of propagation in the gel samples of the concentration fields of transportable substances by method of optical spectroscopy. The main regularities of the variation of the diffusion coefficients in gels with an increase in the concentration of the dispersed phase are determined.**

Keywords— gel; concentration of dispersed phase; diffusion coefficient; critical density

I. INTRODUCTION

Gels are dispersed systems having a liquid dispersion and microstructure due to the forces of intermolecular interaction, the dispersed phase [1]. In gels, the concentration of the dispersed phase forming their structure can range from a few percents to a tenth of a percent. The presence of unique physico-chemical and rheological properties of gels leads to the expansion of areas of their practical use in various fields of science and technology [2].

In recent years, numerous studies have been carried out to practically realize the possibility of growing tissues from stem cells in bioreactors with hydrogels, using additive 3D technologies for this purpose [3, 4]. A capillary network in gels is suitable for providing living cells with nutrients and removing the products of their metabolism. The rheological properties of gels make it possible to form bioreactors of a complex shape by layer-by-layer printing of gel media of different composition and concentration, without violating the survival conditions of biological microobjects. The practical realization of this approach requires the formulation and solution of new fundamental problems of studying the patterns of mass transfer in gels [5, 6].

The properties of the gels depend on the composition of the medium, the method of preparation, and the synthesis conditions [7]. However, even for gels of the same composition, there are difficulties with reproducibility of the values of their basic properties. Nevertheless, for technological applications many properties of gels are similar. For example, such properties are their unsteadiness and anisotropy, caused by the structure and behavior of the transport medium [8].

Many of gels are optically transparent, so it is convenient to use optical methods to study their mass-transfer properties. The determination of the transport coefficients is based on the measurement of the temporal and spatial dynamics of the concentration profiles movement by using colored substances in gels. There are numerous optical methods that are used to study mass-transfer properties of gels including conventional visualization [9], spectral sounding [10], and many others. The advantage of these methods is that they are non-contact, i.e. do not affect the natural course of the matter transport process. Available data [11] suggests that mass transfer in gels of different nature has similar mechanisms.

The aim of this article is to study the fundamental properties of the mass conductivity of gels (for example, gels of silicic acid and agarose gels of various concentrations) using spectral methods for their best use in the creation of bioreactors with aid of additive 3D technologies. It is practically important to establish basic laws of diffusion of substances in gels of different chemical nature and concentration.

II. METHOD AND MATHERIALS

To measure the mass transfer rate in gels of different densities, a method was used based on determining the dynamics of the front of the contrasting tolerated substance along the height of the gel sample with reference to the corresponding time points. It was assumed that the concentration of the diffusing substance decreases in direct proportion to the increase in the intensity of the light passing through the sample.

For this purpose, the spectroscopy method was used. The use of spectral methods with the possibility of optical sensing of gels by their height makes it possible to measure the displacement of isoconcentration surfaces much more accurately at selected intervals of time than it was usually done with photography. As the main element of the experimental setup, the spectrometer of the company Ocean Optics USB2000+ was used together with a standard block for recording and processing spectra. The schematic diagram of the experimental setup used is described in detail in [11].

Based on the measurement of the intensity of the light passing through the gel with the diffusing substance, for each time point, concentration profiles were constructed and their displacement in the time interval was determined. The

minimum value of the relative permeability of light corresponds to the region occupied at that time by the diffusing substance, and the maximum is the region of the still pure gel. Each measured profile corresponds to a certain initial density of the gel-forming solution and the approximate measurement time from the moment of diffusion initiation. The time interval for measuring each profile was about 1 min. The results were calculated from the expression for a self-similar variable for unsteady diffusion [12]

$$x = \sqrt{4Dt} \ . \qquad (1)$$

Here, x is the displacement of the selected concentration for time t from the beginning of the process, D is the diffusion coefficient.

As objects of experimental study, two gels that have different physico-chemical mechanisms of formation were used. One of them, a silicic acid gel, is formed as a result of a chemical reaction, the second, an agarose-based gel, is formed during polycondensation upon cooling of the gel-forming solution.

For practical purposes, the creation of bioreactors based on gels it is interesting to obtain experimental data about the dependence of the mass transfer coefficients in gels and, in particular, on the diffusion coefficients from the initial density of gel-forming solutions.

To determine the properties of mass conductivity, silicate gels with a density in the range 1.04 - 1.08 g/cm^3 were synthesized, the density was checked with an Abbe refractometer. Under the synthesis of gels of lower density than in the above range of values, their properties were not reproduced, and under higher density, the gels had an inhomogeneous structure. When investigating the mass transfer rate in silicate gels, 3.0 % by weight aqueous solution of potassium permanganate $KMnO_4$ was used as the diffusing substance. It is the "true" solution because it forms a molecular mixture with water.

Agarose gels for experiments were obtained by mixing agarose with distilled water, followed by heating to 90°C with convection or microwave methods and further cooling to room temperature. For the experiments, agarose gels with a concentration of 0.4–3.0 % by weight agarose were used. To measure the diffusion rate in agarose gels, a 1.0 % aqueous solution of fuchsin was used in the experiments. In microbiology this substance is sometimes added to nutrient media. Fuchsin (hydrochloric acid rozanilin) $C_{20}H_{20}N_3Cl$ is a substance with a high molecular weight, the aqueous solutions of which have a purple-red color.

Both diffusing substances, even at low concentrations, contrast well with water and gel. Their usage makes it possible to obtain both high-contrast photographs and clear spectra and to accurately determine from them the temporal and spatial dynamics of the concentration profiles.

When studying the mass conductivity of gels, it is important to select such diffusion conditions to avoid in the experiment the influence on the results of the density effects associated with the difference in the densities of gels and diffusing substances. A particular difficulty is the determination of the diffusion coefficient of 1 % solution of fuchsin in pure water and in aqueous solutions of agarose, when the concentration of agarose is less than the critical concentration of gel formation. The problem is that the density of fuchsin is lower than the density of water due to the presence of ethyl alcohol in it, since in pure water fuchsin is insoluble. A system where the solution of fuchsin is below, and the water from above is hydrodynamically unstable and density convection arises in it. When fuchsin is added from above, capillary instability arises because of the presence of fuchsin surface-active properties.

To measure the diffusion coefficient of fuchsin in pure water and aqueous solutions of agarose with low concentration, the experimental procedure described in [11] was used. The idea was to determine the cross profiles of the concentration of fuchsin, formed by the diffusion mechanism from its vertical jet, formed as a result of spontaneous density convection. By increasing the cross-sectional dimension of this jet for the indicated time, the diffusion coefficient of fuchsin can be estimated.

III. EXPERIMENTAL RESULTS

The experiments showed, despite the difference in the amplitude of the concentration profiles during diffusion, determined by the transmission of light, due to the strong effect of the gel density on the intensity of its passage, they are self-similar for different times. From the point of view of the theory of one-dimensional diffusion, when the solution of the problem is expressed through the error function, the argument of which is a self-similar variable, the dependence of the displacement of the isoconcentration surface on time is described by the relation (1). Knowing the corresponding time moments for measuring the concentration and distance values to which their similar points are shifted, the diffusion coefficients were calculated using (1). Usage of the relation (1) for calculation of diffusion coefficient is applicable only when it is independent of the concentration of the diffusing substance.

Based on experimental data on the displacement of isoconcentration surfaces in the diffusion of potassium permanganate in a gel of silicic acid of various densities on Fig. 1 shows the dependence of the corresponding diffusion coefficient from the gel density. It follows that in the range of gel densities for which its reproducible synthesis is possible, the diffusion coefficient decreases several times with increasing density of the gel-forming solution.

The graph of the dependence in Fig. 1 is extrapolated to the diffusion coefficient of potassium permanganate in distilled water, for which gel formation does not occur. On the basis of physical considerations, we can propose a special form of dependence (depicted in Fig. 1) in the region of low densities, when there is no gel formation. In this concentration range, the amount of gel forming substance is not sufficient to form a stable chemically interconnected dispersed phase. It is known [13, 14], when the concentration of the disperse phase is less than the critical concentration of gel formation, stable

gels that have the whole set of inherent properties are not formed. The possibility of determining the critical concentration of the formation of gels by optical methods is discussed below.
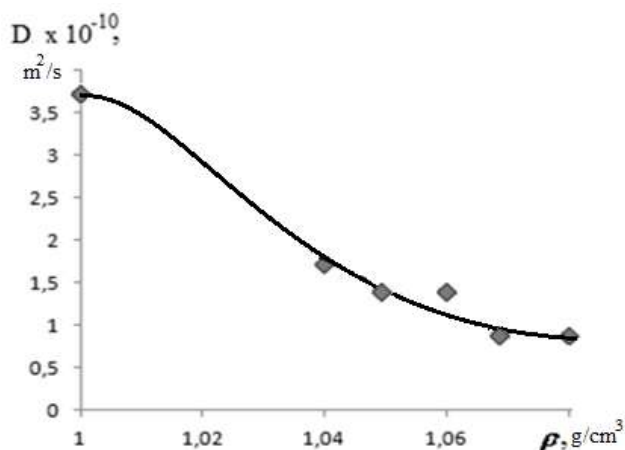

Fig. 1. Dependence of the diffusion coefficient of a 3.0 % solution of potassium permanganate in a gel of silicic acid from the gel density.

In the range of low gel densities, the diffusion coefficient remains practically constant at the level corresponding to water, with a sharp decrease at a density corresponding to the beginning of the stable formation of gels.

The study of the mass transfer of fuchsin in agarose gels is complicated due to the fact that gel is a microdispersed medium and fuchsin is a large organic molecule. Their interaction leads to the appearance of the dependence of the diffusion coefficient, both on the concentration of the gel and on the concentration of the diffusing substance. When calculating these experiments, the use of relation (1) is not justified, therefore the results described below can only be regarded as qualitative.

To study diffusion of fuchsin in an agarose gel, the same procedure as described above was used. As a result, the dependence of the diffusion coefficient of fuchsin from the concentration of agarose gel was obtained (see Fig. 2). From this it follows that in the studied range of agarose concentrations, the diffusion coefficient decreases several times with increase in agarose concentration in the gel forming solution from 0.4 to 3.0 % by weight. Zero concentration of agarose corresponds to the diffusion coefficient of fuchsin in water.

The shape of the graph in Fig. 2 is similar to that shown in Fig. 1. This confirms the analogy in the change in the mass-transfer properties of the gel with increasing concentration of the dispersed phase. It should be emphasized that at concentrations of agarose up to 0.6 % by weight the diffusion coefficient of fuchsin in the gel is only slightly less than its value for distilled water. At higher concentrations of agarose, the diffusion coefficient is much smaller.

IV. DISCUSSION

It has been experimentally shown that the mass conductivity (diffusion coefficient) of gels of different chemical nature depends on the concentration of the dispersed phase. With increasing concentration, the diffusion coefficients of the investigated model substances decrease by several times.
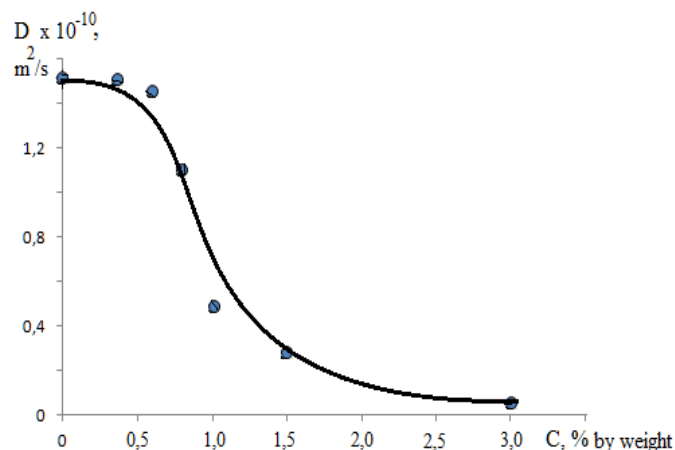

Fig. 2. Dependence of the diffusion coefficient of a 1.0 % solution of fuchsin in an agarose gel from the mass concentration of agarose.

It was found that for small concentrations of the dispersed phase (probably less than the critical concentration of gel formation) the diffusion coefficients of model substances in the gel differ only slightly from their values for water. At large concentrations of the dispersed phase, the mass conductivity of gels is greatly reduced with respect to the low-concentration gels. This behavior is due to the fact that as the concentration of the dispersed phase increases above the critical value, the solution undergoes a phase transition to the gel under certain conditions, and the diffusion effect is the stronger that higher the concentration of the gel-forming solution.

As follows from the obtained results, the value of the critical concentration of gel formation is an important parameter for predicting the mass-transfer properties of gels. The presence of a gel-forming substance, even in the state of the solution, slightly reduces the corresponding diffusion coefficients, but a reduction becomes critical only when the dispersed phase exceeds the critical concentration and conditions for the formation of the gel are realized. Previously, the phenomena associated with the critical concentration of gel formation were studied mainly to determine the conditions for changing rheological properties of gels and it was determined by various rheological methods, see, for example, [15].

However, optical methods can be used to determine critical concentrations of gel formation in some cases. For optically transparent media, we proposed a new method based on the measurement of the refractive indices of gel-forming solutions and gels obtained from them. The method of such measurements is simple, the experimental equipment allows us to restrict ourselves to the use of widespread and uncomplicated equipment (for example, the Abbe

refractometer). Let us consider the possibility of using such a method for determining the critical concentration of gel formation by the example of silicate gels, for this we use the experimental data obtained earlier and published in [16]. The method will be further tested for evaluation of the possibility of its application for determining the critical concentration of the formation of gels obtained by polycondensation.
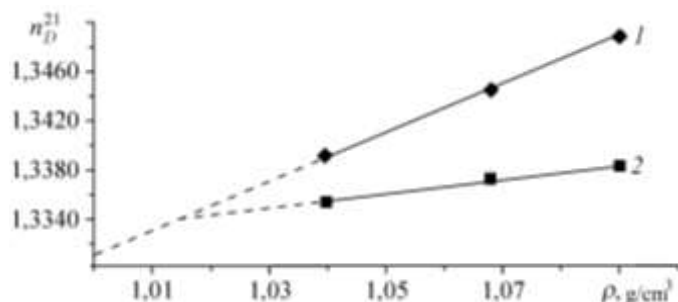

Fig. 3. Refractive indices of solutions of sodium silicate and the corresponding gels: 1 - liquid solution, 2 - gel of appropriate density.

In Fig. 3 shows the results of measurements of the refractive indices of solutions of sodium silicate and the corresponding gels as functions of the density. The measurements were carried out at a temperature of 21°C. It can be seen that the refractive index for a solution is higher in magnitude than for a gel prepared from it. In addition, for the gel there is a slower increase in the refractive index than for the solution with increasing density. The experimental dependence of the refractive index for the gel-forming solution is linearly extrapolated to the value of the refractive index of pure water, taken from the reference data for this temperature.

Similar linear extrapolation of the experimental data was also performed for the dependence of the refractive index of the gel from the density. However, since in the gel the dispersed phase is structured and the gel differs in its optical properties from the solution, the indicated dependence will not go to the value of the refractive index corresponding to pure water (the extrapolated dependences are shown in Fig. 3 with a dashed line). The intersection point of these extrapolation lines determines the density of the gel-forming solution, at which the refractive indices of the solution and gel begin to differ from each other. This density should be taken as critical density of gel formation. According to the calculations, it will correspond approximately to the value of 1.015 g/cm^3.

The presented results only from the methodological point of view describe the possibility of determining the critical density of gel formation by comparing the dependences of the refractive indices of the gel-forming solutions and the gels obtained from them from the density. To increase the accuracy of determining the critical density of gel formation, a much

larger number of experimental points are needed. In this case, nonlinear extrapolation may be required, so that, at lower densities of the gel-forming solution, experimental data will be obtained for the refractive indices of gels, the more accurately the critical density of gelling can be determined.

It is important to note that at the branch point the derivatives of the refractive indices of the gel-forming solution and the gel from the density must be equal, that is, at the critical point of gel formation, the extrapolation curves should touch each other rather than intersect.

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