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YU.F. ZABASHTA, V.I. KOVALCHUK, O.S. SVECHNIKOVA, L.A. BULAVIN

Taras Shevchenko National University of Kyiv, Faculty of Physics
(64/13, Volodymyrs'ka Str., Kyiv 01601, Ukraine)

APPLICATION OF THE LIGHT SCATTERING METHOD TO STUDY THE HYDROGEL SURFACE STRUCTURE

Light scattering at the sol-gel transition in aqueous solutions of hydroxypropyl cellulose with sodium and potassium impurity ions has been studied. It is found that the transition brings about the light reflection associated with the formation of the hydrogel surface. A molecular model of the observed phenomenon is proposed. Assuming that the light scattering is described by the Rayleigh law, the corresponding equations are derived and used to calculate the fractal indices of the hydrogel surface structure. It is shown that the introduction of ionic impurities into the polymer solution leads to the swelling of molecular coils and the reduction of the fractal dimension of the hydrogel surface.

K e y w o r d s: light scattering, hydrogel, fractal dimension.

1. Introduction

It is well known [1] that there are two phase states of the polymer solution: the sol and gel phases. In the latter, unlike the sol phase, there exists a network of polymer chains. The gel phase of an aqueous polymer solution is called hydrogel.

The study of the physical properties of hydrogels is promising in connection with the wide application of hydrogels in biomedical technologies [2–6]. The main areas of hydrogel applications are ophthalmology [7, 8], wound treatment [9, 10], tissue engineering [11, 12], drug delivery systems [13, 14], hygiene products [15, 16], and others. In all those cases, hydrogel, when performing its functions, comes into contact with living tissue. Therefore, the efficiency of a hydrogel application depends to a large extent on the state of the hydrogel surface. In this connection, the study of the structure of this surface is undoubtedly important. No less important is the search for methods that would make it possible to modify the structure of the hydrogel surface in order to increase its efficiency.

The problem of the gel and, in particular, hydrogel surfaces has not been resolved yet. Therefore, it is necessary first of all to determine the methods that are suitable for studying the hydrogel surface. In the presented paper, we consider the possibility of using the light scattering method for this purpose.

2. Experimental Part and Formulation of the Problem

As the experimental object, we selected the 2-wt% aqueous solution of hydroxypropyl cellulose (Alfa Aesar) [17]. The molecular weight of this compound equals 10^5, and the substitution degree is 75.7%. Polymer solutions contained impurities, namely, chlorides of Group I alkali metals (Na and K). The molar concentration of salt in every specimen was identical (0.154 mol/l).

The studies were performed on the installation described in work [18] in detail. In particular, the pri-

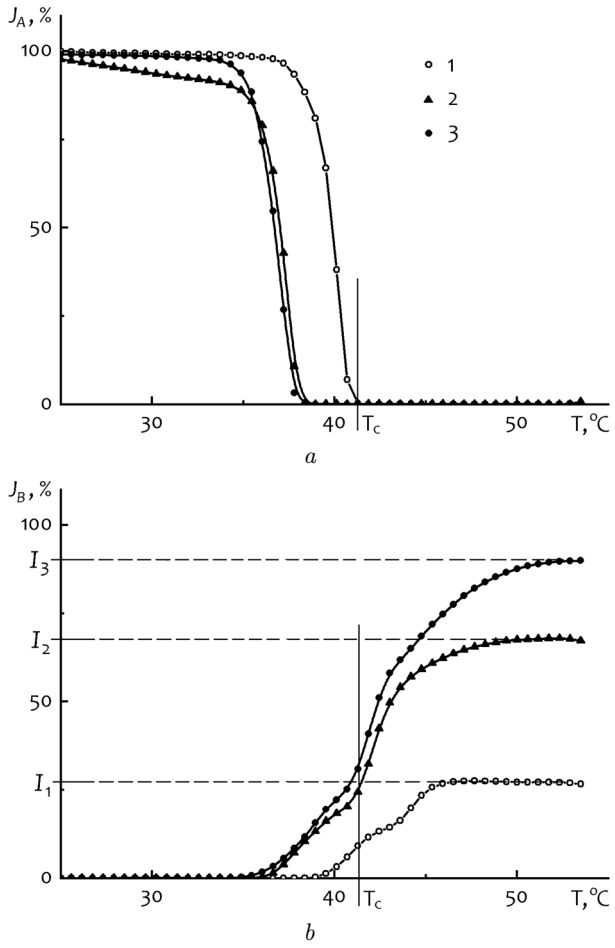


Fig. 1. Temperature dependences of the intensities of the transmitted (J_A, panel *a*) and reflected (J_B, panel *b*) light beams for (*1*) the ion-free specimen, (*2*) the specimen with Na ions, and (*3*) the specimen with K ions. The heating rate is 1.1 °C/min. See other explanations in the text

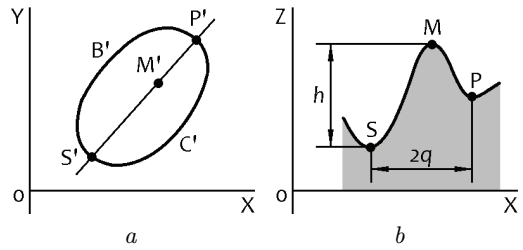


Fig. 2. Protrusion on the gel surface: the view from above (*a*), the protrusion cross-section by a plane parallel to the Z axis (*b*)

mary light beam with a wavelength of 525 nm fell on the surface of the examined solution and formed two beams, transmitted (A) and reflected (B). The intensities J_A and J_B of those beams were measured when the specimen temperature T was increased from 20 to 55 °C at a constant rate. The corresponding $J_{A,B}(T)$ dependences are shown in Fig. 1.

In works [19, 20], it was shown that the dependence $J_A(T)$ is governed by the sol-gel transition. The purpose of this article is to determine the physical mechanism responsible for the experimental temperature dependence of the intensity of the light beam reflected from the hydrogel surface, which is depicted in Fig. 1.

3. Continuum Model of the Gel Surface

The formulated problem will be solved on the basis of the continuum model. Let the gel be considered as a continuous medium, and let us assume that the gel surface is not perfectly smooth, i.e., it contains protrusions of various sizes (see Fig. 2). The equation of the surface is

$$Z = f(x, y). \tag{1}$$

Within the surface area occupied by a protrusion, function (1) behaves as follows. Its maximum is observed at point M, i.e., this is the protrusion top (Fig. 2, *b*). Point M' is the projection of point M onto the XY plane. The protrusion top is surrounded by a "valley", the bottom of which is described by the closed line $S'B'P'C'$ (Fig. 2, *a*). Along this line, function (1) acquires minimum values, the smallest of which is observed at point S'. Let us consider a plane that is parallel to the Z axis and passes through points S' and M'. The protrusion cross-section by this plane is shown in Fig. 2, *b*. Points S' and P' are projections of points S and P, respectively, onto the XY plane.

The protrusion height h and width $2q$ (Fig. 2, *b*) are defined as follows:

$$h = z_M - z_S, \tag{2}$$

$$2q = x_P - x_S. \tag{3}$$

The values of h and q are considered to be random functions of the coordinates (x_M, y_M) of the protrusion top:

$$h = f_h(x_M, y_M), \tag{4}$$

$$q = f_q(x_M, y_M). \tag{5}$$

Let H and Q denote the mathematical expectations of the corresponding random variables h and q. The quantity H will be called the degree of surface roughness.

4. Light Scattering Induced by the Gel Surface

The analysis of Fig. 1, *a* testifies that each $J_A(T)$ dependence can be associated with a temperature T_C above which the intensity J_A practically vanishes. The loss of transparency of the polymer solution is conventionally identified with the complete transition of the solution into the gel phase. Therefore, the examined system is a gel at temperatures $T > T_C$.

According to Fig. 1, *b*, the intensity $J_B(T)$ equals zero below a certain temperature $T_{1C} = T_C - \Delta T_C$, where $\Delta T_C \ll T_C$, as well as at $T > T_C$. Since the gel is opaque at temperatures $T > T_C$, the appearance of a beam with the intensity J_B can only be a result of the primary beam reflection from the gel surface.

By convention, the surface model exhibited in Fig. 2 is attributed to the class of statistically nonplane surfaces. The studies of light scattering by such surfaces have a long (for more than a hundred years) story [21]. It is known that the solution of this problem is reduced to the analysis of a wave equation of a certain type. Instead, in this paper, we will confine ourselves to a qualitative consideration proceeding from assumptions concerning the type of backward scattering, which forms the output beam with the intensity J_B.

Let the following conditions hold:

$$kh \ll 1, \quad kq \ll 1, \tag{6}$$

where **k** is the wave vector of incident light. In this case [22], Rayleigh scattering takes place,

$$j_B \sim k^4 r^6, \tag{7}$$

where j_B is the intensity of light scattered by a single particle of size r. The total scattering intensity

$$J_B \sim n j_B, \tag{8}$$

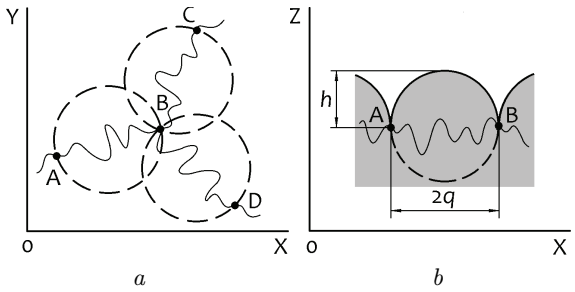
where n is the number of scattering centers per unit volume. It is obvious that

$$n \sim 1/r^3. \tag{9}$$

Hence,

$$J_B \sim k^4 r^3. \tag{10}$$

The continuum model discussed in the previous section is characterized by two spatial parameters, H and Q. Let us assume that the particle size is proportional to the geometric mean of those parameters [21],



a *b*

Fig. 3. Polymer coils at the gel surface: the view from above (*a*), the surface cross-section by a plane parallel to the Z axis (*b*)

$$r \sim (HQ)^{1/2}. \tag{11}$$

Then, formula (10) reads

$$J_B \sim k^4 (HQ)^{3/2}. \tag{12}$$

5. Molecular Model of the Gel Surface

We will assume that the surface nodes of the network are located at the plane (see Fig. 3, *a*, where points A, B, C, and D mark the nodes). Figure 3, *b* illustrates the cross-section of the surface by a plane that passes through points A and B and is parallel to the Z axis. The solid curve in this figure corresponds to the surface boundary. Thin wavy curves in Fig. 3 stand for polymer chains.

In accordance with the classical theory of high elasticity [23], the chains of the polymer network are assumed to be coil-shaped. In Fig. 3, the contours of coils are indicated by dashed curves. Let R denote the average coil radius. Then formula (12) looks like

$$J_B \sim k^4 R^3. \tag{13}$$

The polymer coil is known to be a fractal [23]. Let the fractal dimension of the coil be d, and let us introduce the notation

$$\beta = 1/d. \tag{14}$$

Then the expression for R looks like [1]

$$R = aN^{\beta}, \tag{15}$$

where N is the number of links composing a molecular chain, and a is the link length. Substituting this

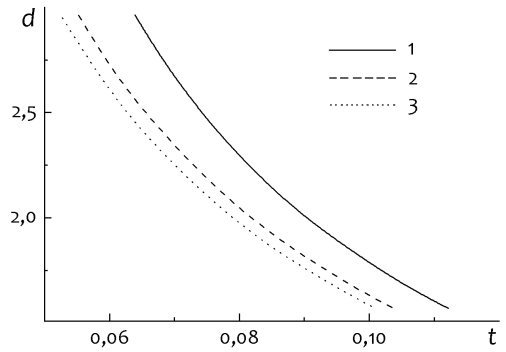


Fig. 4. Dependences of the fractal index d on the parameter t of Eq. (17) for the ion-free specimen (*1*), the specimen with Na ions (*2*), and the specimen with K ions (*3*)

expression into formula (13), we obtain

$$J_B \sim k^4 a^3 N^{3\beta}. \tag{16}$$

Hence, in the framework of the proposed gel surface model, the intensity of the reflected beam is determined by the wavelength of incident light, the length of polymer molecule, and the fractal dimension of the surface.

6. Structure of Polymer Coils Forming the Gel Surface

Let us determine the values of the parameter β that characterizes the fractal structure of polymer coils located at the gel surface. For this purpose, we should analyze the experimental data shown in Fig. 1.

Let I_1 denote the asymptotic value of J_B obtained for a specimen free of ionic impurities, whereas I_2 and I_3 do the same for specimens with Na and K impurities, respectively (see Fig. 1, *b*). The corresponding values of β for polymer solutions without impurities and with ions will be denoted as β_1, β_2, and β_3, respectively. Then, using formula (16), we obtain

$$\begin{cases} (\beta_1 - \beta_2)P = C_1, \\ (\beta_1 - \beta_3)P = C_2, \end{cases} \tag{17}$$

where

$$P = \lg N, \quad C_1 = \frac{1}{3}\lg\frac{I_1}{I_2}, \quad C_2 = \frac{1}{3}\lg\frac{I_1}{I_3}. \tag{18}$$

The value of N for hydroxypropyl cellulose equals $N = 300$ [24]. The values of the parameters $C_{1,2}$, according to the data of Fig. 1, *b*, are as follows: $C_1 = -0.133$ and $C_2 = -0.174$.

Each of two equations in system (17) is an equation of a plane in the Cartesian coordinates $(\beta_1, \beta_2, \beta_3)$. Accordingly, the solution of system (17) is the intersection of those planes, i.e., a straight line. The parametric equation of the latter has the form

$$\begin{cases} \beta_1 = P^2 t + C_1/P, \\ \beta_2 = P^2 t, \\ \beta_3 = P^2 t + (C_1 - C_2)/P. \end{cases} \tag{19}$$

From whence, it follows that the inequality $d_1 > d_2 > d_3$ always holds true for the fractal index (14) at an arbitrary t-value. Figure 4 demonstrates an example of the calculated dependences of the parameter d on the parameter t.

Thus, the introduction of Na and K ions into the hydroxypropyl cellulose solution reduces the fractal dimension of aggregates, d. At the same time, as follows from formula (13) and Fig. 1, *b*, the presence of ions increases the roughness of the gel surface, R. This result is in full agreement with the results of work [25], where, with the help of mathematical simulation methods, it was shown that just such a dependence of the fractal index d on the surface roughness takes place at small R values (when the Rayleigh scattering condition is obeyed).

7. Conclusions

Using the light scattering method, the surface of hydrogels formed in aqueous solutions of hydroxypropyl cellulose as a result of the sol-gel transition has been studied. On the basis of the continuum model for hydrogel, a molecular model of the gel surface is proposed. This model made it possible to relate the experimentally obtained data on the light scattering intensity to the fractal properties of the hydrogel surface.

It is found that the formation of the gel surface structure in the polymer solution continues after the termination of the sol-gel transition. This process is accompanied by the surface loosening and the increase of the surface roughness. The introduction of ions into the polymer solution leads to the growth of the surface roughness degree in comparison with the solution free of those ions. The surface loosening is a result of the swelling of polymer coils that form the gel surface.

In our opinion, the swelling degree of polymer coils in the solution of hydroxypropyl cellulose increases,

if ions are introduced into the solution. It can occur due to the screening of electrostatic interaction forces between polymer links and the appearance of "water–ion" bonds that pull water molecules away from the hydrated shell of polymer chains, thereby reducing the number of intermolecular "polymer–polymer" bonds.

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Ю.Ф. Забашта, В.І. Ковальчук,
О.С. Свєчнікова, Л.А. Булавін

ЗАСТОСУВАННЯ МЕТОДУ
РОЗСІЯННЯ СВІТЛА ДЛЯ ВИВЧЕННЯ
ПОВЕРХНЕВОЇ СТРУКТУРИ ГІДРОГЕЛЮ

Досліджено спричинене золь-гель переходом розсіяння світла у водних розчинах гідроксипропілцелюлози з домішками іонів натрію і калію. Встановлено, що після завершення переходу виникає відбиття світла, пов'язане із формуванням поверхні гідрогелю. Запропоновано молекулярну модель спостереженого явища. У припущенні, що розсіяння світла описується законом Релея, ми отримали рівняння, за допомогою яких обчислено фрактальні показники поверхневої структури гідрогелю. Показано, що додавання іонних домішок у полімерний розчин приводить до набухання молекулярних клубків та зменшення фрактальної розмірності поверхні гідрогелю.

Ключові слова: розсіяння світла, гідрогель, фрактальна розмірність.