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Swelling behaviour of a polyelectrolyte network under load

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The kinetics of swelling of a strongly charged hydrogel is studied. The influence of external load on the rate of swelling and on the equilibrium degree of swelling is experimentally investigated. With the help of a sensitive technique it is shown that two different mechanisms governing the process of swelling may be clearly determined. The first one (at the beginning of swelling) is connected with the 'ordinary' swelling of a neutral network, and the second one corresponds to the largest part of the kinetic curve and is connected with additional electrostatic interactions. The dynamics of hydrogel swelling, which corresponds to strong electrostatic interactions, is analysed by the equation of motion of the hydrogel boundary. The mathematical approach is based on the modern theory of the qualitative solution of differential equations. It allows one to obtain a correlation between static and dynamic parameters of the swelling process and the dependence of these parameters on applied load. © Elsevier Science Ltd.

(Keywords: polyelectrolyte hydrogel; swelling dynamics; influence of load)

INTRODUCTION

The importance of studies of the physicochemical properties of highly swelling hydrophilic networks have been discussed in many recent publications[1–3]. Such materials are already produced for absorption applications (e.g. baby diapers), but also they have enormous potential applications. They can be used as an environmental agent to purify water and also as 'intelligent' materials, changing their shape in response to external inputs.

For all the above mentioned cases the kinetics of polyelectrolyte hydrogel swelling in different conditions is one of the main subjects to be studied. Models of the swelling behaviour of hydrophilic neutral gels are given, e.g. in refs 4–8. Time-dependent response and the kinetics of swelling of ionic networks under pH and ionic strength changes have been reported[9–13]. The influence of external load on the equilibrium degree of swelling of a weakly charged gel has been discussed[14], but the thermodynamic approach used does not give a good quantitative agreement with experimental data. To our knowledge there are no papers describing the influence of external load on the *kinetics* of swelling of a strongly charged hydrogel. On the one hand, these results may be important for practical applications. On the other, detailed study of hydrogel behaviour under load gives new knowledge for understanding the mechanism of gel swelling.

In our work we studied the kinetics of swelling in water of a strongly charged polymer network with and without load. Due to the specially developed sensitive technique we show that during different time intervals of the swelling process different mechanisms are governing the hydrogel swelling. The dynamics of hydrogel swelling which corresponds to strong electrostatic interactions will be described by the equation of motion of the hydrogel boundary. We shall show that by knowing static characteristics under different load values it is possible to predict dynamic characteristics of the swelling process in this region.

EXPERIMENTAL

The hydrogel used in this study is a strongly charged gel based on sodium polyacrylate/polyacrylic acid in a molar ratio of 0.75/0.25 cross-linked by *N*,*N*′-methylenebisacrylamide (with a mole fraction of the crosslinking agent with respect to the monomer of 0.06%), kindly provided by Atochem, a French company. The initial state is a powder of dry gel particles with a size of about 1 mm. The equilibrium degree of swelling in water is $350\,\mathrm{g\,g^{-1}}$.

The kinetics of gel swelling was recorded on the home-made apparatus schematically presented in *Figure 1*. The principle of measurements is as follows. A thin layer of 0.003 g of a dry gel powder (8) is placed in a glass vessel. A plastic tube (5) with a piston (6) is moved down on this layer. Water is poured into the vessel (7). Small holes in

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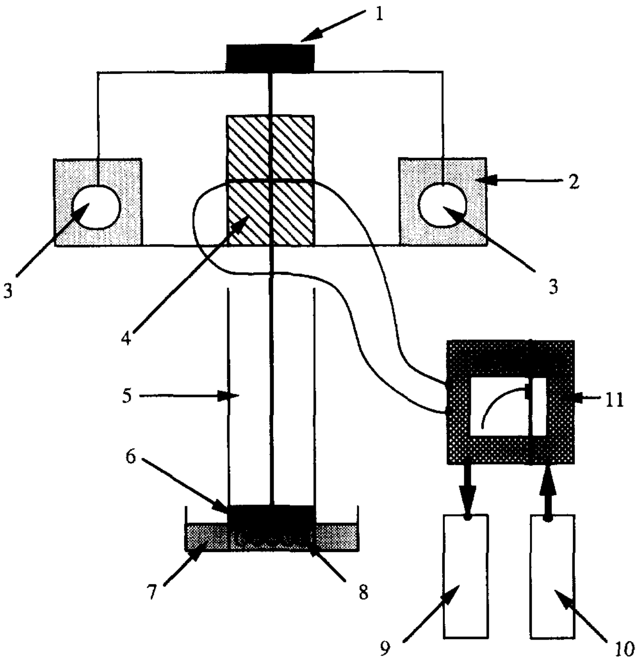

Figure 1 Experimental set-up for measuring kinetics of hydrogel swelling: load (1), counterweight (3) of the piston in water (2), induction coil (4), plastic tube (5) with the moving piston (6), hydrogel (8) swelling in water (7), automatic recorder (9), alternative power generator (10) and transfer (alternating to direct current) (11)

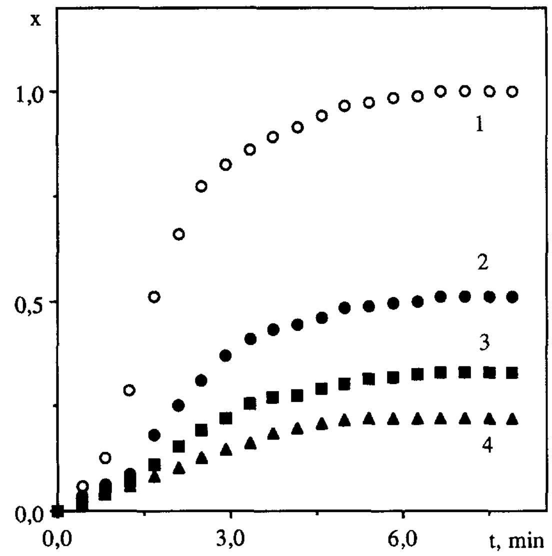

Figure 2 Kinetics of hydrogel swelling in water under different load: changes in coordinate x (position of the piston or hydrogel boundary) with time under $M = 0$ g (1), 20 g (2), 30 g (3) and 40 g (4)

the wall of the tube provide water free access to the gel. The hydrogel starts to swell and pushes the piston up. As the end of the piston is moving inside an induction coil (4), the resistance is changing and an electric signal is passed to an automatic recorder (9). This allows one to record directly changes in the hydrogel degree of swelling with time.

In order to exclude the influence of the weight of the piston we used a counterweight (3) placed in water (2). By adjusting the piston and the tube we tried to minimize friction. The external load was changed by placing a load of different weight (1) on the top of the piston.

RESULTS AND DISCUSSION

The kinetic curves of the hydrogel swelling (in other words, changes of coordinate x with time), with and without load, are presented in *Figure 2*. For convenient comparison we reduced all the experimental data to the maximum coordinate value which corresponds to a hydrogel swollen at equilibrium state without load.

The discussion will be focused on the following phenomena:

(a) Swelling dynamics: shape of the kinetic curve of the gel free swelling; dependence of the swelling kinetics on the applied load.
(b) In equilibrium state: dependence of the equilibrium degree of swelling on the load.

Correlation between static and dynamic parameters of the whole process of swelling will be also analysed.

It is well known that several forces contribute to the swelling of a polyelectrolyte network. Generally speaking, they are: polymer–solvent interaction, elastic deformation of polymer chains and electrostatic forces. During the process of swelling it is necessary to take into account the force of friction.

The kinetic curve of the free hydrogel swelling in water (*Figure 2*, curve 1) shows a sigmoidal shape. The beginning of the process seems to be linear, then, when the gel degree of swelling is about 50 g g^{-1}, the network becomes 'diluted' enough for electrostatic forces to start to play the main role, and the rate of swelling increases significantly. When the gel is almost swollen a slow approach to equilibrium state takes place.

From our measurements it is possible to see clearly the difference in the rates of swelling connected with 'ordinary' swelling of a polymer network in a solvent (the beginning of the process) and 'polyelectrolyte' swelling. One should keep in mind that, in general, the gel has to be considered as a three-dimensional object; in other words, when a gel is swelling in a solution from the dry state it takes time for a network to swell from the surface to the core. Thus, the beginning of swelling consists of several processes coupled together: interaction with the solvent, time-dependent solvent penetration inside the network, which induces a polymer density gradient and leads to the appearance of stresses[4], etc. The high values of the degree of swelling of a strongly charged network in the equilibrium state are determined by the presence of electrostatic forces. The presence of a load slows down all the rates of swelling and their difference becomes less noticeable. However, it is the 'polyelectrolyte' mechanism that makes the main contribution to the swelling of a strongly charged network.

Theoretically, the swelling kinetics of neutral and charged networks have been discussed in several papers. The approach used is based on the solution of a diffusional equation in partial derivatives[5–12]. The solution is given as an expansion in a series of diffusional modes. This approach can be used only if the initial equation is linear. Thus, it is valid only in the region close to the equilibrium state when the diffusion coefficient (or friction coefficient) is constant. However, in a paper by Candau *et al.*[6] it was justified that the friction coefficient of a network swelling in a solvent depends on polymer concentration. This effect may be neglected if a network does not swell greatly. In other words, the approach proposed by Tanaka and Fillmore[5], and further developed in refs 6–12, may be used for the description of swelling kinetics of a charged network at the beginning of the process.

We shall try to describe the swelling kinetics of a strongly charged gel in the region of 'polyelectrolyte' swelling. For the reasons mentioned above (the dependence of diffusional or friction coefficients on polymer concentration) the initial model has to be non-linear. We shall use an approach based on solving equations in ordinary derivatives.

Theory: general approach

The swelling of a charged network at enough high dilution is determined by a balance of extension (electrostatic) and contraction (elastic) forces. As was shown in ref. 15 electrostatic forces may be described through the action of the electric field of a double layer which appears at the hydrogel–solution boundary due to the thermal motion of free counter-ions. When a hydrogel is placed in water this approach is equivalent to the Donnan theory, which takes into account the osmotic pressure of free ions[15]. The diffusional approach used by Budtova *et al.*[15] allows one to reduce extension forces to ones applied directly to the hydrogel boundary. The same conclusion can be made for elastic forces[16].

For simplicity let us consider a sample of a charged gel as an infinite plane. In this case we can assume that the forces of extension and contraction are applied directly to a single mass point on the hydrogel boundary.

The diffusional process of water penetration inside the gel can be described as the effective friction of this mass point. As the swelling process is slow we can neglect the term with the second derivative of the mass point coordinate with respect to time. Thus, the effective friction is proportional to the velocity of the mass point.

In the presence of external load the motion of this mass point is determined by an ordinary differential equation of the first order:

$$k(x)\frac{\mathrm{d}x}{\mathrm{d}t} = F_1(x) - F_2(x) - PS \qquad (1)$$

where $k(x)\,\mathrm{d}x/\mathrm{d}t$ is the force of friction, $k(x)$ being the friction coefficient, $F_1(x)$ is the resultant force of extension, being in our approach electrostatic force, $F_2(x)$ is the elastic force of contraction, and PS describes the influence of external pressure P on the sample with area S.

The forces $F_1(x)$ and $F_2(x)$ and coefficient $k(x)$ depend on several hydrogel parameters: degree of cross-linking, mesh size M_c, functionality of crosslinking junctions, etc. We shall try to give a general description of the kinetics of hydrogel swelling in the 'polyelectrolyte' region, not solving directly equation (1) with exact values of gel parameters. This approach is based on the method of the qualitative theory of analysis of ordinary differential equations[17].

In our case this method can be used as follows. In the equilibrium state under a certain load (coordinate x_0 means the equilibrium degree of swelling) equation (1) becomes

$$F_1(x_0) - F_2(x_0) - PS = 0 \qquad (2)$$

When deviation $\Delta x = x - x_0$ from the equilibrium value x_0 is not large we can use the Tailor expansion of the left-hand side of equation (1), leaving only linear terms:

$$\frac{\mathrm{d}(\Delta x)}{\mathrm{d}t} \approx \frac{\partial}{\partial x}\left(\frac{F_1(x) - F_2(x) - PS}{k(x)}\right)\bigg|_{x_0} \Delta x \qquad (3)$$

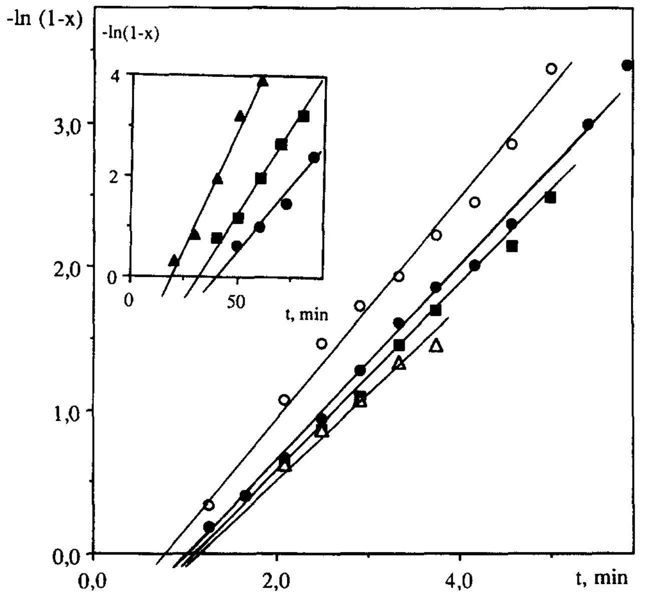

Figure 3 The same kinetic curves in the 'polyelectrolyte' region presented on a semi-logarithmic scale. Notation is the same as in *Figure 2*. Inset: analogous dependences calculated from Figures 3 and 5 of ref. 13

The value of the factor before Δx has the meaning of a time constant, which describes the kinetics of the gel approach to equilibrium state:

$$\frac{1}{k(x_0)}\frac{\partial}{\partial x}(F_1(x) - F_2(x))|_{x_0} = -\frac{1}{\tau} \qquad (4)$$

We put '−' before $1/\tau$ because the resultant force applied to the mass point decreases during the approach to the equilibrium state, and thus the partial derivative in equation (4) is negative.

Thus, the main equation (1) becomes very simple:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -\frac{x}{\tau} \qquad (5)$$

The value of τ depends on the coordinate of the equilibrium point x_0, in other words, on the value of the applied load.

The solution of equation (5) describes the asymptotic approach of the hydrogel to the equilibrium state. It is given by the expression:

$$x = x_0\left(1 - \exp\left(-\frac{t - t_0}{\tau}\right)\right) \qquad (6)$$

Here, t_0 is a certain constant which characterizes the real time of the beginning of 'polyelectrolyte' swelling. In our case it will be calculated from experimental data.

The same approximation formula is given in refs 5–12. In these papers τ has the meaning of the relaxation time of the slowest diffusional mode. This means that τ depends on coefficients of the initial diffusional equation as described in ref. 5. These coefficients were supposed to be constant, being a combination of hydrogel parameters: shear modulus, osmotic compressional modulus and osmotic longitudinal modulus. In our case, τ has a non-linear dependence on the hydrogel degree of swelling [see equation (4)]. This will allow us to describe

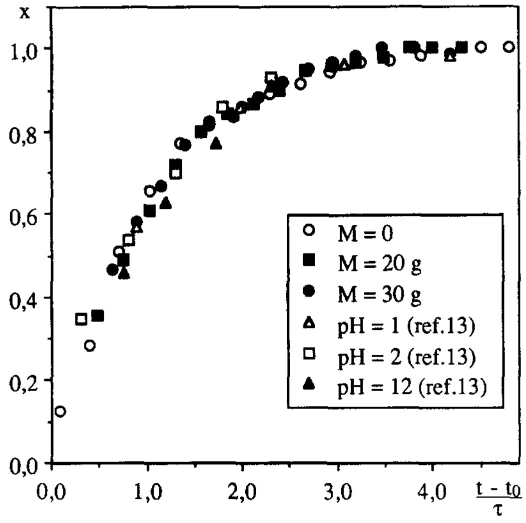

Figure 4 Kinetic master plot for the region of 'polyelectrolyte' swelling: changes in coordinate x with reduced time $(t - t_0)/\tau$ for our data and data from ref. 13

the influence of external load on hydrogel swelling behaviour.

Comparison with experiment

Kinetic master plot. In *Figure 3* experimental kinetic curves in the region of 'polyelectrolyte' swelling (from data shown in *Figure 2*) are presented on a semi-logarithmic scale. It is clear that the dependences are linear which means that 'polyelectrolyte' swelling may be described by the exponential law given by equation (6).

The slope of each line [determined by $1/\tau$, see equation (6)] is different: it decreases with increase in the load. Each line crosses the abscissa at a fixed time $t > 0$. This parameter may be used as an effective time t_0 of the beginning of 'polyelectrolyte' swelling process.

Using the determined parameters τ and t_0 it is possible to construct a master plot (*Figure 4*). All the data fit well the exponential dependence [equation (6)]. This shows the validity of our approach for the description of hydrogel swelling in the 'polyelectrolyte' region.

To show that our approach is valid for other ionic networks we performed the same data treatment for results obtained in ref. 13 for 78/22 mol% 2-hydroxyethyl methacrylate (HEMA)/2-(dimethylamino)ethyl methacrylate at pH 1 and 2 (*Figure 5* of ref. 13) and for 78/22 mol% HEMA/methacrylic acid at pH 12 (Figure 3 of ref. 13). The shape of the kinetic curves in this case is the same as in ours. The values of $1/\tau$ and t_0 were calculated from kinetic dependences presented on a semi-logarithmic scale (see inset of *Figure 3*). Using the parameters obtained, all the data were plotted on the same graph (*Figure 4*).

It is clear that the swelling behaviour of this gel in the 'polyelectrolyte' region may be described in a similar way to the sample we used in our studies. Equation (4) is valid for the case when there is not a load, but the ionic strength of the solvent is changed. Here, $F_1(x)$ will depend on the difference between the concentration of free ions inside and outside the hydrogel. This difference may be described by the phenomenon of concentration redistribution of free ions in the presence of a charged network[18].

*Influence of load**. In this section we shall describe the influence of applied load on the equilibrium degree of swelling. This will also allow us to find the correlation between static (coordinate x_0) and dynamic (parameter τ) characteristics of a hydrogel.

According to equation (2) the pressure of applied load in the equilibrium state is proportional to the difference of forces $F_1(x)$ and $F_2(x)$. We shall roughly estimate the dependence of this difference on coordinate x and compare the result with experimental dependence of load values on the equilibrium degree of swelling.

Let us consider the same infinite plane gel sample. The forces of expansion $F_1(x)$ and contraction $F_2(x)$ according to the simplest model are given by the expressions:

$$F_1(x) = RTn/x \tag{7}$$

$$F_2(x) = Bx \tag{8}$$

where R is the universal gas constant, T is the temperature, n is the number of moles of ionogenic groups in the sample (which is fixed), and B is an undetermined elastic constant.

The expression for $F_1(x)$ was chosen from the following assumptions. As was shown in the paper by Budtova *et al.* the expression for the swelling pressure of a hydrogen in water, given by diffusional[15] and thermodynamic[2] approaches, is the same. Both theories show that $F_1(x)$ is directly proportional to the concentration of mobile counter-ions. For the case of a plane gel sample its volume is directly proportional to x. As concentration is inversely proportional to volume, $F_1(x)$ is inversely proportional to x. Equation (8) is the simplest form of Hooke's law.

Thus, the equation describing the dependence of the difference between expansion and contraction forces (or, in other words, the pressure of applied load) on coordinate x_0 (coordinate of the gel boundary in the equilibrium state) may be written as follows:

$$PS = F_1(x_0) - F_2(x_0) = \frac{RTn}{x_0} - Bx_0 \tag{9}$$

The constant B may be determined as follows: when $P = 0$, then $RTn/x_0 = Bx_0$. However, we also know that without any load $x_0 = 1$ (see *Figure 2*). Thus, $B = RTn$ and equation (9) may be rewritten as

$$P \approx \text{const}\left(\frac{1}{x_0} - x_0\right) \tag{10}$$

In *Figure 5* experimental correlation between the coordinate of the hydrogel boundary in the equilibrium state under different loads and the mass of applied load M is presented in coordinates $(1/x_0 - x_0)$ *versus* M.

In this coordinates theory (equation (10)) gives a linear dependence of P (or M) on $(1/x_0 - x_0)$ passing through the origin of the coordinates. Experimental points lie approximately on the mentioned straight line. The deviations may be caused by a rough approximation of elastic forces by Hooke's law.

Correlation between static and dynamic parameters. The part of the kinetic curve which corresponds to 'polyelectrolyte' swelling is characterized by dynamic

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* We should like to note a curious detail: the work performed by 0.003 g of hydrogel swelling and pushing a load of 30 g to a height of 1 cm up is the same as the work needed for lifting this gel sample to a height of 100 m

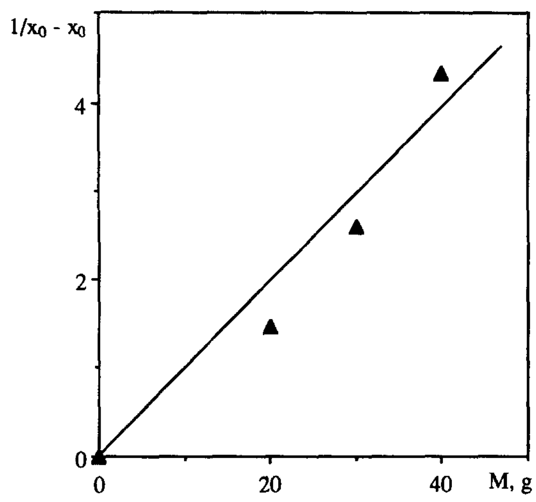

Figure 5 Experimental correlation between the position of the hydrogel boundary in equilibrium state x_0 under different loads and the weight M of the applied load in coordinates $(1/x_0 - x_0)$ *versus* M. Theory predicts a direct proportionality between M and $(1/x_0 - x_0)$, which is shown by a straight line

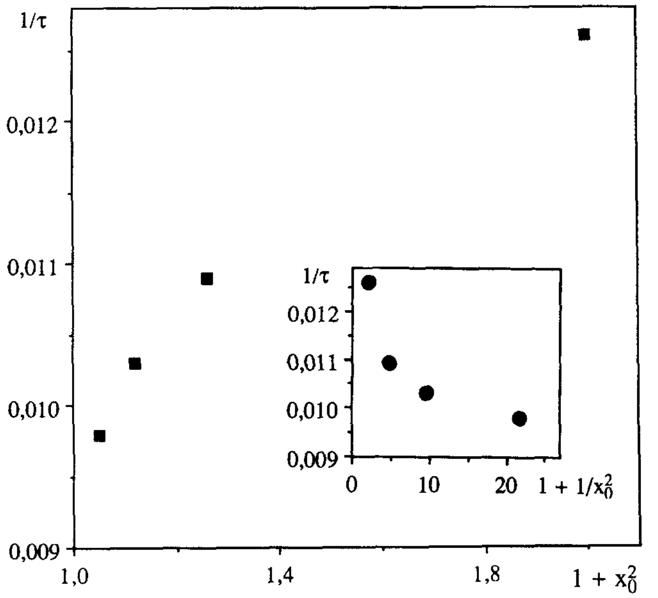

Figure 6 Dependence of the time constant $1/\tau$ on the position of the hydrogel boundary in the equilibrium state x_0 under different loads in coordinates $1/\tau$ *versus* $(1 + x_0^2)$. According to equation (13) $1/\tau$ must be directly proportional to $(1 + x_0^2)$. Inset: the same dependence in the assumption of a constant friction coefficient. Here, theory predicts a linear dependence with a positive slope in coordinates $1/\tau$ *versus* $(1 + 1/x_0^2)$. Experimental data give the opposite result

parameter τ, which describes the rate of approach to the equilibrium state [see equation (6)] and static parameter x_0 which corresponds to the coordinate of the hydrogel boundary in the equilibrium state under a certain load. We shall describe theoretically the dependence of $1/\tau$ on x_0 and compare it with experimental results.

The correlation between $1/\tau$ and x is given in the general case by equation (4). In terms of the same simple model the expressions for $F_1(x)$ and $F_2(x)$ are given by equations (7) and (8). Let us examine the expression for the friction coefficient $k(x)$. Usually, the friction coefficient of a polymer network swelling in a solvent is supposed to be constant (see e.g. refs 5–12). However, this is not correct (and it will be shown later) for strongly charged hydrogels which can swell several hundred times. We shall try to analyse the behaviour of a friction coefficient taking into account the following qualitative assumptions.

Any simple mathematical model of a dynamic system is using direct proportionality of dynamic characteristics on derivatives of variations which are changing in time. In our case we consider hydrogel swelling as a quasi-stationary process. This means that the concentration of dissociated ionogenic groups may be considered to be homogeneous at any time. Thus, we assume that the dynamic term in equation (1) is directly proportional to the derivative of free ions concentration with time:

$$k(x)\frac{\mathrm{d}x}{\mathrm{d}t} = -\mathrm{const}\,\frac{\mathrm{d}N}{\mathrm{d}t} \tag{11}$$

where N is the concentration of free ions.

As N is inversely proportional to the volume of the gel and as we consider the gel to be a plane, N is inversely proportional to coordinate x. Thus, from equation (11) one can obtain

$$k \approx \frac{1}{x^2} \tag{12}$$

Substituting the expressions for $F_1(x)$ [equation (7)], $F_2(x)$ [equation (8)] and $k(x)$ [equation (12)] into the general formula [equation (4)] we have

$$\frac{1}{\tau} \approx 1 + x_0^2 \tag{13}$$

In order to compare the obtained result with experimental data we shall plot them in coordinates $1/\tau$ *versus* $(1 + x_0^2)$ (see *Figure 6*). It is clear that the experimental points fit well with the trend predicted by theory.

For comparison, we plot the dependence of $1/\tau$ on x_0 in the assumption of a constant friction coefficient. In this case the dependence of $1/\tau$ is described by direct proportionality to $(1/x_0^2 + 1)$, which means that $1/\tau$ has to increase with the increase in $(1/x_0^2 + 1)$. Experimental data plotted in these coordinates (see inset of *Figure 6*) show an opposite tendency.

The results obtained show that the friction coefficient of a strongly charged hydrogel swelling in water is not a constant. It decreases rapidly with the increase in the degree of swelling.

CONCLUSIONS

Studies of the swelling behaviour of a polyelectrolyte hydrogel under load give the following results.

- The kinetic curves of hydrogel swelling consist of two parts according to swelling mechanisms governing the process: the beginning corresponds to the swelling of a neutral hydrophylic network and the following largest part with higher rate of swelling corresponds to the swelling due to electrostatic interactions. This part is described by exponential law with the time constant depending on applied load.
- The non-linear theoretical model of 'polyelectrolyte' swelling of a network is developed. It is based on consideration of the equation of the motion of an effective mass point on the hydrogel boundary. This equation is in ordinary derivatives, which allows one to take into account the changes in friction coefficient during the swelling process. The approach used gives a

correlation between static and dynamic parameters of the swelling gel.

- The friction coefficient of a strongly charged network swelling in water is not constant; it decreases rapidly with increase in the degree of swelling of the gel.

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