Theoretical Description of Polyelectrolyte Hydrogel Collapse in Electric Field

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Abstract

Theory of collapse of polyelectrolyte hydrogels under the influence of direct electric current is developed. The theory is based on the consideration of the motion of gel-solution boundary. It is shown that this boundary is moving with constant velocity on the first stage of the collapse (some part of hydrogel stayed undeformed). This velocity is theoretically determined by analysis of boundary conditions only (electric current density conservation). It is shown that on the first stage of the process hydrogel collapse caused by direct electric current is described completely by Faraday's law analog. Hydrogel collapse is described by exponential form of Faraday's law analog on the second stage. On this stage the whole specimen is deformed. The comparison of proposed theory and results obtained early is carried out. It is shown that the theory is in good accordance with experimental data.

Introduction

Reversible collapse of polyelectrolyte hydrogels and its applications are continuously studying in current literature. Thus, on this base biomimetic devices [1,2], ecological technologies [3], etc may be developed. Y.Osada et al. reported a number of experiments demonstrating wide possibilities of application of hydrogels for transformation of energy from the one form to another [4]. Recently we also proposed the modification of the method of purification of water [5], which may be used in military systems of deactivation.

Different attempts of complete theoretical description of polyelectrolyte hydrogels collapse under the influence of direct electric current are widely known also. These attempts mostly are connected with detail consideration of phenomenon, which takes place on the gel-solution boundary. Thus, in Ref [2] collapse of hydrogel was interpreted on the base of analysis of changing of moveable ions concentration near an electrode under the influence of direct electric current. In Ref [6] the changing of osmotic pressure caused by DC was calculated numerically. The time-dependent distribution of concentration by nu-

merical solving of equations on motion was analyzed for this purpose.

This paper [6] is the most complete theoretical description of collapse of polyelectrolyte hydrogels, which is known at present. In other words, one can say that now only numerical solution of the problem exists under consideration. In this paper we are aimed to show that the theoretical description of collapse of polyelectrolyte gels may be completely given without consideration of concrete processes taking place on the gel-solution and gel-electrode boundaries in analytical form.

Basic model

First of all we'll try to show that the theoretical description of hydrogel collapse under the influence of DC may be reduced to the analysis of motion of hydrogel boundary. In Ref. [7] it was shown that the linear dependence of change of hydrogel mass on time is in good accordance with experimental data during the first stage of the processes. Hydrogel specimen collapsing under DC influence in different moments is schematically presented at Fig.1 (Ref. [7]).

This figure shows that collapse actually takes

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place just near electrode. In other words, only one part of the specimen change its volume (I). The other parts of the specimen (II) simply are moving in space. The cylindrical specimen of finite radius is presented at Fig 1.
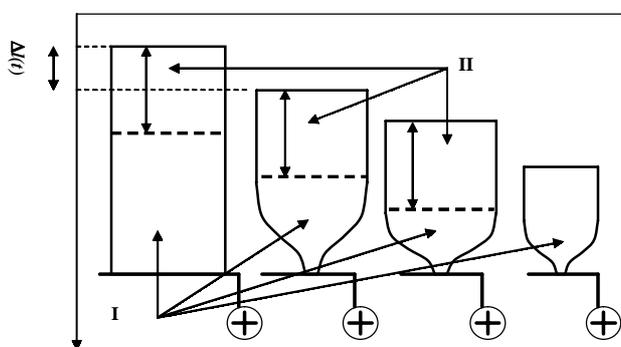

Fig. 1. Schematic picture of polyelectrolyte gel collapse under the influence of DC.

One can easy to see that a part of the specimen is moving without changing of its volume. Moreover, supposing that the mass (volume) of collapsed part is negligible in comparison with the mass (volume) of swollen part, one can found a simple relation between the hydrogel boundary velocity and changing of specimen mass in time.

$$vS\rho = S\rho \frac{dl}{dt} = \frac{dm}{dt} \qquad (1)$$

where v is the velocity of gel – solution boundary, S – cross section of the specimen, l – the length of the specimen, m – its mass.

Formula (1) is valid at the first stage of the collapse for cylindrical specimen while the volume of definite part (II) of the specimen stay unchanged.

Derivative $\dfrac{dm}{dt}$ is constant at the beginning of the collapse and one can say that the gel boundary is moved with the constant velocity.

Thus the first step of theoretical description of polyelectrolyte gel collapse is reduced to calculation of this velocity which may be supposed to be constant. Let us try to determine this value without consideration of collapse mechanism in details.

Motion of gel-solution boundary

Let us consider the collapse of infinite plane specimen, placed in low-molecular salt solution. In such system carriers of electric charge of both signs are moved outside and inside the gel. The concentration of the carriers depends on the coordinate x only while the specimen is infinite plane one. Moreover, both gel and solution may be considered as quasi-neutral objects because the dimension of the specimen much more exceed the Debye's length. Consequently magnitude of direct current inside and outside the hydrogel is determined by concentrations of moveable ions and electric field only.

$$j_{int}^{\pm} = b^{\pm} n_{int}^{\pm} E_{int} \qquad (2)$$

$$j_{ext}^{\pm} = b^{\pm} n_{ext}^{\pm} E_{ext} \qquad (3)$$

where $j_{ext}^{\pm}$, $(j_{int}^{\pm})$ and $n_{ext}^{\pm}$, $(n_{int}^{\pm})$ is the magnitude of positive/negative ions flow and their concentrations outside (inside) the hydrogel, E_{ext}, E_{int} is magnitude of electric field outside and inside hydrogel, $b^{\pm}$ are coefficients of mobility of positive and negative charged carriers.

Now we show, that the gel solution boundary can not stay in the rest under such conditions. Indeed, in this case both positive and negative ions flows inside and outside the specimen should be equal (any processes of dissociation or association do not take place at gel-solution boundary)

$$j_{int}^{+} = b^{+} n_{int}^{+} E_{int} = j_{ext}^{+} = b^{+} n_{ext}^{+} E_{ext} \qquad (4)$$

$$j_{int}^{-} = b^{-} n_{int}^{-} E_{int} = j_{ext}^{-} = b^{-} n_{ext}^{-} E_{ext} \qquad (5)$$

Concentrations of positive and negative ions are not independent due to quasi-neutrality requirement: $n_{int}^{+} = N_0 + n_{int}^{-}$ (we suppose that the network is uniformly charged) and $n_{int}^{+} = n_{ext}^{-}$. Using these relations one can write instead of (4) and (5)

$$(n_{int}^{-} - N_0) E_{int} = n_{ext}^{-} E_{ext} \qquad (6)$$

$$n_{int}^{-} E_{int} = n_{ext}^{-} E_{ext} \qquad (7)$$

Dividing equation (6) by equation (7) we get:

$$(n_{int}^{-} - N_0)/n_{int}^{-} = 1 \qquad (8)$$

Consequently relations (4-5) may be valid when network charge is equal to zero. Thus equation (8) means that boundary of charged network have to be moved[1].

Let us suppose now that the boundary move with constant velocity. The equations of conservation of ions flow magnitude in moving reference system (which has the same velocity in respect to laboratory one) may be written as

$$j_{int}^{\pm} = (b^{\pm} n_{int}^{\pm} \mp v) E_{int} = j_{ext}^{\pm} = (b^{\pm} n_{ext}^{\pm} \mp v) E_{ext} \qquad (9)$$

Using requirement of quasi-neutrality one can

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[1] The boundary may move when the specimen is moving as whole too. The description of superfast electrophoresis based on this approach was obtained in Ref. [8].

rewrite equations (9) as

$$(b^+[n_{int}^- + N_0] - \nu)E_{int} = (b^+ n_{ext}^- - \nu)E_{ext} \quad (10)$$

$$(b^- n_{int}^- + \nu)E_{int} = (b^- n_{ext}^- + \nu)E_{ext} \quad (11)$$

The concentration of moveable ions n_{ext}^- is equal to the concentration of surrounding 1:1 electrolyte solution. Knowing this value, one can easy calculate

external electric field magnitude (2). Solving equations (10) and (11) we get expressions for velocity of gel-solution boundary

$$\nu = \frac{b^+ b^- E_{int} N_0}{(b^+ + b^-)(n_{int}^- - n_{int}^-) + b^- N_0} \quad (12)$$

and internal electric field magnitude

$$E_{int} = \frac{E_{ext} n_{ext}^- (b^+ + b^-)[(n_{int}^- - n_{ext}^-)(b^+ + b^-) + N_0 b^-]}{N_0(b^+ + b^-)[b^- n_{int}^- + b^+(n_{int}^- - n_{ext}^-)] + n_{int}^-(n_{int}^- - n_{ext}^-)(b^+ + b^-)^2} \quad (13)$$

Further calculations may be easy carried out in practically important case when concentration of network charges much more exceed concentration of moveable ions

$$N_0 >> n_{int}^- \quad (14)$$

Besides, the effect of concentration redistribution is pronounced under such conditions [9]:

$$n_{ext}^- >> n_{int}^- \quad (15)$$

(gel mainly sorb pure water when concentration of salt is low and moveable ions mainly are concentrated in surrounding solution [9]). Using conditions (14) and (15) equations (12) and (13) may be significantly simplified

$$E_{int} = -E_{ext} \frac{N_0 b^- - n_{ext}^-(b^+ + b^-)}{N_0 b^+} \quad (16)$$

Sign "−" in formula (16) shows that polarization effect in collapsing gel turns to appearance of inverse electric field. The most simple result obtained for the velocity of gel-solution boundary under considering conditions may be presented in next form:

$$\nu \approx - b^+ E_{ext} \quad (17)$$

Resulting expression (17) shows that velocity of gel-solution boundary is determined by the velocity of motion of counterions. This result is quite clear in physical sense. Indeed, the mechanism of gel collapse is of different nature. Nevertheless countrions should be moved from initial position under the influence of some electric field which have to be inverse. Expression (17) shows that the motion of counterions is the limiting factor in hydrogel collapse.

Analog of Faraday's law

One can use connection (1) between velocity of

gel-solution boundary and mass losses for the cylindrical specimen. Using expression (17), we get

$$\frac{dm}{dt} \approx \rho S b^+ E_{ext} \quad (18)$$

where q is elementary charge, S – cross section of the specimen. Density of ionic flow is connected with the total electric current as

$$J = qS(j^+ + j^-) \quad (19)$$

Electric current inside hydrogel is determined mainly by positive charged carriers.

$$J = qSN_0 b^+ E_{int} \quad (20)$$

Consequently, instead of (18) one can approximately write (we supposed, that concentration of network charges much more exceed concentration of moveable ions in surrounding solution)

$$\frac{dm}{dt} \approx \rho \frac{J}{qN_0} \quad (21)$$

ρ is the mass of unit of hydrogel volume. The mass of dry polymer in this volume is MN_0/N_A, where N_A is Avogadro number and M is molecular mass of monomer unit. Consequently degree of swelling of hydrogel may be expressed as $Q = \frac{\rho N_A}{MN_0}$. Thus, expression (21) may be rewritten as

$$\frac{dm}{dt} \approx -QM \frac{J}{F} = const \quad (22)$$

This is exactly expression for the Faraday's law analog, empirically obtained in Ref [7].

Result (22) describes correctly the first stage of hydrogel collapse only. On this stage part (I) of the specimen does not change the geometric share. On

the next stage one should take into account the dependence of average concentration of network charges on the time. In other words the resulting form of the differential equation, which describes polyelectrolyte gel collapse may be written as

$$\frac{dm}{dt} = -Q(t)M\frac{J}{F} \qquad (23)$$

where $Q(t)$ is hydrogel degree of swelling just near gel-solution boundary. In approximation of first order equation (23) it leads to the exponential rule of hydrogel collapse.

Comparison of theoretical and experimental results

Experimental data obtained in Ref. [7] are presented in Fig.2. Approximation curves are presented at the same figure by dash lines. Phase portraits of curves 3,4,5 (Fig.2) are presented at Fig.3 (a,b,c).

Derivative of the considered function $\frac{dm}{dt}$ is postponed on ordinate axis, and values of this function m are postponed on an abscissa axis. Derivatives $\frac{dm}{dt}$ at different moments were calculated numerically:

$$\frac{dm}{dt}(t_i) \approx \frac{1}{10\Delta t}\left[2m(t_{i+2}) + m(t_{i+1}) - \right.$$

$$\left. - m(t_{i-1}) - 2m(t_{i-2})\right], t_i = i\Delta t \qquad (24)$$

Derivatives at $t = 0$ were calculated numerically using least square method applied to first few experimental points. It is easy to see that derivative $\frac{dm}{dt}$ is approximately constant in the beginning of collapse. In other words the first stage of hydrogel collapse is correctly described by Faraday's law analog in linear form. Oppositely, on the second stage the hydrogel collapse is described by exponential law.

The dependence of derivative $\frac{dm}{dt}$ on m represents the straight line. Exponential dependence of gel mass on time takes place when degree of swelling is directly proportional to hydrogel mass (elastic deformation leads to increasing of functional groups concentration on the gel-solution boundary):
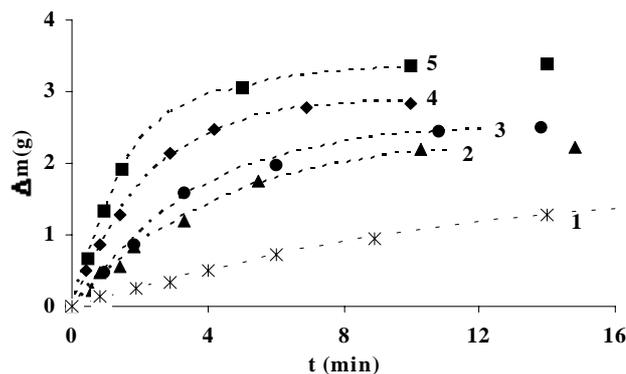

Fig. 2. Kinetic dependences of sample weight changing under direct electric current (1) 1.4 mA, (2,3) 4.2 mA, (4,5) 4.3 mA. Approximation curves are given by dashed lines.
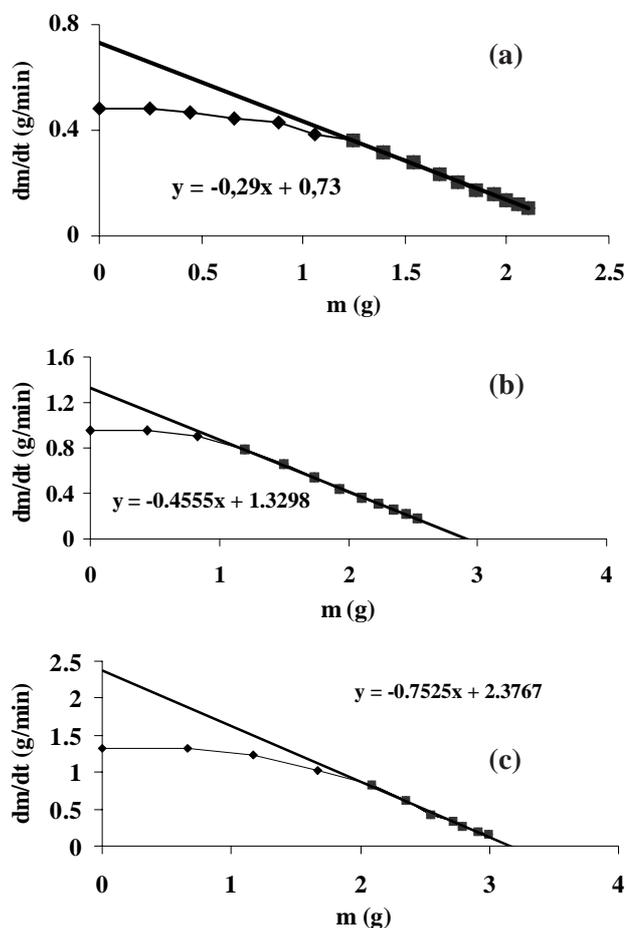

Fig. 3. Phase portraits of curves 3, 4, 5 (Fig. 2). Equations of linear approximation are given directly in the figures.

$$Q(t) = \frac{m(t)}{m_{dry}} \qquad (25)$$

Substituting (25) in (23) one can get differential equation of first order [10] which describes the second stage of gel collapse.

The comparison of production $Q_0 M \dfrac{J}{F}$ and experimentally obtained values $\left. \dfrac{dm}{dt} \right|_{e=0}$ is presented at Fig. 4. It is easy to see that direct proportionality between these parameters takes place

$$\frac{dm}{dt} = -\gamma Q_0 M \frac{J}{F} \qquad (25)$$

Thus analog of Faraday's law is really valid when the coefficient γ is taken into account. Experimental data presented in Fig 4 show that $\gamma = 2.0 \pm 0.4$. Obtained result shows that one electron passing through hydrogel leads to collapse of approximately 2 functional groups. One can suppose that under considered conditions the effective network charge is really less than the charge, which appears when all functional groups are dissociated.
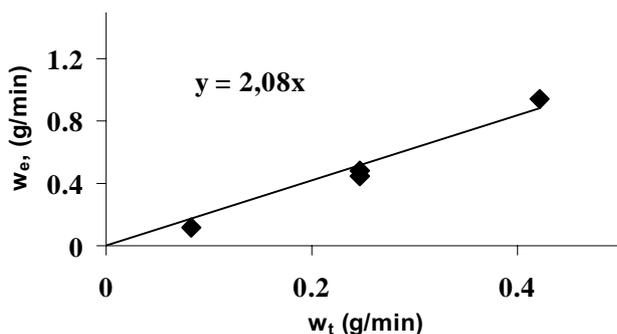

Fig. 4. Comparison of theoretical and experimental data: dependence of derivative $w_e = \left. \dfrac{dm}{dt} \right|_{t-0}$, calculated on the basis of experimental data on theoretically calculated parameter $w_t = QM \dfrac{J}{F}$.

Conclusions

Collapse of polyelectrolyte hydrogels may be considered as two-stage process. Some part of the specimen does not change the form on the fist stage. This part is moving as whole. Theoretical description of this stage may be reduced to analysis of motion of gel-solution boundary, which take place with constant velocity. Theoretical analysis shows that this velocity is determined by mobility of counterions when polymer network is strongly charged. In this case collapse of polyelectrolyte hydrogel is described completely by the linear analog of Faraday's law.

References

1. Tanaka T., Nishio I., Sun S.T. & Ueno-Nishio S. Science 218: 467 (1982)
2. Osada Y. Gong J.-P. Prog. Polym. Sci. 18: 187 (1993)
3. T.Budtova, I.Suleimenov J. Appl. Polym. Sci., 57: 1653 (1995).
4. Mitsumata T., Ikeda K., Gong J.-P., Osada Y. Appl. Phys. Lett. 73: 2366 (1998)
5. Suleimenov I., Pereladov Yu. Reports of MA of AF RK (in Russian) N1: 24 (2002)
6. Doi M., Matsumoto M., Hirose Y. Macromolecules, 25: 5504 (1992)
7. Budtova T.V., Suleimenov I.E., Frencel S.Ya. Polymer Gels and Networks, 3: 387 (1995).
8. Suleimenov I., Bekturov E. Reports of NAS of RK (in Russian) N6: 24 (2001)
9. Budtova T.V., Bel'nikevich N.G., Suleimenov I.E., Frencel S.Ya. Polymer, 34: 5154 (1993)
10. Bekturov E.A., Suleimenov I.E. Polymeric hydrogels (in Russian). Gylym, Almaty (1998). 240 p.