

Physical Principles of Using Polyelectrolyte Hydrogels for Purifying and Enrichment Technologies

T. BUDTOVA* and I. SULEIMENOV

Institute of Macromolecular Compounds, Russian Academy of Sciences, Bolshoi prosp. 31, 199004 St.-Petersburg, Russia

SYNOPSIS

The main physical regularities which allow one to use a strongly charged hydrogel in purifying and/or enrichment technologies are analyzed. The proposed cyclic method is based on the two known phenomena—the salt concentration redistribution in the presence of the polyelectrolyte hydrogel and the reversible gel contraction under electric current. It is shown that in order to obtain high degrees of purification and/or concentration the salt concentration must be lower than that of the polymer. Under these conditions, there is no dependence on the nature of the salt and the cycle may be repeated several times without regeneration of the gel. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polyelectrolyte hydrogels are polymer networks based on crosslinked polyelectrolytes. They possess many interesting physicochemical properties, being able to sorb large amounts of water and to change their volume and properties according to the changes of the surrounding medium. Different possibilities of their applications are now under consideration and some of them are already used in practice. For example, hydrogels may be used as thickening additives and superabsorbents,^{1,2} drugs for therapeutic purposes³ and other biomedical applications,⁴ and different chemomechanical converters.⁵ However, the possibilities of polyelectrolyte hydrogels being used for purifying and processing low concentrated salt solutions have not yet been studied.

In the known methods of purifying technologies, the power and/or resources greatly increase while the degree of purification is increased (this concerns, e.g., the methods of electrodialysis). The traditionally used methods of precipitation lead, on the one hand, to increase of the chemicals. On the other hand, to purify the low concentrated salt solution, one must use large vessels because of the low rate of precipitation in this case. The known ion-ex-

changing methods are also not sufficient enough, because the rate of obtaining of clear water sharply decreases for the stricter requirements for the degree of purification. Besides, there may be some difficulties with the regeneration of the working materials.

In this article, the possibility of using strongly charged hydrogels for purifying low concentrated salt solutions is justified. We propose to use them as three-dimensional membranes in the regime which is somewhat opposite to ion sorption. The method is based on two known phenomena—the salt redistribution in the presence of the polyelectrolyte hydrogel⁶ and the reversible gel contraction under the influence of electric current.^{5,7,8} The combination of these effects allows one to develop a two-staged cyclic regime. In the first stage, the hydrogel swells in the salt solution, sorbing almost clear water. In the second stage, the water is released from the gel under constant electric current.

The aim of this article was to describe the main physical regularities which allow one to use the strongly charged hydrogel in such a cyclic regime. An example of this process is calculated.

RESULTS AND DISCUSSION

Salt Redistribution in the Presence of the Strongly Charged Hydrogel: Theory

Let us examine the process which occurs in the first stage of the cycle. The strongly charged hydrogel is

* To whom correspondence should be addressed.

placed in the solution of a 1 : 1 electrolyte (as an example, we consider the hydrogel based on cross-linked sodium polyacrylate). The ionogenic groups of the gel, being crosslinked, are fixed in space. Under these conditions, the phenomenon of the salt concentration redistribution in the presence of the hydrogel takes place.⁶ The mechanism of this effect is in many instances analogous to the Donnan one, when different concentrations of mobile ions are settled at different sides of a semipermeable membrane. The boundary hydrogel solution may be considered as the membrane which is not permeable for COO⁻ ions. Thus, it is possible to write the equation for the chemical potentials of the mobile ions of the system for the both sides of the boundary hydrogel solution when equilibrium is attained (the Donnan correlation⁹):

$$n'_1 n'_2 = n''_1 n''_2 \quad (1)$$

where n'_1 and n'_2 are the concentrations of the positive ions inside (area I) and outside (area II) the gel, respectively, calculated in g equiv/L; n'_2 and n''_2 are the concentrations of the negative ions in the same areas, respectively. To determine the mobile ions' concentrations, it is necessary to add the conditions of quasi-neutrality in- and outside the hydrogel:

$$\begin{aligned} n''_2 &= n'_1 \\ n'_2 + N_0 &= n'_1 \end{aligned} \quad (2)$$

where N_0 is the concentration of COO⁻ groups inside the gel. To close the set of eqs. (1) and (2), the correlation for the mass balance for the low molecular weight component must be written:

$$V_1 n'_2 + V_2 n''_2 = C_0 V_0 \quad (3)$$

where V_1 and V_2 are the volumes taken by the hydrogel and the solution, respectively; C_0 is the initial concentration of the salt solution; and $V_0 = V_1 + V_2$ is the volume of the whole system.

The solution of the set (1)–(3) gives the formula for calculating the salt concentration outside the hydrogel C_{out} in the equilibrium state:

$$C_{out}/C_p = \frac{(1-w)(2C_0/C_p + 1) - \sqrt{(1-w)^2 + 4w^2(C_0/C_p + 1)C_0/C_p}}{2(1-2w)} \quad (4)$$

$C_p = N_0 V_1/V_0$ is the concentration of the ionogenic groups in the system; $w = V_1/V_0$ is the part of the whole system occupied by the gel.

In Figure 1, the dependencies of C_{out}/C_p vs. C_0/C_p are given for the different values of parameter w (for convenient comparison, all the concentrations are calculated for the total volume of the system hydrogel + solution). In these coordinates, the bisector $C_{out} = C_0$ (dashed line) indicates the hypothetical homogeneous salt distribution in the system. It is clear that all the curves are above the bisector. In other words, the concentration of the low molecular weight component outside the hydrogel is higher than inside it. Thus, it is possible to say that when $C_0 \ll C_p$ the hydrogel sorbs almost clear water.

In Ref. 6, it was shown that there is good agreement between the mentioned theoretical results and the experimental studies (we investigated the concentration redistribution of the salts Na₂S₂O₃ and K₃[Fe(CN)₆] in the presence of crosslinked sodium polyacrylate). All the experimental data fall on the same curve given in the reduced coordinates C_{out}/C_p vs. C_0/C_p .⁶ This means that in the process of the interaction of the hydrogel with the salt solution the main role played is not the absolute value of the salt concentration, but the relation C_0/C_p (certainly, we are describing a system of finite dimension, where the volume, occupied by the gel, can be compared with the volume of the whole system). Thus, the

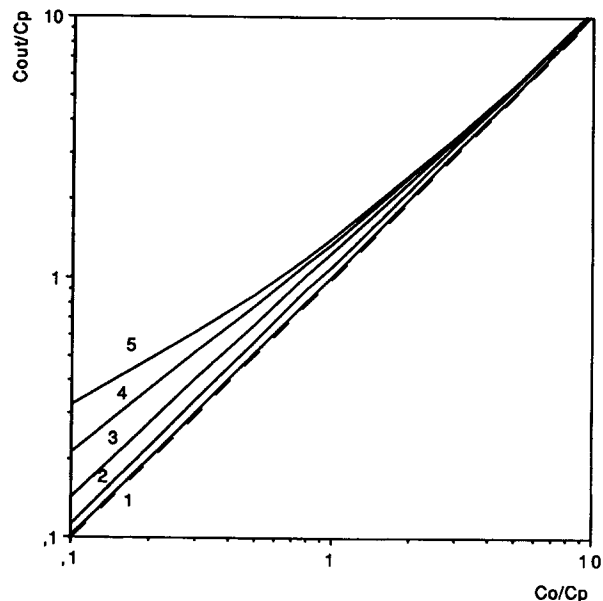


Figure 1 The salt redistribution in the presence of the hydrogel. The curves are calculated by eq. (4) for the values of (1) $w = 0.01$, (2) 0.1, (3) 0.3, (4) 0.6, and (5) 0.95. Curve 1 almost coincides with the bisector (dashed line).

choice of the regime of the purifying cycle may be made by fitting the amount of the polymer with respect to the initial salt concentration.

The effect of the concentration redistribution is more pronounced in the area of the low salt concentrations when $C_0 \ll C_p$. This is quite clearly seen in Figure 2, where the dependence of C_{out}/C_0 on C_0/C_p for different values of parameter w are given. This correlation was obtained by solving the initial set of equations¹⁻³:

$$C_{out}/C_0 = \frac{(1-w)(C_0/C_p + 2) - \sqrt{(1-w)^2(C_0/C_p)^2 + 4w^2(C_0/C_p + 1)}}{2(1-2w)} \quad (5)$$

Using the equation of the mass balance (3) and eq. (5), one can obtain the dependence of the salt concentration inside the gel C_{in}/C_0 on its initial value C_0/C_p :

$$C_{in}/C_0 = \frac{1}{w} [1 - (1-w)C_{out}/C_{in}] \quad (6)$$

These dependencies are given in Figure 3 for the different values of parameter w .

The values C_{out}/C_0 and C_{in}/C_0 characterize the degree of the salt concentration outside the hydrogel and the degree of purification inside it, respectively. They demonstrate the opposite behavior in respect

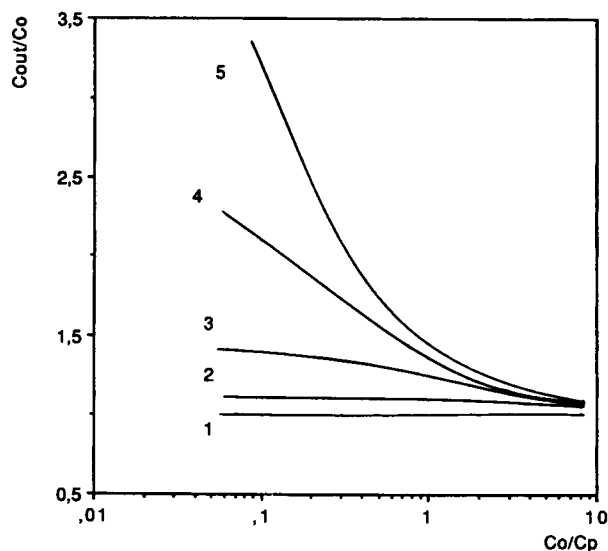


Figure 2 The dependence of the degree of the salt concentration outside the gel C_{out}/C_0 on the initial salt concentration C_0/C_p , calculated for the values of (1) $w = 0.01$, (2) 0.1, (3) 0.3, (4) 0.6, and (5) 0.95.

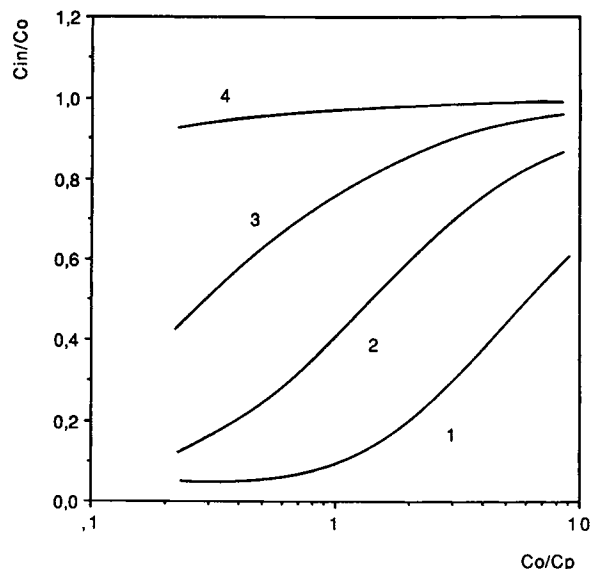


Figure 3 The dependence of the degree of purification of the solution inside the hydrogel C_{in}/C_0 on the initial salt concentration C_0/C_p , calculated for the values of (1) $w = 0.1$, (2) 0.3, (3) 0.6, and (4) 0.95.

to the initial salt concentration: The ratio C_{out}/C_0 decreases and C_{in}/C_0 increases with increase of C_0/C_p (see Figs. 2 and 3). This means that for the region of high salt concentrations ($C_0 \gg C_p$) the effectivity of the process of concentration as well as the process of purification diminish.

The other peculiarity of the process of the salt concentration outside the gel is its increase with the increase of parameter w . This is quite natural (taking into consideration that the strongly charged gel acts as a membrane): When the hydrogel takes up most of the volume of the system, a small change of the salt concentration inside the gel leads to big salt concentration changes outside. On the contrary, the effectivity of the purification process inside the hydrogel increases with decrease of the volume taken up by the hydrogel. The reasons here are the same: The limit of the effectivity of purification corresponds to the traditional thermodynamic problem describing the hydrogel behavior in an infinite solvent:

$$\lim_{w \rightarrow 0} C_{in} = \sqrt{(C_0)^2 + (N_0/2)^2} - N_0/2$$

If $C_0 \ll N_0$, the salt concentration inside the gel will be as follows:

$$\lim_{w \rightarrow 0} C_{in} \approx C_0^2/N_0$$

It is a well-known fact that there is a strong dependence of the hydrogel degree of swelling (and, thus, the amount of the volume occupied by the gel) on the salt concentration.^{5,6,10,11} When the salt concentration is high enough ($C_0 \gg C_p$), the hydrogel collapses. However, when the initial salt concentration is low— $C_0 < C_p$ —the contraction is rather small.^{6,10} Thus, when $C_0 \ll C_p$ in the first approximation, it is possible to assume that the degree of gel swelling is equal to $(0.8 + 0.1)Q$, where Q is the hydrogel degree of swelling in water. This will significantly simplify the calculation of the parameters of the purifying cycle.

All the above-mentioned concerned the salts of monovalent metals. The ions of these metals do not chemically crosslink the hydrogel substance. Another situation occurs during the hydrogel interaction with polyvalent metal salt solutions. In this case, the concentration redistribution depends essentially on the magnitude of C_0/C_p .¹² If $C_0 > C_p$, the hydrogel plays the role of an ion exchanger and the chemical reaction of crosslinking between the metal ions and the gel takes place. On the contrary, in the region of the low salt concentrations, $C_0 \ll C_p$, the polyvalent metal ions do not penetrate inside the gel.¹² When $C_0 \approx C_p$, the process has a complicated cooperative character. But for our purposes, it is quite important that in the region of the low salt concentrations the regularities of the hydrogel interaction with the polyvalent metal salt solution are the same as with the monovalent metal salt solutions. This means that in the region of $C_0 \ll C_p$ it is possible to use the proposed purifying cycle for the salts of any chemical nature.

Hydrogel Behavior Under Constant Current

The second stage of the cycle is the water release from the hydrogel. There are some external actions which lead to the reversible hydrogel contraction and thus to water release. For example, the hydrogel may collapse because of the presence of a precipitator,¹³ under mechanical loading,¹⁴ or under the influence of constant electric current.^{5,7,8} It is obvious that while using the first method the problem of the water separation from another solvent arises once more. The second method (e.g., centrifugation) is connected with using complicated equipment with high-energy input and long times of the process. On the contrary, the application of the potential difference on the hydrogel leads to a quick enough reversible water release (10–20 min) under not very high values of constant electric current (less than 100 mA). As was shown in Ref. 8, it is possible to

control the rate of the hydrogel contraction and thus to run the time parameters of the whole cycle. This follows from the fact that for the low degrees of the gel contraction the law which is analogous to the Faraday one is fulfilled.⁸ It means that the hydrogel mass change Δm is directly proportional to the value of the electric charge passed through the sample:

$$\frac{\Delta m}{QM} \approx \frac{3}{2} F^{-1} J \Delta t \quad (7)$$

where Q is the degree of the hydrogel swelling in the equilibrium; M , the mol mass of the monomer; F , the Faraday constant; J , the value of the current; and Δt , the time of contraction.

An Example of the Cycle

To give an idea of the work of the purifying cycle, let us consider the example of the hydrogel swelling in water and its subsequent contraction under constant electric current. (We assume that for the low concentrated salt solutions all the main regularities are the same as in pure water.) The experimental electric scheme is given in Figure 4. The dry hydrogel[†] (mass 0.02 g) was placed in water in the cell with two electrodes. The dependence of swelling in time is given in Figure 5 (curve 1). Then, the current (12.5 mA) was switched on. The contraction in time

[†] We used the gel which was kindly provided by the Production Association "Orgsteklo," Dzerzhinsk, Russia. The sample was the powder based on sodium polyacrylate, crosslinked by *N,N'*-methylenebisacrylamide. The dimensions of the particles were near 1 mm.

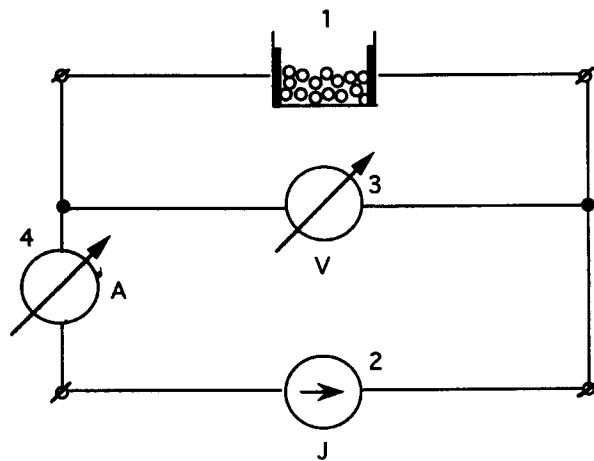


Figure 4 Experimental electric scheme: (1) the cell; (2) constant current source B5-49 (made in Russia) (3) voltmeter; (4) ammeter.

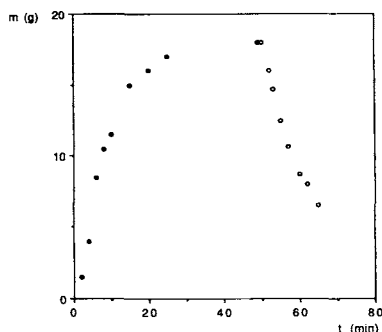


Figure 5 The kinetics of the hydrogel (mass of the dry particles 0.02 g, diameter 1 mm) swelling in water (curve 1) and contraction under the constant current (12.5 mA) (curve 2).

is given in Figure 5, curve 2. It is necessary to note that the electrodes must be made of the material which excludes the ion emission under the current. In the other case, the gel may collapse because of the chemical reaction between its substance and the metal ions and the whole process will not be reversible.

The obtained curves may be used for constructing the approximate diagram of the cycle swelling-contraction (Fig. 6). Part AB corresponds to the hydrogel swelling (see Fig. 5, curve 1), and Part BC, to its contraction (see Fig. 5, curve 2). The cycle may be repeated several times. The parts of the curves were selected according to the following reasons: On the one hand, it is obvious that the most preferable regions are the ones with the highest rates of swelling and contraction. On the other hand, there must be a compromise between the mass change and the duration of the whole cycle. In fact, the increase of the amount of the sorbed and, as a consequence, the released water leads to increase of the duration of the whole cycle because of the flat parts on the swelling and contraction curves (see Fig. 5). Thus, for the effective work of the cycle, it is better not to swell the hydrogel up to the equilibrium state. In the same way, one must not contract the gel under the current more than in 1.5–2 times, taking into consideration that this is exactly the region where the analog of the Faraday law is valid.

The productivity of the cycle swelling-contraction may be increased by different methods: First of all, it is possible to use some other samples with the improved rate of swelling. Then, according to the "Faraday law," the rate of contraction may be increased due to the increase of the value of the current.

Concluding the article, we present Table I, demonstrating the work of the purifying cycle. Calculations

were performed for the volume of the system hydrogel + solution equal to 1 L. As an example, the solution of KCl was chosen. All the concentrations were calculated for the whole volume of the system. The initial concentrations were chosen from the condition $C_0/C_p < 0.5$. As it is not necessary to swell the gel up to the equilibrium state, we put its final degree of swelling at 700 g/g (we assumed that the degree of swelling in water in the equilibrium of a hypothetical hydrogel is 1000 g/g). The values of the salt concentrations in- and outside the gel (C_{in}/C_p and C_{out}/C_p) as well the degree of purification and the degree of concentration (C_{in}/C_0 and C_{out}/C_0) were calculated according to eqs. (4)–(6). The amount of the purified water, Δm , was chosen according to the possibility of using the "Faraday law" (the contraction must not be too high). The time Δt during which the hydrogel contracts on the value Δm under the current 0.1 A was calculated by eq. (7). The duration of the whole cycle is not given because it depends on the kinetics of the hydrogel swelling. The cycle may be repeated several times without regeneration of the gel.

From the given examples in Table I, it is clear that one must choose the initial parameters of the cycle (in particular, the initial hydrogel concentration) depending on the aim of the work. If it is necessary to purify the solution from the low molecular weight salt, it is better to use low values of w : $w \approx 0.3$. On the contrary, for concentrating the solution, the high values of w ($w \approx 0.7$ – 0.8) are preferable.

CONCLUSIONS

The possibility of using the strongly charged hydrogels for purification and/or concentration of the di-

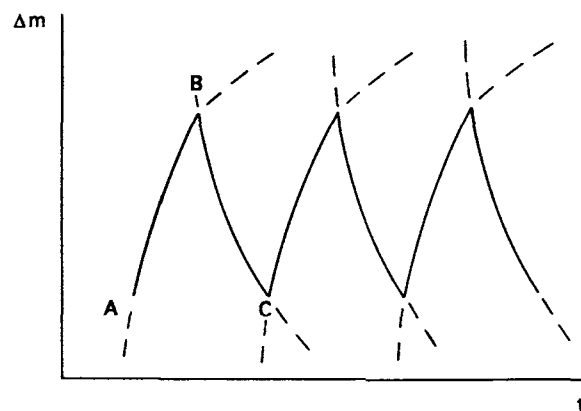


Figure 6 Scheme of the cycle: curve AB, swelling; curve BC, contraction.

Table I The Main Parameters of the Cycle, Calculated for the System Hydrogel (Crosslinked Sodium Polyacrylate, Monomer Mol Mass 94) + KCl Solution (Mol Mass 74)

C_p	C_0	W	C_{out}	C_{in}	C_{out}/C_0	C_{in}/C_0	Δm (g)	Δt (min)
1.14	0.09	0.8	0.25	0.05	2.8	0.6	200	22
1.14	0.14	0.8	0.34	0.09	2.4	0.6	200	22
1.14	0.28	0.8	0.53	0.22	1.9	0.8	200	22
0.86	0.07	0.6	0.14	0.018	2.1	0.3	150	17
0.86	0.11	0.6	0.20	0.042	1.8	0.4	150	17
0.86	0.21	0.6	0.35	0.120	1.7	0.6	150	17
0.43	0.03	0.3	0.05	0.001	1.4	0.02	100	11
0.43	0.05	0.3	0.07	0.006	1.4	0.1	100	11
0.43	0.11	0.3	0.14	0.050	1.3	0.5	100	11

Concentrations are calculated in g/L for the whole volume of the system (1 L). Δt is calculated for the current 0.1 A.

luted water-salt solutions is demonstrated. The proposed two-staged cyclic regime is based on the phenomena of low molecular weight salt redistribution in the presence of the hydrogel and its reversible contraction under constant electric current. It is essential that in these conditions the gel contraction is reversible for the salts of any chemical nature; thus, the polymer may be used in the cycle several times.

REFERENCES

1. I. Ahmed and A. Mordi-Araghi, *TRIP*, **2**, 92 (1994).
2. F. Askari, S. Nafisi, H. Omidian, and S. A. Hashemi, *J. Appl. Polym. Sci.*, **50**, 1851 (1993).
3. W. T. K. Stevenson and M. V. Sefton, *TRIP*, **2**, 98 (1994).
4. A. S. Hoffman, *Polym. Sci. Technol.*, **8**, 33 (1975).
5. Y. Osada, *Adv. Polym. Sci. Polym. Phys. Ed.*, **82**, 1 (1987).
6. T. V. Budtova, N. G. Belnikevich, I. E. Suleimenov, and S. Ya. Frenkel, *Polymer*, **34**, 5154 (1993).
7. T. Tanaka, I. Nishio, S. T. Sun, and S. Ueno-Nishio, *Science*, **218**, 467 (1982).
8. T. Budtova, I. Suleimenov, and S. Frenkel, *Polym. Gels Networks*, to appear.
9. S.-T. Hwang and K. Kammermeyer, *Membranes in Separations*, Wiley, New York, 1975.
10. J. Ricka and T. Tanaka, *Macromolecules*, **17**, 2916 (1984).
11. V. V. Vasilevskaya and A. R. Khokhlov, *Vysokomol. Soed.*, **A28**, 316 (1991).
12. T. V. Budtova and S. Ya. Frenkel, *Vysokomol. Soed.*, **B33**, 856 (1991).
13. I. Ohmine and T. Tanaka, *J. Chem. Phys.*, **77**, 5725 (1982).
14. S. G. Starodubtzev, N. R. Pavlova, V. V. Vasilevskaya, and A. R. Khokhlov, *Vysokomolec. Soed.*, **B27**, 485 (1985).

Received November 28, 1994

Accepted January 19, 1995