# Comprehensive characterization of superabsorbent polymer hydrogels

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## Summary

An approach to the quantitative description of superabsorbent polymer hydrogels is exemplified by partially hydrolyzed polyacrylamide gels obtained by three-dimensional radical copolymerization or radiation cross-linking of the polymer. The modified swelling theory has been used to develop a system of experimental and computational methods for the evaluation of the supergels network parameters. The possibility of applying these methods to the analysis of the network formation process is also discussed.

## Introduction

Hydrophilic polymer networks capable to retain huge volumes of water by swelling, the so-called superabsorbent hydrogels (SAH), are of the great interest in view of their practical uses. Among the recent of them the application of SAH in agriculture for improvement of water-holding capacity of soils is the most attractive [1, 2]. There are many other promising applications of SAH.

Optimization of SAH characteristics for different aims claimes for a quantitative assessment of the network parameters which are the key variables in the analysis of both the synthesis of SAH and their efficiency. To approach this problem, it would be useful to consider SAH, which are usually polyelectrolyte gels, on the basis of the existing theories [3-6], in particular, by using the formalism of the Donnan theory [7, 8].

In principle, the following levels are possible in the characterization of SAH. The first one is an experimental determination of hydrogel swelling degree as a function of the external conditions. The second is the evaluation of the network parameters with the help of swelling theory and, finally, the prediction of the swelling degree and practical efficiency of SAH in a broad range of conditions. All these possibilities are discussed in the present study where measurements of the elastic modulus and potentiometric titrations are also used for the characterization of SAH.

## Experimental

The SAH were obtained by copolymerization of acrylamide (AA) and acrylic acid (AAc) in the presence of N,N'-methylene-bis-acrylamide [9] or by $\gamma$-radiation cross-linking of high-molecular AA-AAc copolymers in aqueous solutions [10]. The copolymerization was initiated with ammonium persulfate - tetramethylethylenediamine (2 : 1) in 10% aqueous solution of the monomers at 45°C. The cross-linking agent content was varied between 0.005 and 0.13 mol.% with respect to the sum of the monomers. The initiator concentration

was of 0.88 mM. The radiation cross-linking was performed in 3-10% aqueous solutions under $^{60}$Co $\gamma$-radiation at a dose rate of ca. 50 rad/s and doses of 0.5-10 Mrad. The gels were examined immediately or after preliminary drying. To obtain samples with a well defined geometry the synthesis was performed in glass tubes 2-5 mm in diameter.

The degree of free swelling was determined by placing the gel sample of regular shape in a large volume of liquid and measuring its dimensions with a microscope. The swelling degree of shapeless samples (powder, granules) was measured by a volumetric method with a specially designed device which automatically determines the volume of the solution outside the gel [11].

The gel swelling under load was studied with an apparatus described elsewhere [8]. In a first method the equilibrium sample volume was determined at a constant load. In the other case the sample volume was fixed and the relaxation of the swelling pressure was monitored as described [12]. The range of the pressures was within 1-20 kPa and the device sensitivity was about 100 Pa.

The elastic modulus of SAH swollen at equilibrium was obtained from penetration measurements [13]. The equilibrium swelling degree of the samples in these experiments was varied by changing the NaCl concentration in the outer solution.

The potentiometric titration were performed under inert atmosphere at room temperature. We used an OP-211 pH-meter fitted with an OP-8071 electrode (Radelkis, Hungary).

In all the experiments distilled water (conductivity 3 $\mu$Sm/cm) was used as the solvent. The gel swelling behavior was studied in solutions of neutral salts (NaCl, CaCl$_2$) and acid (HCl). When possible, ion concentrations in the solution in equilibrium with the gel was determined by direct potentiometry. In the other cases the ion concentrations were regarded as coincident with the given ones. To exclude the effect of the SAH' ion-exchange properties the swelling experiments were made in a few steps: the outer solutions were replaced by fresh ones until the gel swelling degree ceased to change.

Results and Discussion

The set of quantitative characteristics of SAH includes dependencies of the equilibrium swelling degree on the external mechanical load and the ionic composition of the surrounding solution.

Starting with a relatively simple case when the mechanical forces at the network boundary are equal to zero, then, according to the theory, one has to consider only the concentrations and charges of mobile ions and also the constants of their association with the ionic groups of the network. The effect of the external load during the experimental studies of the SAH is usually excluded in the conditions of the so-called free swelling. Typical dependencies of the swelling degree of SAH on the concentration of some cations obtained in such conditions are shown in Fig. 1. The swelling is strongly suppressed by the ions present in the solution. The higher the charge of the ions, the lower their concentration ensuring the same suppression of swelling. The strongest suppression effect, other conditions being the same, is exhibited by ions capable to associate with the ionic groups of network, in particular by hydrogen ions. As the ionic concentration increases, the degree of swelling tends to the low limit ($W_{net}$) which is likely to correspond to the swelling of the same but uncharged network.
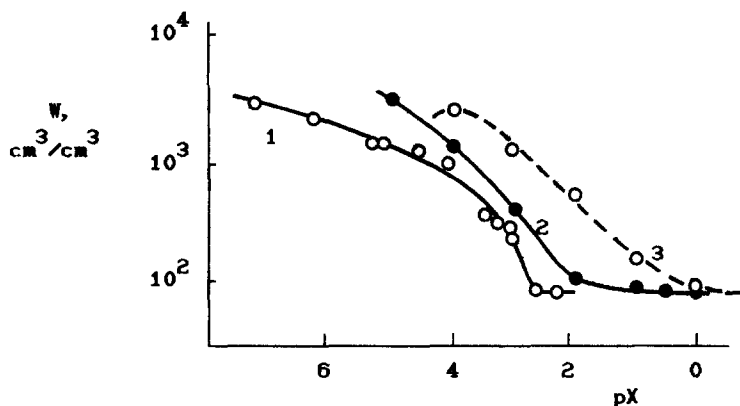
Fig. 1. Dependence of the swelling degree of SAH (sample 2, see Table 1) on the concentration of $H^+$ (1), $Ca^{2+}$ (2) and $Na^+$ (3) in the outer solution. Dashed curve 3 is obtained by calculation . X is the molar concentration of ions.

As a rule, the swelling of charged networks is independent of the size and chemical nature of small ions [7]. Exceptions include $H^+$ and some of the multi-charge cations, e. g., $Cu^{++}$ [14] giving stable associates with the network charges. Therefore the ionic suppression curves similar to those of Fig. 1 are universal to some extent and can be regarded as the key characteristics of SAH. They allow to estimate the swelling degree of SAH in practically any ionic situation, which is important for application purposes.

The dependence of swelling degree on the external forces applied to the network is another significant characteristic of SAH which can be obtained by direct methods. Fig. 2 shows the results of experiments on swelling of SAH in a cylindrical cell. It is evident that there exists a strong dependence of the swelling degree on the small load applied to the gel. These data can be considered in the opposite sense, too, as a measure of the SAH swelling pressure.

The behavior observed agrees well with the theory. The important feature of the behavior is a substantial difference between three- and one-dimentional modes of network swelling at relatively large changes of sample size. That leads to different equilibrium volumes of the gel. During free swelling the network obviously undergoes an isotropic deformation. In swelling experiments at fixed volume the equilibrium swelling pressure also corresponds to the practically isotropic equilibrium deformation of network. Therefore in this case (Fig. 2, curve 3) the W value extrapolated to the zero pressure coincides with the free swelling degree. By contrast, in experiments with a fixed load the gel swells uniaxially. In this case (Fig. 2, solid curve 1) the limiting degree of swelling at a load tending to zero is far below the free swelling degree.

The data in Figs. 1 and 2 in combination with the existing theory of swelling allow to estimate the SAH network parameters. For solving this problem the hydrogel is regarded as a partially charged flexible polymer network with a regular structure, cross-link density $n_c$ or average number of units in the subchain $\bar{x}_c = 1/(n_c.v)$, where v is the molar volume of the monomer unit. In the following f is the cross-link functionality, $\beta$ the
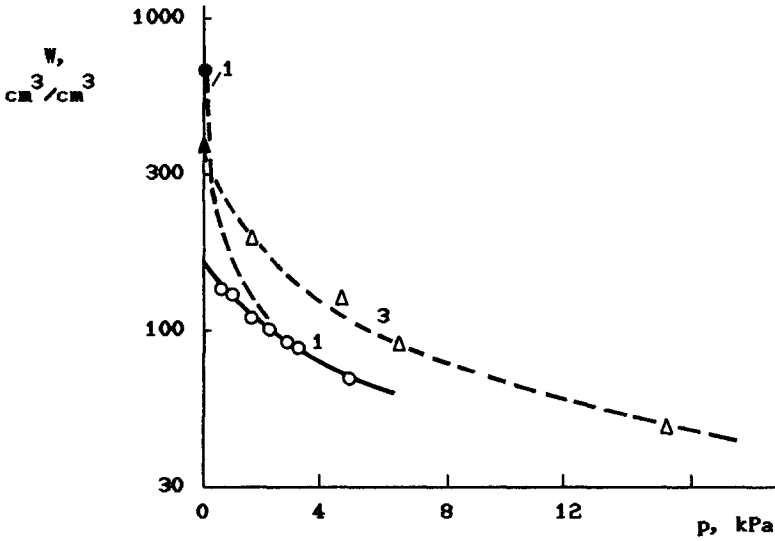
Fig. 2. Influence of pressure on the swelling degree of SAH in 0.01 M NaCl. Points on the y-axis correspond to the free swelling ; solid curve -uniaxial, dashed curves - isotropic swelling as obtained by calculation. Here and in Fig. 3 the curves numbers correspond to the sample numbers in Table 1.
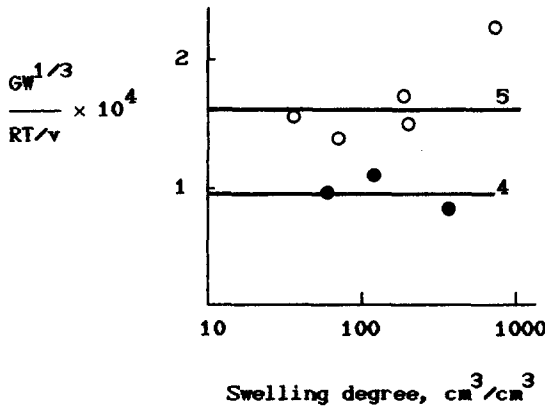


Fig. 3. The reduced shear modulus of SAH swollen at equilibrium as a function of the swelling degree.

fraction of the ionizable (carboxyl) groups , $K_H$ their dissociation constant and $\chi$ the thermodynamic parameter of polymer-solvent interaction. For simplicity we consider the case when the gel-solution system contains only one type of ions capable to associate with the ionized network groups, viz., hydrogen ions.

The swelling pressure of a network is known to consist of network ($\pi_{net}$) and ionic ($\Delta\pi_{ion}$) contributions. In the case of isotropic swelling the former can be expressed as follows [3]:

$$\pi_{net} = (RT/v) \{(1/2 - \chi)\phi^2 - (\phi/\bar{x}_c)[(\phi_0/\phi)^{2/3} - 2/f]\},$$

where $\phi$ is the volume fraction of polymer in the gel; $\phi_0 = \bar{x}_c^{-1/2}$ is the volume fraction of polymer in a reference ideal state [6]. The ionic pressure is due to the difference between the concentrations of freely mobile ions in the gel ($C_i^*$) and in the outer solution ($C_i$):

$$\Delta\pi_{ion} = RT \sum (C_i^* - C_i).$$

The swelling equilibrium is governed, firstly, by the equality of the external (p) and swelling pressure:

$$\pi_{net} + \Delta\pi_{ion} = p, \qquad (1)$$

and, secondly, by the equality of the chemical potentials of the mobile ions on both sides of the gel boundary, which can be expressed through the ion charges $Z_i$ and the distribution coefficient $K_D$ (Donnan ratio):

$$C_i^*/C_i = K_D^{z_i} \qquad (2)$$

and, finally, by the dissociation constant of ionizable groups:

$$K_H = \alpha C_H^*/(1 - \alpha), \qquad (3)$$

where $\alpha$ is the degree of dissociation of these groups, $C_H^*$ is the concentration of the hydrogen ions in the gel. Equations (1)-(3) together with the gel electroneutrality condition

$$\sum Z_i C_i^* - \alpha\beta\phi/v = 0 \qquad (4)$$

fully determine the swelling degree ($W = 1/\phi$) as a function of external conditions ($C_i$, pH, p, T) and network parameters ($n_c$, $\chi$, $\beta$ , $K_H$). These equations can be solved numerically and used for determining the network molecular structure parameters.

It should be noted that the above relationships provide rather fragmentary description of the SAH swelling behavior. The situation can be improved by the introduction of empirical functions $\pi_{net}(\phi)$ [7] or $K_H(\alpha)$ [8], however, the corresponding theories cannot be applied to network parameters characterization. Anyhow, in the case of the above formalism the network parameters can be obtained from the functions $W(C_{Na})$ or $W(p)$.

In our calculations we started with the $W_{net}$ value which, as stated above, corresponds to the non-charged state of the network. This value, with the use of Eq. (1) at $\Delta\pi_{ion} = p = 0$ and $\chi = 0.48$ [15], leads unambiguously to

$n_c$ and $\bar{x}_c$. The $\beta$ value was found as a fitting parameter for the experimental curves $W(C_{Na})$ and $W(p)$ (at $K_H = 7.10^{-8}$ M, RT/v = 135 MPa). The corresponding results for the swelling degree are given in comparison with the experimental data in Figs. 1 and 2. Thus we put forward an approach for calculating the SAH network parameters.

Some of the values estimated for the SAH under study are listed in Table 1. For the SAH prepared by three-dimensional polymerization there exists a quite satisfactory coincidence between the expected and measured network densities, which can be regarded as a verification of the above approach on the model systems.

A still further indication of the validity of the network parameters calculated has been obtained by the use of the traditional shear modulus (G) measurements for the gels swollen at equilibrium (see Table 1). It should be noted that for SAH, in accordance with the classical theory [3] the reduced shear modulus $GW^{1/3}$ is practically independent of the swelling degree (Fig. 3). Therefore in the case of SAH unlike the strongly cross-linked polyacrylamide gels [16] the shear modulus measurements permit a fairly unambiguous determination of the cross-links density.

The $\beta$ values obtained by the various procedures are also in a rather good correlation with each other (Table 1) although the parameters determined from the ionic suppression curves do not fit precisely the real

Table 1. Characteristics of superabsorbent hydrogels

| Number of sample[a] | $W_{max}$,[b] $cm^3/cm^3$ | $W_{net}$,[b] $cm^3/cm^3$ | $10^5 \cdot n_c$,[c] $mol/cm^3$ | $\beta$,[g] % |
|---|---|---|---|---|
| 1 | 22000 | 110 | 1.4; $0.60^{[d]}$ | 20; $20^{[h]}$ |
| 2 | 3300 | 88 | 2.1 | $11^{[h]}$; $4.0^{[i]}$ |
| 3 | 1900 | 62 | 3.6; $3.6^{[d]}$ | $25^{[h]}$; $4.0^{[i]}$ |
| 4 | -- | 60 | 3.7; $5.2^{[e]}$ | 30 |
| 5 | 800 | 37 | 7.9; $8.0^{[e]}$ | 30 |
| 6 | 290 | 26 | 14.0 | 30; $30^{[h]}$ |
| 7 | 10000 | 230 | 0.50; $0.55^{[f]}$ | 5.0 |
| 8 | 6700 | 160 | 0.86; $1.1^{[f]}$ | 5.0 |
| 9 | 3300 | 57 | 4.0; $2.8^{[f]}$ | 5.0 |
| 10 | 1800 | 56 | 4.1; $14.3^{[f]}$ | 15; $11^{[h]}$; $10^{[i]}$ |
| 11 | 1330 | 55 | 4.3; $14.3^{[f]}$ | 5.0; $7.7^{[h]}$; $5.0^{[i]}$ |
| 12 | 530 | 50 | 5.0; $14.3^{[f]}$ | 9.4; $9.8^{[h]}$; $9.2^{[i]}$ |

[a] 1-6 - obtained by radiation cross-linking, 7-12 - by three-dimensional copolymerization; [b] limiting upper and lower values of the swelling degree on the $W(C_{Na})$ curve; [c] from $W_{net}$ at $\chi = 0.48$; [d] from the $W(p)$ curve; [e] from the modulus of elasticity; [f] from the cross-linking agent content; [g] from the AAc/AA ratio; [h] from the $W(C_{Na})$ curve at $K_H = 7.10^{-8}$ M; [i] from titration.

number of ionogenic groups. These discrepancies may be caused by a certain imperfection of the swelling theory used.

The approach proposed opens a way to the evaluation of the results of synthesis. In the case of three-dimensional polymerization a convenient criterion for this analysis is a relationship between the network densities (or $\bar{x}_c$ values) calculated from the cross-linking agent content ($n_c^{th}$) and determined experimentally ($n_c^{exp}$). For moderately swellable polyacrylamide gels the $n_c^{th}/n_c^{exp}$ ratio is great and depends strongly on both the cross-linking agent fraction and the total concentration of the monomers [17]. With lowering the cross-linking agent content the ratio decreases and tends to a constant value. Our data corresponds to the very low concentrations of the cross-linking agent and strongly confirm this tendency. One probable reason for the difference between the expected and observed network structures is likely to consist in an incomplete conversion of the reactive groups of the cross-linking agent.

For the SAH obtained by radiation cross-linking of polyacrylamide in aqueous media the literature contains no reliable guidelines. This method of SAH synthesis for some reasons can be even more attractive as compared with the direct "chemical" synthesis from monomers. The characteristics of the SAH obtained by irradiation turn out to be quite satisfactory. Our results opens a possibility of the more detailed analysis and optimization of the radiation cross-linking process, for instance as it has been proposed [18].

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