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Polymer 46 (2005) 121–127

polymer

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Solvent release from highly swollen gels under compression

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Received 16 April 2004; received in revised form 28 September 2004; accepted 13 October 2004
Available online 11 November 2004

Abstract

The behaviour of a strongly charged polyelectrolyte gel under uniaxial compression was studied experimentally, demonstrating gel deformation and solvent loss at the same time. A theoretical interpretation used was based on a thermodynamic approach developed for weakly charged gels. The proposed approach was considered as a first approximation of the solution of the problem on gel volume loss under compression. It predicts solvent release under compression for both weakly charged and neutral gels, being more pronounced for polyelectrolyte hydrogels. A qualitative agreement between experiments and proposed theoretical model was obtained.

Keywords: Gel; Compression; Solvent release

1. Introduction

Hydrogels are highly swelling chemically cross-linked hydrophilic (polyelectrolyte) polymer networks. They swell/contract several hundred times and absorb/release solvent in response to changes in the surrounding medium (solvent quality, presence of ions or linear polymers) and to the applied external fields (electric field, temperature). Hydrogels are widely used as superabsorbents and they are promising materials for food, cosmetic and pharmacological applications because of their intelligent absorption/release properties.

Even being swollen several hundred times, hydrogels keep their shape. In most of the applications and during processing, gels are under a mechanical stress. What will happen if such a gel is compressed or deformed? Will it just deform and then break at high stresses or solvent will also be released? The release of fluid from a mechanically compressed gel is an important phenomenon that has to be considered for gel applications, for example, when micro-gel is used as a drug carrier. Release is then positive if an active compound is supposed to be ejected from a compressed/sheared micro-gel particle when applied on the skin (for example, in the case of a cream composed of a suspension of micro-gel particles). Release is negative when solvent is ejected during processing, in other words, before application. As for hydrogels used as superabsorbents, the applied pressures are not high enough for the release to be noticeable (as it will be shown in the following).

The mechanical properties of hydrogels have been intensively studied during the past decade, but still there are debates on the theoretical interpretation of different deviations from the classical rubber-elasticity laws, observed experimentally. One of the reasons is that because hydrogels contain charged groups and counter-ions, the chains between the cross-links are highly extended and they are far from a Gaussian coil.

Different ways of measuring gel elastic modulus are described in literature, the most common ones being the uniaxial compression [1–6] and the penetration technique [7]. Hydrogels are usually deformed less than 10–20% [1–7] and experimental results are interpreted either by the classical network-elasticity theory or by using a scaling approach [8], supposing that there is no volume loss.

Two ways of performing compression experiments are

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doi:10.1016/j.polymer.2004.10.046

used: when gel is placed in a bath of solvent in which it was swollen [4,5,7] and when gel is in the air [1,3,6]. In the first case, the solvent molecules inside and outside the gel can easily exchange. It is thus supposed that gel is in the equilibrium state. However, there is no way to see if there is any solvent release from the gel (i.e. to measure gel volume change) as a reaction to compression or deformation. The understanding of the compression experiments performed in the open air [1,3,6] is much more complicated: the influence of the plates' surface roughness should be considered (see the influence of a one nanometer water layer on the measured gel elastic modulus [2]); the boundary conditions for a gel-in-air (not equilibrium) differ as compared with the case of a gel-in-solvent (equilibrium state). The penetration technique [7] does not interfere with the gel sample as much as compression, and thus the interpretation of penetration results is more adequate.

Only few publications consider the gel volume change caused by compression [9]. In Ref. [9] compression is used to perform osmotic deswelling and to measure the swelling pressure and the diffusion coefficient. In some cases, experiments are performed quicker than solvent is released [3,6]. Recently we showed that a swollen hydrogel microparticle based on a cross-linked sodium poly(acrylate-co-acrylic acid) and immersed in a silicon oil releases solvent under shear [10,11]. However, aside of one example shown in Ref. [10] where the volume of released solvent was estimated from experimental data, there are no experimental or theoretical results demonstrating gel volume change caused by a mechanical action. In this paper, we consider a simple case—a uniaxial compression—and we bring the evidence of an immediate volume loss of a polyelectrolyte gel after the application of compression. Both effects (gel volume loss caused by shear or compression) considered together show that solvent release due to a mechanical action is not a negligible phenomenon. It complicates the interpretation of the mechanical experiments but has to be taken into account.

2. Experimental section

2.1. Materials

Two types of polyelectrolyte gels were used:

1. Stockosorb®; 410K ('potassium gel' in the following): it is a poly(potassium acrylate-*co*-acrylamide) with a molar ratio of 0.7/0.3, chemically cross-linked by *N*,*N*′-methylenebisacrylamide, kindly provided by Stockhausen company. The gel was initially in the form of dry grains of size ~10–15 mm^3. The grains were swollen in distilled water up to equilibrium (swelling degree being around 140–150 g/g) and gel disks with a diameter of about 10–12 mm and height of about 1–1.5 mm were cut from them. In order to study the influence of gel swelling degree and to show that volume loss takes place for gels swollen less than at equilibrium, less swollen gels were prepared by combining water evaporation and using a blotting paper to absorb water from the gel disks swollen at equilibrium. In order to homogenise water distribution in the less swollen sample, gels were left to equilibrate for a few days. As a result, compression experiments were performed on hydrogels with several initial swelling degrees of $Q=140$ g/g (equilibrium state), 100, 60 and 20 g/g.
2. A poly(sodium acrylate-*co*-acrylic acid) gel ('sodium gel' in the following) was synthesised by free-radical copolymerisation [12] from partially neutralised acrylic acid (75% of the monomers) cross-linked with *N*,*N*′-methylenbisacrylamide in a proportion of 300 mole to 1, respectively. The monomer concentration in the initial aqueous mixture was 25% (w/w). Nitrogen was bubbled through the monomer mixture to eliminate dissolved oxygen and 0.5% w/w of *N*,*N*′,*N*′-tetramethylethylenediamine (TEMED) was added as a conditioner. The polymerisation reaction was initiated by ammonium persulfate (0.06% w/w). The mixture was put in glass cylindrical tubes (0.7 cm diameter) and heated in an oven at 40 °C in nitrogen atmosphere for 1 h. The gels were then allowed to set at room temperature for another 24 h. Gel cylinders were removed from the moulds and washed in demineralised water during 2 weeks while refreshing water every day. Disks with approximately the same size as potassium gels were cut. The equilibrium swelling degree in water was 200 g/g.

2.2. Methods

The compression experiments were performed with a RMS-800® rheometer, manufactured by Rheometrics, with plate-plate geometry. The plates were coated with a sandpaper to help fixing a wet gel sample on the plate. The excess of water from samples swollen at equilibrium was carefully removed with a blotting paper. As shown in Fig. 1, a gel disk (1) was put on the fixed lower plate (2), the upper plate (3) moved vertically down at a constant speed of 10^{-3} mm/s and the force exerted due to deformation was

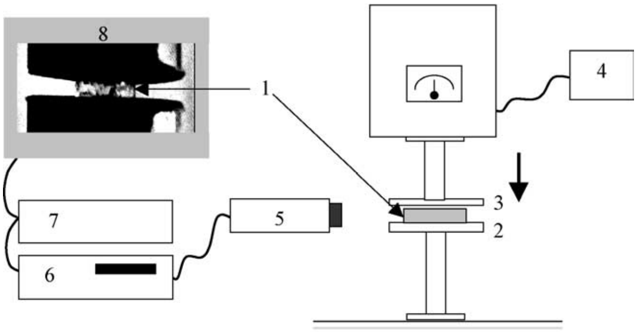

Fig. 1. Compression experimental set-up. See explanations in the text.

measured in time (4). The changes in the gel disk diameter measured at sample half-height during compression were recorded by a CCD camera (5) coupled to a video-recorder (6), frame code generator (7) and monitor (8). The gel height equal to the gap between the plates was automatically recorded by the rheometer. All data discussed here correspond to the gel samples before any breakage, which was easy to detect by a sharp drop of the normal force. No barrel distortions occurred. The recorded sequences of images of compressed gel were analysed image by image with the help of image analysis software Visilog 5.3 from Noesis 2000. The experimental error in gel diameter measurement with CCD camera is ±0.1 mm, in gel height determined by the rheometer ±1 μm.

As far as experiments were performed in the open air, the rate of water evaporation was checked. It was about 1.3×10^{-3} mg/s for a potassium gels swollen at equilibrium and slightly decreasing to $1.2\times10^{-3}-1.0\times10^{-3}$ mg/s for gels at lower swelling degrees. The rate of water evaporation from sodium gels was about 5×10^{-3} mg/s. As it will be shown later, within the compression measurement time (<15 min) the evaporation effect is negligible as compared to the loss of water caused by compression.

3. Results and discussion

3.1. Qualitative observations

During compression experiments, a gel (either potassium or sodium) disk of any swelling degree deforms and a certain amount of water is released. The release of water can be easily noticed at the end of each compression experiment: droplets were left on the lower plate when the gap was opened and the gel disk removed.

Another visual proof of water release during a quick compression experiment is that a cylindrical gel sample had a concave shape (see scheme in Fig. 2a), while due to the friction between the gel and the plates' surface the gel should have a convex shape (see scheme in Fig. 2b). Because of water released near the descending upper plate [9], accumulated on the lower plate due to gravity and kept around the gel by capillary forces, the apparent sample shape became concave.

It should be noted that Fig. 2 is schematic and shows the result of special tests to visualise water release. Systematic experiments where gel deformation and volume loss were measured have been performed on gel disks with diameter being 10 times larger than its height (see Section 2.1). Because in the systematic experiments the speed of the upper descending plate was low, gel adapted a cylindrical shape by sliding with minor 'barrel' distortions. The sample volume was calculated as a cylinder volume with the diameter measured at a half-height of the gel disk, this approximation being acceptable within experimental errors.

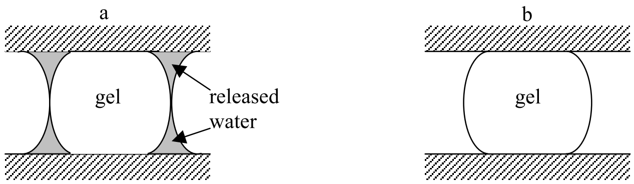

Fig. 2. (a) Schematic presentation of solvent release from a compressed gel (concave shape) and (b) compressed gel without released solvent (convex shape).

An important question is when does water release start. Is there a certain threshold pressure value or is water released immediately as soon as pressure is applied? To answer this, the following test was performed on both sodium and potassium gels. A gel swollen at equilibrium was compressed in steps with increasing deformation. Between each step the gap was kept constant. As soon as water is released, the sample size and thus the disk height should decrease due to the volume loss and a decline of the normal force should be expected.

This is exactly what was observed in experiments. No threshold pressure value needed to trigger water release was found: as soon as the first step of the gel compression was performed and the disk was under load, a decrease in the normal force was observed. It is a direct indication of the volume loss. This is an important phenomenon that is usually not taken into account when mechanical characteristics of hydrogels are determined. At small deformations the loss of volume is low, but as it will be shown in the following, at large deformations it may be more than 30% from the potassium gel initial volume.

In the next sections, gel deformation and volume loss as a function of pressure will be discussed. It should be kept in mind that the studied system—a gel under the continuous compression—is very complex and there are several reasons to consider it to be not at equilibrium. First, as far as water is released during compression, the gel swelling degree changes continuously during the experiment and as far as experiments are performed in the air, the gel is not in the equilibrium state. Second, aside of the potassium gels initially swollen to 140 g/g and sodium gels initially swollen at 200 g/g, all the other samples, that are swollen less, are not in the equilibrium state. And third, the state of a compressed (and thus deformed) gel initially swollen at equilibrium which, for example, had lost 50% of its volume, is not the same as the state of a free gel which is just swollen twice less than at its equilibrium, so such cases cannot be compared. Thus only general trends and a qualitative comparison with a theory developed for compressed gels (see Section 3.4) will be discussed.

3.2. Deformation–pressure dependencies

The deformation–pressure dependencies $D(P)/D_0=f(P)$ (D_0 being the initial disk diameter and $D(P)$ the disk diameter at pressure P) for a potassium gel disk is presented in Fig. 3 for different initial swelling degrees. The inset (a) shows the beginning of the deformation–pressure curves for two potassium gel disks swollen at $Q_0 = 140$ g/g. Similar results were observed for the sodium gel.

The deformation–pressure curves for both potassium and sodium gels show an 's-shape'. The first region with very low D/D_0 values corresponds to the beginning of compression. The deformations are low because as far as the reaction of the gel to compression is solvent release, the normal forces generated are very low. At the beginning, the decrease of the gap size leads mainly to volume loss, but not to gel diameter increase. This is shown in the inset (b) in Fig. 3, where the dependence of the deformation D/D_0 on the relative gap size H/H_0 (H_0 being the initial gap size or the initial gel height and H being the gap size in the course of experiment) for sodium and potassium gels swollen at equilibrium is given. The experimental points D/D_0 vs H/H_0 obviously differ from the dependence calculated for the case of volume conservation, as $D/D_0 = \sqrt{H_0/H}$. This is the indication of the gel volume loss.

With further compression, the deformation–pressure dependencies are linear up to the moment when the diameter becomes extended in about 25%. Less gel was swollen at the beginning, higher forces are generated in order to reach the same deformations as for more swollen gels (compare, for example, curves 4 ($Q_0 = 20$ g/g) and 1 ($Q_0 = 140$ g/g) in Fig. 3). This is an expected result, because the lower gel is swollen, the higher is its elastic modulus. Above $D/D_0 \cong 1.25$, the deformation–pressure curves deviate from the linear regime indicating threshold of strain saturation of the gels.

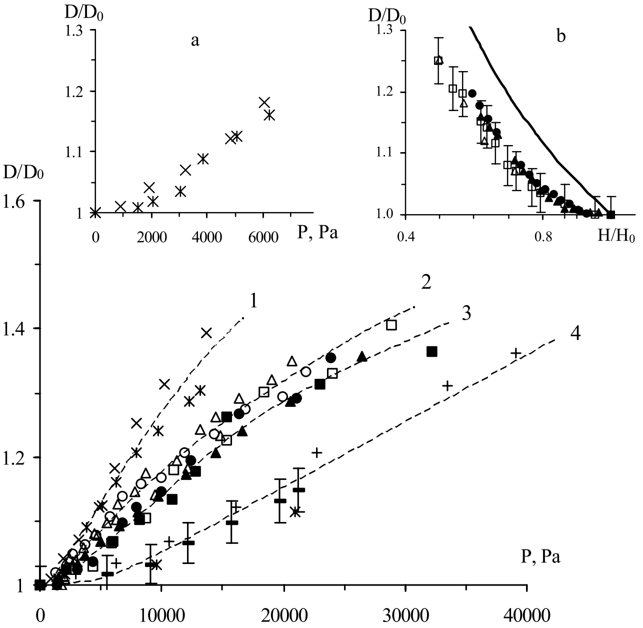

Fig. 3. Deformation as a function of pressure for potassium gels with initial swelling degrees of 140 g/g (1), 100 g/g (2), 60 g/g (3) and 20 g/g (4). Lines are given to guide the eye. (a): beginning of deformation for two potassium gel disks swollen at equilibrium (140 g/g). (b): Beginning of deformation as a function of the relative gap size H/H_0 for potassium gel (open symbols) and sodium gel (shaded symbols). Continuous line corresponds to the case of a constant volume.

No strain saturation at $D/D_0 > 1.2$ was observed for sodium gels. Higher deformations were leading to gel breakage. As it will be shown in Section 3.3, sodium gels release less water than potassium gels at the same deformations. Having similar equilibrium swelling degrees, sodium gels seem to be more fragile but better keeping water.

3.3. Volume change as a function of applied pressure

As far as gel disk size changes were recorded continuously as a function of the applied deformation, it was straightforward to calculate the dependence of the volume $V(P)$ on the pressure. An example of a set of experiments performed on several potassium gel disks of $Q_0 = 140$ g/g and $Q_0 = 60$ g/g is shown in Fig. 4. Different sets of data correspond to the disks of various initial sizes.

It is evident that potassium gel looses solvent due to compression. Two regions with different rates of the volume loss can be distinguished: a steep decrease at the beginning of the compression and a slow decrease (the slope being 8–10 times smaller) at high deformations associated with high pressures. Similar results were obtained for all the other gels. The volume loss at the beginning of compression is larger for more swollen gels: while the 'rate of release' (amount of solvent released per pressure unit) for potassium gels swollen at equilibrium is 0.007–0.008 mm^3/Pa, it drops down two fold for potassium gels swollen at $Q_0 = 60$ g/g. The reason of this 'rate of release' decrease is clear: farther the hydrogel is from its initial state corresponding to $P = 0$, more difficult it is to extract solvent from it. As far as sodium or potassium polyacrylate are extremely hydrophilic substances, it is very difficult to extract water from such hydrogels up to their completely dry state.

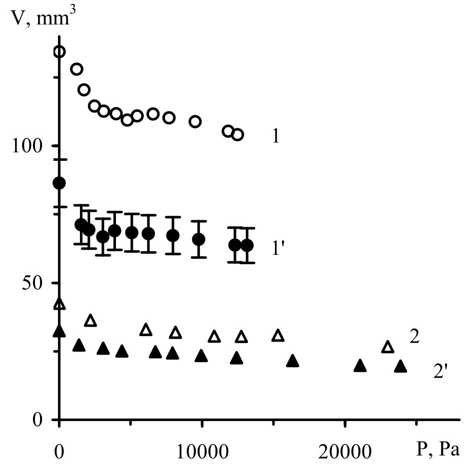

Fig. 4. Example of the volume change as a function of pressure for potassium gels of different initial volumes, swollen at 140 g/g (1 and 1′) and at 60 g/g (2 and 2′).

In order to compare the data obtained for gels of different swelling degrees and of different sizes, a relative volume $V(P)/V_0$ (V_0 being the initial gel volume) was plotted as a function of pressure (Fig. 5 for potassium gels, inset-for sodium gels). For potassium gels, all data fall together within the 10% experimental error. There is no significant influence of the gel initial swelling degree on its relative volume loss under compression. As well as for $V(P)$, the relative volume as a function of the applied pressure can be roughly described by two lines with the slopes differing in 6–7 times (see broken lines in Fig. 5). The lower is gel initial swelling degree, the higher is its shear modulus, thus it can sustain higher deformations before breakage and thus more water can be released.

In Section 3.4 a theoretical prediction describing charged hydrogel behaviour under compression will be given. One should keep in mind that the gels in the experiments described above are not fully in the equilibrium state (evaporation rate not completely negligible, friction coefficient not taken into account, etc.). Thus the only qualitative conclusions that could be derived from the experiments are as follows: (i) there is a significant volume loss due to the compression and (ii) there are two regions with different rates of the solvent release. These two points will be compared with a qualitative theoretical approach that we developed for a uniaxially compressed hydrogel.

3.4. Theoretical predictions

The theoretical analysis used is based on the thermodynamic approach developed for weakly charged polyelectrolyte gels [13,14]. The hydrogel studied experimentally is strongly charged and far from equilibrium. Up to now, no theory describing the behaviour of such systems was developed. Thus the proposed approach should be considered as a first approximation of the solution of the problem on gel volume loss under compression. The comparison between theoretical predictions and experimental results will be only qualitative.

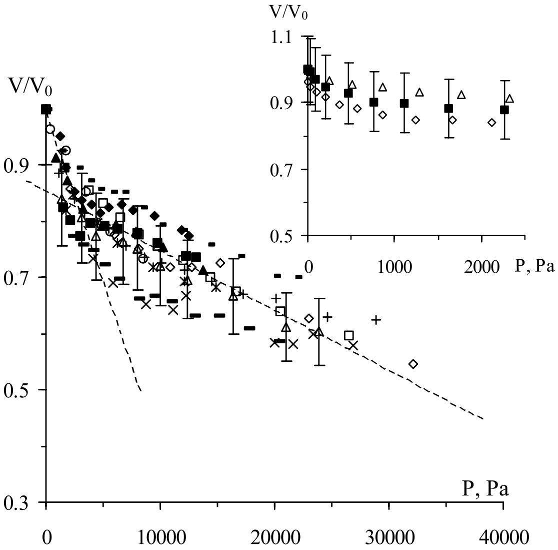

Fig. 5. Dependence of the relative volume on pressure for all potassium gels. Broken lines show two regions with different slopes. Inset: the same for sodium gels.

Let us consider a cylindrical sample of a hydrogel swollen at equilibrium in water up to volume V. We assume that the gel contains ν internodal chains and the average number of monomers per the chain is N. The monomer concentration in the swollen hydrogel is $n=\nu N/V$. Each chain contains N/m charges separated by m monomers. The electrical neutrality of the system is provided by $\nu N/m$ counter-ions.

As far as the main goal is to examine whether the hydrogel volume changes when applying a uniaxial compression, the swelling degree of a gel before and after compression has to be calculated. The uniaxial symmetry of our problem results into two relevant swelling degrees: along the z-axis, α_z, and in the perpendicular (radial) direction, α_r. They are defined as $\alpha_z=L/L_{\text{ref}}$ and $\alpha_r=R/R_{\text{ref}}$, L and R being the length and radius of the cylindrical sample under compression and L_{ref} and R_{ref} are the length and the radius in the reference state corresponding to the Θ-condition of polymer chains connecting neighbouring cross-links. In the reference state the monomer concentration is $n_0=\nu N/V_{\text{ref}}$. In the limiting case of the overlap threshold of the chains the monomer concentration depends on degree of polymerisation as $n_0=d^{-3}N^{-1/2}$ (d being the persistent length).

At the stress free state, the swelling degrees result into $\alpha_{0z}=L_0/L_{\text{ref}}$ and $\alpha_{0r}=R_0/R_{\text{ref}}$, where L_0 and R_0 represent sizes of the sample at $P=0$. Generally speaking, the swelling degrees α_{0z} and α_{0r} differ from each other if lateral Laplace pressure is taken into account.

The volume of a compressed and free gel can be expressed as $V=\alpha_z\alpha_r^2V_{\text{ref}}$ and $V_0=\alpha_{0z}\alpha_{0r}^2V_{\text{ref}}$, respectively. Our purpose is to estimate the relative volume change as a function of pressure:

$$\frac{V(P)}{V_0}=\frac{\alpha_z\alpha_r^2}{\alpha_{0z}\alpha_{0r}^2} \tag{1}$$

Due to the axial symmetry, two components of the stress tensor, σ_{zz} and σ_{rr} are relevant in our problem. They represent the elastic response to the applied uniaxial compression P and the lateral Laplace pressure $\Gamma=\gamma/R$ caused by the interfacial tension γ. The equilibrium state is described by the following equations

$$P=\frac{1}{\alpha_r^2V_{\text{ref}}}\frac{\partial F}{\partial\alpha_z}\quad\text{and}\quad\Gamma=\frac{1}{2\alpha_r\alpha_zV_{\text{ref}}}\frac{\partial F}{\partial\alpha_r} \tag{2}$$

where F is the free energy of the polyelectrolyte gel. Eq. (2) will be used in deriving dependencies of swelling degrees α_z and α_r on the applied pressure.

The free energy of a polyelectrolyte gel is represented as a sum of four contributions [15]:

$$F = F_{\mathrm{el}} + F_{\mathrm{int}} + F_{\mathrm{tr}} + F_{\mathrm{C}} \tag{3}$$

The first term, F_{el}, is the elastic energy of a swollen network. For a weakly charged gel it may be expressed with a proper accuracy as a sum of elastic energies of ν Gaussian coils composing the sample (cf. Refs. [13,14])

$$F_{\mathrm{el}} = \frac{1}{2}\nu kT\left[2\alpha_r^2 + \alpha_z^2 - \frac{2}{f}\ln(\alpha_r^2\alpha_z)\right] \tag{4}$$

where T is temperature, k is the Boltzmann constant, and f is the functionality of cross-links of the network.

The second term, F_{int}, owes its origin to the Van der Waals interactions between the uncharged monomers. For the highly swollen gel it may be written in terms of virial expansion

$$F_{\mathrm{int}} = \nu kTN[Bn + Cn^2] \tag{5}$$

where B and C are the second and the third virial coefficients respectively. The second one is of the order of $B \sim d^3\Delta T/T$ representing deviation of polymer system from Θ-temperature ($\Delta T = T - \Theta$) while the third virial coefficient is $C \sim d^6$. It is important to bear in mind that monomer concentration n of the swollen gel depends on the concentration n_0 in the reference state as $n = n_0/\alpha_z\alpha_r^2$.

The third contribution to the total free energy corresponds to the free energy of the gas of counter-ions entrapped in the polyelectrolyte gel (see Ref. [15]):

$$F_{\mathrm{tr}} = kT\frac{\nu N}{m}\ln\left(\frac{n}{m}\right) \tag{6}$$

We neglect the escape of counter-ions into the released solvent because of high electric potential arising while electro-neutrality is violated. As a result, the small amount of ions released does not bring any important contribution to the free energy.

The free energy F_C of electrostatic interactions of the polyelectrolyte gel may be identified with free energy of Coulomb interactions in electrically neutral plasma with concentration of charges n/m. In the Debye–Hückel approximation this energy may be written as

$$F_C = -kT\nu\left(\frac{l_{\mathrm{XL}}}{d}\right)^{3/2}\frac{N}{m}\left(\frac{nd^3}{m}\right)^{1/2} \quad \text{where} \quad l_{\mathrm{XL}} = \frac{q^2}{\varepsilon kT}$$

is the Bjerrum length [15]. For the aqueous system under consideration this length is equal to $l_{\mathrm{B}} = 0.7$ nm at room temperature. It is of the same order as dimension of monomers of the hydrogel, $d = 0.8$ nm, and we can put $l_{\mathrm{B}}/d \cong 1$. Thus, in the case of weekly charged hydrogels the contribution of electrostatic interactions to the free energy can be written as

$$F_C = -kT\nu\frac{N}{m}\left(\frac{nd^3}{m}\right)^{1/2}. \tag{7}$$

Substituting Eqs. (4)–(7) to Eq. (3) and using Eq. (2), we obtain the following correlations between hydrogel swelling degrees and the uniaxial and Laplace pressures:

$$P = kTn_0\left[\frac{f\alpha_z^2 - 1}{Nf\alpha_r^2\alpha_z} - \frac{Bn_0\alpha_r^2\alpha_z + 2Cn_0^2}{\alpha_r^6\alpha_z^3} - \frac{1}{m\alpha_r^2\alpha_z} + \frac{1}{2m\alpha_r^3\alpha_z^{3/2}}\left(\frac{n_0d^3}{m}\right)^{1/2}\right], \tag{8}$$

$$\Gamma = P + \frac{kTn_0}{N}\left(\frac{1}{\alpha_z} - \frac{\alpha_z}{\alpha_r^2}\right). \tag{9}$$

Note that the last term in Eq. (8), appearing due to the electrostatic interaction of charges, is much smaller than the term related to the osmotic pressure of the counterions. Below we will neglect the Laplace pressure Γ supposing that interfacial tension γ between the swollen gel and water is about zero.

Calculating numerically the swelling degrees from Eqs. (8) and (9), we can obtain with help of Eq. (1) the relative volume of the polyelectrolyte gel as a function of the applied pressure P. The results are presented in Fig. 6 for three ratios: $N/m = 0$, 5, and 10 at two values of polymer volume fractions $\phi_0 = n_0d^3 = 0.25$ and 0.1 in the reference state. We took $N = 100$ and cross-link functionality $f = 4$. In this case the value $\phi_0 = 0.1$ corresponds to the overlap threshold of polymer chains. The considered values of the second and the third virial coefficients, $B = 4d^3$ and $C = 0.08d^6$, provide a high swelling of the gel.

The zero value of N to m ratio corresponds to the case of neutral networks. An increase of N/m results in the increase of the number of charges leading to the increase of the translational entropy of counterions and of electrostatic interactions in the gel (cf. Eqs. (6) and (7)) and thus to the increase of the initial swelling degrees α_{0r} and α_{0z} in a free-stress state. Fig. 6 shows that the more there are charges per chain, the smaller is the relative volume $V(P)/V_0$ of a polyelectrolyte gel at a given value of the applied pressure.

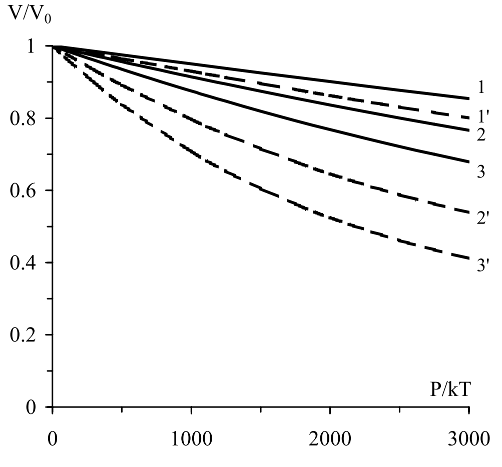

Fig. 6. Theoretical predictions of the volume loss for a weakly charged polyelectrolyte gels: $N/m = 0$ (neutral gel) (1, 1′); $N/m = 5$ (2, 2′) and $N/m = 10$ (3, 3′). The continuous lines correspond to monomer volume fraction $\phi_0 = 0.25$ and broken lines to $\phi_0 = 0.1$.

This result indicates that in the case of highly charged hydrogels, the uniaxial compression indeed should lead to a noticeable volume loss. Even using a qualitative approach developed for weakly charged polyelectrolyte gels, the trend of the theoretical curve is similar to the one observed in the experiment (compare curve 3 of Fig. 6 and Fig. 5). Fig. 6 also shows that decrease of polymer concentration leads to the increase of relative volume loss of polymer gels under the compression (broken curves).

The physical understanding of the solvent release under the mechanical action on a hydrogel is as follows. For the neutral gels the applied pressure restricts repulsion between monomers caused by the Van der Waals interactions resulting in some decrease of the sample volume. In the case of the polyelectrolyte hydrogels, another much stronger phenomenon contributes to gel swelling—the osmotic pressure of counterions. Being partially compensated by the uniaxial compression, this contribution is diminished thus leading to a larger solvent release than from the neutral networks. The decrease of polymer concentration results in amplification of this effect. Actually, both the Van der Waals repulsion of monomers and the osmotic pressure of counterions would be diminished in this case leading to a larger compression with a smaller lateral swelling. As a result it increases solvent release.

4. Conclusions

The evidence of solvent release from a compressed strongly charged polyelectrolyte gel based on sodium or potassium poly(acrylate-co acrylic acid/acrylamide) was demonstrated experimentally. The volume loss occurs at any initial gel swelling degree, even if the gel is far from its equilibrium state. The theoretical approach developed qualitatively correlates with the experiment: it shows that solvent release takes place for weakly charged and neutral gels, being more pronounced for polyelectrolyte hydrogels.

Acknowledgements

Part of this work was financially supported by the Réseau de Recherche et d'Innovation Technologiques Matériaux et Procédés (France). SP thanks CNRS for the financial support of his stay in Cemef of Ecole des Mines de Paris. JW is grateful to Erasmus EC program for the financial support of his stay in Cemef. Authors are grateful to Patrick Navard (Ecole des Mines de Paris, Cemef) for helpful discussions and to F. Horkay (National Institute of Health, Maryland, USA) for advises on sodium gel synthesis.

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