Osmotically Active and Passive Counterions in Inhomogeneous Polymer Gels

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ABSTRACT: The concepts of osmotically passive and active counterions are introduced for spatially inhomogeneous polyelectrolyte systems. Osmotically passive counterions appear as a result of the trapping of counterions in wells of inhomogeneously distributed electric potential. This effect is additional to the well-known Onsager−Manning condensation (i.e. condensation on the line of charges), which also produces counterions that are osmotically passive. The simplest theory of the swelling of inhomogeneous polyelectrolyte gels taking into account the effect of osmotically passive counterions is developed. It is shown that such gels swell less than the corresponding counterparts with homogeneously distributed charges on the gel chains because osmotically passive counterions are no longer contributing to the exerting of osmotic pressure. Some experimental confirmations of the effect of osmotically passive counterions are discussed.

1. Introduction

Polyelectrolyte gels contain charged monomer units and counterions. When a piece of such gel is immersed in a large amount of water, the counterions cannot escape outside the gel because of the condition of macroscopic electroneutrality. Being forced to reside inside the gel, they try to occupy as much volume as possible because in this way they gain some translational entropy. As a result, they create an exerting osmotic pressure leading to the gel swelling. The exerting of the osmotic pressure of counterions plays a very essential (often dominant) role in the behavior of polyelectrolyte gels. In particular, it determines the two basic properties of the gels: their superabsorbing ability with respect to water and their pronounced collapse transition.[1,2]

Thus, the osmotic pressure of counterions is a very important factor, which governs many of the gel properties, and therefore, it is necessary to be able to calculate it correctly. The easiest way to do this is to assume that counterions can be considered as an ideal gas that is uniformly distributed within the gel sample. This approach suggests that all counterions are free to move in the overall volume of the gel. In this case, the osmotic pressure of counterions π can be expressed as

$$\pi = nk_BT \tag{1}$$

where n is the concentration of counterions, which in this case is equal to the number of counterions divided by the gel volume. However, if we try to calculate the swelling ratio of the gel within this framework, it turns out to be much higher than it is experimentally observed. Therefore, eq 1 significantly overestimates the experimental results.

Below, we describe two specific experimental results recently obtained in our laboratory[3,4] which illustrate the above-mentioned fact.

The first result concerns the deswelling of polyelectrolyte gels in low-molecular-weight salt solutions.[3] When a polyelectrolyte gel is immersed in a salt solution, it shrinks because of the decreasing difference betweem the osmotic pressure inside and outside the gel. The gel shrinking should be observed starting from some characteristic salt concentration, c^*, which is on the order of the concentration of free counterions inside the gel that determines the intranetwork osmotic pressure. However, when the value of c^* was compared in Jeon et al.[3] with the total concentration of counterions available in the gel volume, it was concluded that only a small fraction of gel counterions contributes to the osmotic pressure, i.e., is osmotically active. At the same time, there is a large fraction of osmotically passive counterions. As suggested in Jeon et al., an obvious reason for this is an Onsager−Manning condensation of counterions on the highly charged network chains.[5] However, even taking into account this type of condensation, still there is a rather large deviation of the calculated concentration of free counterions from the experimental value.[3]

Moreover, when the monomer concentration during gel formation decreases, this deviation becomes more pronounced. As is known,[6] the lower the concentration of monomer during gel formation, the more heterogeneous is the gel obtained. Therefore, the experimental data suggest that the fraction of osmotically passive counterions increases with increasing gel inhomogeneity. One may suggest that, in the inhomogeneous polyelectrolyte gel in the relatively highly charged polymer-rich regions, the local potential wells are formed, which additionally entraps some of the counterions. The data presented in Jeon et al.[3] evidence that the fraction of counterions trapped by charge inhomogeneities may be rather high.

Another way to introduce the inhomogeneous distribution of charges in the gel consists of the incorporation of charged macromolecules in the neutral gel. This was done for polyacrylamide hydrogel with polyelectrolyte rods PPP3 (see Philippova et al.[4] for the details of the chemical structure of this polymer). The rods are embedded in the gel but not covalently attached to it. In this case, the charged units belong only to the rods, whereas the rod-free space in the gel volume does not contain charged units at all. The rods bring with them their counterions, and the latter create the exerting osmotic pressure that causes the gel to swell.

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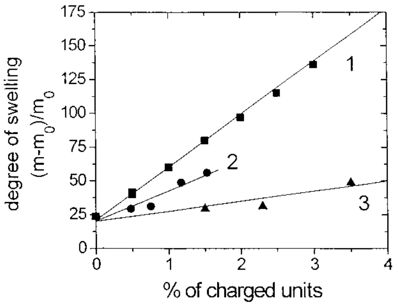

Figure 1. Dependence of the degree of swelling of polymer gels on the fraction of charged units for model copolymer gel with random distribution of charged units in (1) the gel volume and for the gel with embedded rigid-rod polyelectrolyte (2) with and (3) without correction for Onsager–Manning condensation.

In Zeldovich et al.,[7] the swelling of the gel with entrapped rods (inhomogeneous distribution of charges) was compared with that of the model gel with more or less randomly distributed charges (the amount of charged units being approximately the same). The model gel was prepared by free-radical copolymerization of neutral (acrylamide) and charged (sodium salt of 2-acrylamido-2-methyl-1-propanesulfonic acid) monomers. Figure 1 depicts the degree of swelling of the gels as a function of the fraction of charged units. A striking effect is evident: the swelling of the rod-containing gel is much less than that of the model gel (cf. curves 1 and 3). Therefore, in the gel with entrapped rods, a large fraction of counterions does not contribute to the osmotic pressure; i.e., these counterions are osmotically passive. Obviously, one part of the osmotically passive counterions are condensed on the rods via an Onsager–Manning mechanism. If we take into account the correction for the Onsager–Manning condensation, we obtain curve 2 (Figure 1), which is still far from the line for the copolymer gel. Therefore, the Onsager–Manning condensation does not explain the whole magnitude of the observed effect. Thus, along with passive counterions condensed in the molecular vicinity of the rods via an Onsager–Manning mechanism, there is some other fraction of osmotically passive counterions. It seems reasonable to suggest that the existence of these counterions is related to the inhomogeneous distribution of charged units within the gel. A schematic illustration of this fact is given in Figure 2. In addition to counterions, which are in the molecular vicinity of the rods and which are condensed by an Onsager–Manning mechanism, there are counterions trapped by local potential wells on a larger spatial scale. These counterions also do not contribute to the osmotic pressure.

Therefore, these experimental data suggest that there can be two types of osmotically passive counterions: (1) counterions condensed via an Onsager–Manning mechanism and (2) counterions trapped by charge inhomogeneities. Moreover, the contribution of the last type of counterion, which was never taken into account in the literature, can be rather significant.

It is clear that in the presence of osmotically passive counterions, the exerting osmotic pressure can no longer be expressed via eq 1. Only osmotically active counterions should be accounted for in this formula, and therefore, the swelling of the gel must be significantly lower. The aim of the present paper is to develop a theory for this effect for a simple model of an inhomogeneous gel. In the next section, we formulate this model and derive the main formulas. The results and discussion are presented in Section 3.

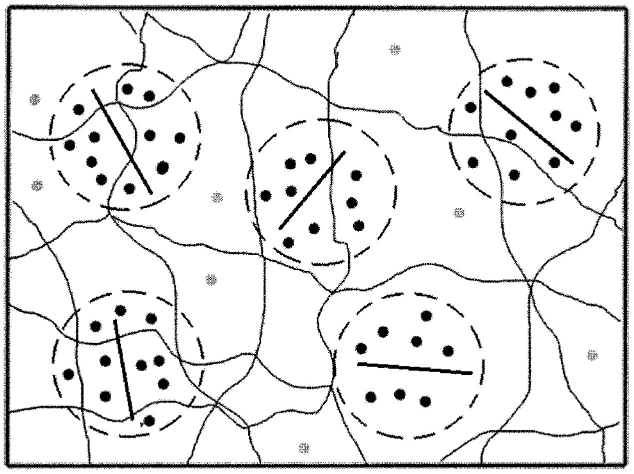

Figure 2. Schematic picture of counterion distribution in a gel with embedded charged rods. Some counterions (black) are trapped in electrostatic potential wells and are osmotically passive, whereas other ions (gray) remain osmotically active.

2. Inhomogeneous Gel: Model and Free-Energy Expression

The inhomogeneities in real gels can be rather complex: they can be either quenched, because of the statistical nature of the cross-linking process during the synthesis of the gel, or they can be induced by external factors (decrease of solvent quality, and so on).[8] The detailed study of these inhomogeneities requires from us the knowledge of the peculiarities of the distribution of subchain lengths, its spatial correlation functions in the gel, etc.

However, despite all of these complications, we can expect that the behavior of an inhomogeneous charged gel is governed by two main factors: the polyelectrolyte effect and elastic tension. Because of the spatial variations of polymer density, the polyelectrolyte gel develops a spatial profile of immobilized electric charge on the gel chains. This effect can have a large influence on the behavior of counterions within the gel, because of the trapping of counterions in local potential wells in polymer-rich areas. As a result, the osmotic pressure of counterions decreases, and the swelling ratio of an inhomogeneous gel should be lower than that of a homogeneous one.

Another factor connected to inhomogeneity is that the elastic forces, arising when the gels swells, are no longer evenly distributed over all subchains but can have a complicated profile connected with the local cross-link density. This effect alters the overall gel elastic modulus and therefore affects the swelling properties.

For qualitative analysis of the main effects described above, we will use the simplest possible model. Namely, we will make the calculations within the framework of a two-phase model of the gel, as shown in Figure 3 (similar approaches have been recently applied to single polyelectrolyte chains and microgels[9]). Our model gel consists of regions of higher density of polymer chains, caused by locally higher cross-link density, separated by regions with lower polymer content. In this model, the actual continuous distribution of subchain lengths is roughly replaced by an assumption that the gel consists of subchains of two different degrees of polymerization N_1 and N_2, and the spatial structure is

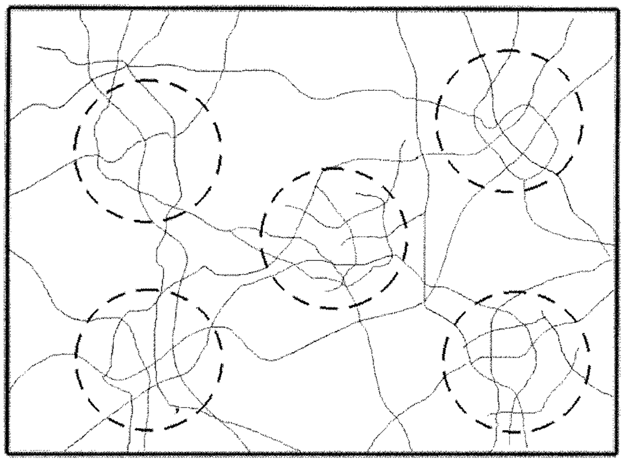

Figure 3. Schematic picture of an inhomogeneous gel. Regions with higher local cross-link density are marked by dashed circles.

depicted as clusters (core) of chains of length N_1 imbedded in a matrix of chains of length N_2 (shell). By varying the parameters of the model, namely N_1, N_2, the core size R_0, and the average separation between the cores D_0, we can hope to describe qualitatively any inhomogeneity pattern occurring in real gels.

Let us consider the case when $N_2 > N_1$ (the core is denser than the shell) and $R_0 < D_0$, so that core size is less than the distance between neighboring cores. With this choice of parameters, the model system resembles the presumed picture of the gel microstructure shown in Figure 3, small, dense aggregates in a loosely cross-linked matrix. It is assumed that polymer chains in both core and shell have the same (constant) charged unit fraction; namely, let σ be the average number of monomer units between quenched charged groups along the chain.

The two-phase model gel can be characterized by swelling ratios α_1 and α_2 of the core and the shell, respectively, and the bulk swelling ratio α of the macroscopic sample. Here, we define the swelling ratio α as the ratio of the end-to-end distance of the polymer chain to its Gaussian size or, for the gel, the ratio of the size of the gel sample to its size under reference conditions, where the subchains are assumed to be closest to Gaussian.

To derive the free energy of the system and to establish the relation between α_1, α_2, and α, we need to agree on a method of calculation of swelling characteristics that does not depend on the details of the mutual positions of denser clusters in the more dilute matrix. Let us assume that the space per one core–shell is of spherical shape and consists of the central highly cross-linked region with subchain length N_1 and radius R_0 (core) surrounded by a spherical layer with radius D_0 consisting of chains of length N_2 (shell) (Figure 4). The subscript 0 denotes the reference state (normally corresponding to synthesis conditions[6] or swelling of uncharged gels in θ-solvents[10]). Then, the macroscopic swelling ratio α is given by

$$\alpha = \frac{\alpha_1 R_0 + \alpha_2 (D_0 - R_0)}{D_0} \tag{2}$$

We will consider the case when $D_0 > R_0$ or even $D_0 \gg R_0$, i.e., when the core size is small as compared to the distance between nearest aggregates.

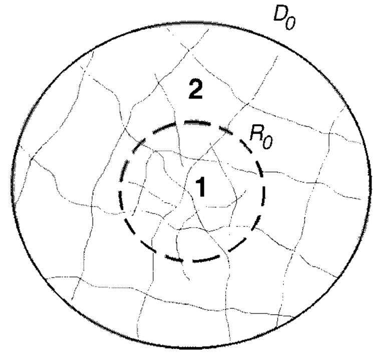

Figure 4. Core–shell model of microheterogeneity in a gel. Chains with degree of polymerization N_1 are confined into a sphere of radius R_0, forming the core (1). The shell (2) consists of chains of length N_2 and has a diameter D_0.

The free energy of the macroscopic gel is proportional to the free energy of the core together with its surrounding shell. The simplification represented by Figure 4 is in the spirit of our simplest model and does not lead to any loss of generality.

The nonionic part of the free energy of the core can be expressed as follows:[10]

$$\frac{F_1}{k_B T} = \frac{4\pi}{3} R_0^3 \nu_{0,1} \left[\frac{3}{2} (\alpha_1^2 + \alpha_1^{-2}) + \frac{B n_{0,1}}{\alpha_1^3} + \frac{C n_{0,1}^2}{\alpha_1^6} \right] \tag{3}$$

where $\nu_{0,1} \approx 1/(a^3 N_1^{3/2})$ is the average cross-link density in the reference state (the state where the gel chains are most close to Gaussian ones), $n_{0,1} \approx 1/a^3 N_1^{1/2}$ is the monomer unit density in the reference state, and B and C are the second and third virial coefficients of the non-Coulombic interaction of monomer units, respectively.

Similarly, for the free energy of the shell we can write

$$\frac{F_2}{k_B T} = \frac{4\pi}{3} (D_0^3 - R_0^3) \nu_{0,2} \left[\frac{3}{2} (\alpha_2^2 + \alpha_2^{-2}) + \frac{B n_{0,2}}{\alpha_2^3} + \frac{C n_{0,2}^2}{\alpha_2^6} \right] \tag{4}$$

with $\nu_{0,2} \approx 1/(a^3 N_2^{3/2})$ and $n_{0,2} \approx 1/a^3 N_2^{1/2}$.

We are interested chiefly in the properties of the swollen state of the inhomogeneous gel with hydrophilic monomer units, and therefore, we suppose that the gel is immersed in a good or θ-solvent. Because a polyelectrolyte gel is highly swollen under these circumstances, we can also neglect all compression-related ($\sim\alpha^{-2}$) elastic terms in the free energy. Therefore we retain only the leading terms in powers of α, neglecting the second and the fourth terms in eqs 3 and 4.

Thus, our final expression for the nonionic part of the free energy takes into account the elastic expansion of a polymer chain and the excluded volume repulsion of monomer units.

The ionic part of the free energy consists of the translational entropy of the counterions and their electrostatic interactions. Within our two-phase framework, this energy per aggregate can be written as

$$\frac{F_{\mathrm{ion}}}{k_B T} = N_1 \ln \frac{N_1 a^3}{V_1} + N_2 \ln \frac{N_2 a^3}{V_2} + l_B (N_1 - Q_1)^2 \left[\frac{1}{R_0 \alpha_1 + (D_0 - R_0)\alpha_2} - \frac{1}{R_0 \alpha_1} \right] \tag{5}$$

The first two terms represent the translational entropy of small ions, and the third term is the electrostatic energy of the system, considered as a spherical capacitor (see also Kramarenko et al.[9]). In these expressions, $l_B = e^2/\epsilon k_B T$ is the Bjerrum length, N_1 and N_2 are the numbers of counterions residing in the core and the shell, respectively, and Q_1 is the immobilized charge on polymer chains in the core. The volumes V_1 and V_2 of core and shell are given by

$$V_1 = \frac{4\pi}{3} R_0^3 \alpha_1^3$$

$$V_2 = \frac{4\pi}{3} \{[R_0\alpha_1 + (D_0 - R_0)\alpha_2]^3 - R_0^3\alpha_1^3\}$$

For subsequent calculations, we will also introduce the fraction of counterions β within the core, defined as $\beta = N_1/Q$.

Thus, the free energy of the system F is given by

$$F = F_1 + F_2 + F_{\text{ion}} \tag{6}$$

The electroneutrality condition is satisfied by setting

$$N_1 + N_2 = \frac{\nu_{0,1} V_{0,1} N_1}{\sigma} + \frac{\nu_{0,2} V_{0,2} N_2}{\sigma} \tag{7}$$

where $V_{0,1}$ and $V_{0,2}$ are the volumes of the corresponding phases in the reference state.

The expression for the free energy, eq 6, depends essentially on the parameters α_1, α_2, and β. It is worth noting that these parameters are not independent: they are connected via a boundary condition of elastic equilibrium on the boundary of the core and the shell. Physically, the expansion of chains in the shell will induce a mechanical stress on chains in the core and vice versa. The difference of counterion osmotic pressure on the different sides of the boundary surface also contributes to this effect.

In its general form, this boundary equilibrium condition can be written as

$$\pi_{1,\text{elastic}} + \pi_{1,\text{osmotic}} = \pi_{2,\text{elastic}} + \pi_{2,\text{osmotic}} \tag{8}$$

where π is pressure and the indices 1 and 2 correspond to the core and the shell, respectively.

To get the explicit form of this equation in our case, note that the force of elastic expansion of a single polymer chain is $\sim k_B T\alpha/a\sqrt{N}$ and the unperturbed size of the chain is $\sim aN^{1/2}$, so its cross section is a^2N.

We assume that the chains of the core and the shell are grafted to core–shell boundary surface with a superficial density of $\sim 1/(a^2N_i)$ chains per unit area ($i = 1$ for the core and $i = 2$ for the shell) on the corresponding sides. Thus, the force per one side per unit area (pressure from each side) is

$$P = \frac{k_B T}{a} \frac{\alpha}{\sqrt{N}} \frac{1}{a^2 N} = \frac{k_B T}{a^3} \frac{\alpha}{N^{3/2}}$$

Therefore, for two uncharged gels consisting of chains of length N_1 and N_2, we get

$$\alpha_1 N_1^{-3/2} = \alpha_2 N_2^{-3/2} \tag{9}$$

The physical meaning of this relation is very clear: in a dense gel, the chains will expand only slightly to yield a given total force, whereas in a lightly cross-linked gel consisting of fewer long chains, the swelling ratio will be much higher.

In the case of a polyelectrolyte gel, one should subtract the osmotic pressure of small ions from eq 9, which gives the final relationship between equilibrium values of α_1 and α_2:

$$\frac{\alpha_1}{N_1^{3/2}} - \frac{N_1 a^3}{V_1} = \frac{\alpha_2}{N_2^{3/2}} - \frac{N_2 a^3}{V_2} \tag{10}$$

Now, to find out the equilibrium state of our model gel, we should minimize the free energy with respect to one of the swelling ratios (say, α_1) and the fraction of counterions within the core β. The swelling ratio α_2 then can be found from the boundary condition, eq 10. The corresponding equations take the following form:

$$\frac{V_2}{V_1} \frac{\beta}{1 - \beta} = \exp\left\{2 l_B (Q\beta - Q_1) \left[\frac{1}{(D_0 - R_0)\alpha_2 + R_0\alpha_1} - \frac{1}{R_0\alpha_1}\right]\right\} \tag{11}$$

$$\frac{\alpha_1}{N_1^{3/2}} = \frac{N_1 a^3}{V_1} = \frac{\alpha_2}{N_2^{3/2}} - \frac{N_2 a^3}{V_2} \tag{12}$$

$$\frac{\partial F[\alpha_1, \alpha_2(\alpha_1, \beta), \beta(\alpha_1, \alpha_2)]}{\partial \alpha_1} = 0 \tag{13}$$

The system of equations, eqs 11–13, has been solved numerically for different values of parameters N_1, N_2, R_0, D_0, and σ, and the results are presented in the next section.

3. Results and Discussion

The first issue that we should treat here is the proper choice of the parameters of our model, so that the resulting physical picture would be the closest to a real inhomogeneous gel. We have chosen $l_B = 0.7$ nm, which corresponds to an aqueous system at room temperature, $R_0 = 20$ nm, and $D_0 = 50$ nm. Inclusions of denser cross-linked gel of the size 20 nm scattered in the gel with 50 nm average separation from each other is our initial guess for the inhomogeneities produced in the course of the formation of a statistically disordered gel. Here we present the results for these values of R_0 and D_0 to illustrate our main points; if numerical data for other values of parameters are needed, they can be easily calculated. However, analysis shows that the main qualitative features of the solution remain the same for any reasonable choice of parameters R_0 and D_0. For the monomer size a we have set $a = l_B$, suggesting that polyelectrolyte chains are flexible, which is the usual assumption in this kind of calculation (for N-isopropylacrylamide, for example, $a = 0.812$ nm[11]).

However, it is more difficult to figure out the reasonable ratio of subchain lengths N_1 and N_2 that would represent the experimental situation. We have chosen $N_1 = 100$, and we varied $N_2/N_1 > 1$ as a free parameter. Although it is not easy to say which value of N_2/N_1 corresponds to real gels, we can still think that the ratio of maximum and minimum average polymer densities in a real statistically inhomogeneous gel is not very high; namely, it is of order of unity (2 can be chosen as an estimate). As is known, the polymer density in the reference state as a function of the degree of polymer-

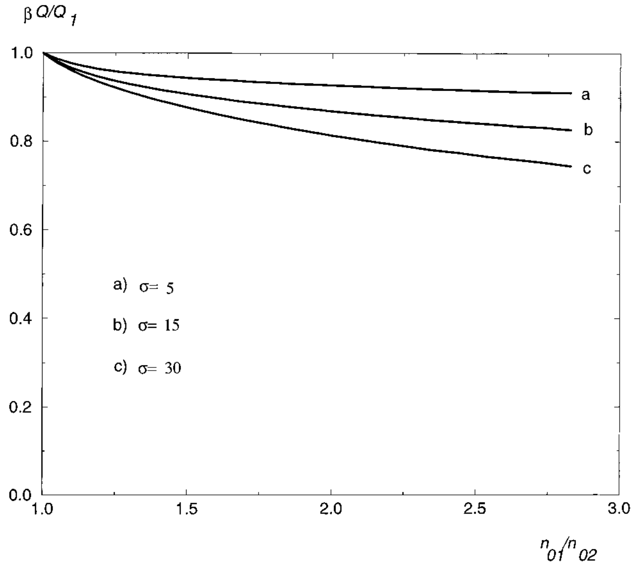

Figure 5. Dependencies of the ratio of the number of ions within the core βQ to the number of immobilized charges in the core Q_1, on the inhomogeneity of the gel (ratio of the maximum and minimum polymer densities) for different values of distance between charged units, σ, along the chain (indicated in the figure). $R_0 = 20$ nm and $D_0 = 50$ nm.

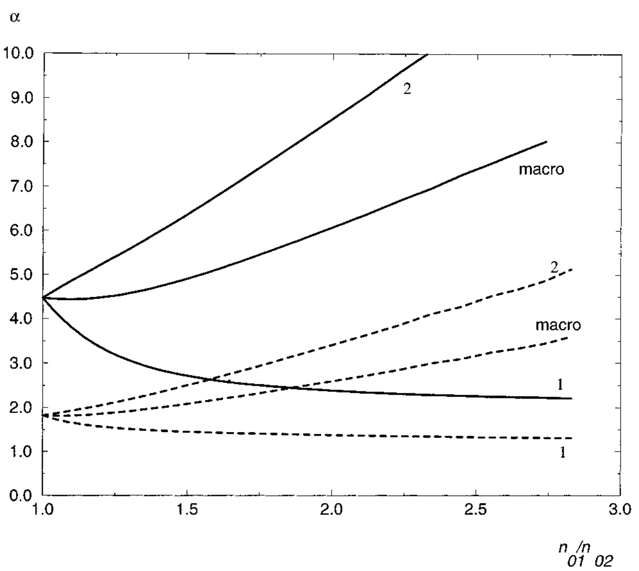

Figure 6. Dependencies of the swelling ratios of (1) the core, (2) the shell, and (macro) the macroscopic swelling ratio of the gel α on the degree of gel inhomogeneity. Solid curves: $\sigma = 5$, $R_0 = 20$ nm, and $D_0 = 50$ nm. Dashed curves: $\sigma = 30$, $R_0 = 20$ nm, and $D_0 = 50$ nm.

ization N can be estimated[10] as

$$n_0 \sim \frac{1}{a^3\sqrt{N}} \tag{14}$$

Accordingly, in our model, the ratio of the maximum polymer density to the core and the minimum in the shell is equal to

$$n_{0,1}/n_{0,2} = \sqrt{N_2/N_1} \tag{15}$$

Therefore, we expect that inhomogeneities in real gels correspond to the values of N_2/N_1 around 4. As we will show later, in this regime, the dependence of gel macroscopic parameters on N_2/N_1 is not very strong, so the particular value of N_2/N_1 seems to be not very important.

We have performed the calculations for the values of σ equal to 5, 15, and 30, which correspond to the charged-unit fractions usually encountered in weakly charged polyelectrolyte gels.

First, let us consider the effect of inhomogeneity on the spatial distribution of counterions as a function of $n_{0,1}/n_{0,2} = \sqrt{N_2/N_1}$ for different values of σ. (Figure 5). We characterize the distribution of counterions by the quantity $\beta Q/Q_1$, which is the ratio of the number of counterions residing in the core to the number of ions on polymer chains within the core. We can see that $\beta Q/Q_1$ is not far from unity; therefore, most of the core counterions are trapped by the core and are osmotically passive. On the other hand, $\beta Q/Q_1 < 1$, which means that some counterions escape from the core into the shell of our model gel, therefore increasing the osmotic pressure in the shell. This leads to the further expansion of polymer chains in the less dense shell and to the increase of the macroscopic gel swelling ratio. Figure 5 also shows that the effect of counterion dissipation from the core is more pronounced for less charged gels. The reason for this is the electrostatic attraction in the gel of higher charge that favors the distribution of counterions according to the distribution of the opposite charge on the polymer chain, so that the conditions close to electroneutrality should observed for the core and the shell separately. Because this attraction is proportional to the square of the total charge of the core, the ion distribution where many of the charges of the core are not compensated by counterions (i.e., $\beta Q/Q_1$ is significantly less than 1) is possible only for weakly charged gels.

The swelling ratios of the core α_1 and of the shell α_2 and the macroscopic swelling ratio α are shown in Figure 6. In the limit $n_{0,1}/n_{0,2} \rightarrow 1$ (homogeneous gel), all of these values coincide with each other and with the swelling ratio of the homogeneous polyelectrolyte gel (see below). This proves the self-consistency of our model. We can see that α and α_2 increase with an increase in the ratio $n_{0,1}/n_{0,2}$. There are primarily two reasons for this phenomenon: first, counterions escaped from the core increase the osmotic pressure inside the shell, and second, at a given counterion concentration, the shell swelling ratio increases with the length of shell subchains just as it should be in the homogeneous gel (see eqs 17 and 18). It is worth noting, however, that the core swelling ratio α_1 is decreasing with $n_{0,1}/n_{0,2}$. This is caused first by decreased counterion concentration in the core resulting in less osmotic pressure and second by the elastic tensions that are developed in the inhomogeneous gel. All three swelling ratios increase with the increase of the gel charge (decreasing σ) (Figure 6), in the same way as in the case of an ordinary polyelectrolyte gel.

It is interesting to compare the macroscopic swelling ratio of an inhomogeneous gel with that of a homogeneous polyelectrolyte gel. For this purpose, we introduce an equivalent homogeneous gel with the same charge and number of monomer units in the volume as in the inhomogeneous gel under consideration. The total number of monomer units S_{inh} in the part of the inhomogeneous gel shown in Figure 4 is

$$S_{\mathrm{inh}} = \frac{4\pi}{3}\nu_{0,1}R_0^3N_1 + \frac{4\pi}{3}\nu_{0,2}(D_0^3 - R_0^3)N_2$$

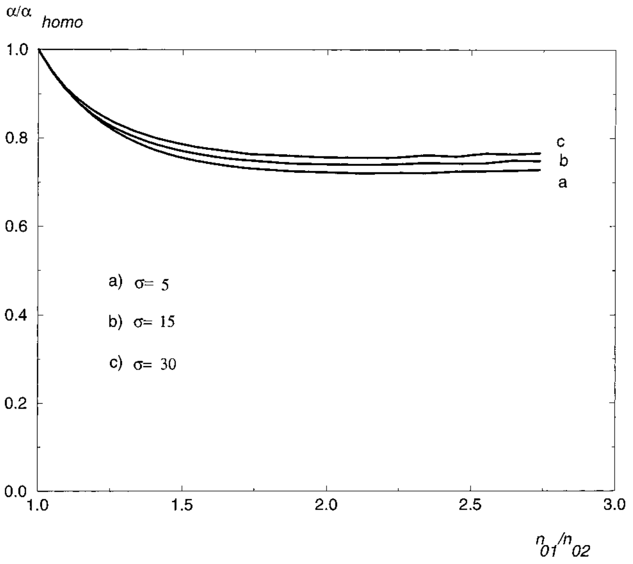

Figure 7. Comparison of the swelling ratio of an inhomogeneous gel α and the swelling ratio of the equivalent homogeneous gel $\alpha_{\rm homo}$ as a function of the degree of gel inhomogeneity $n_{0,1}/n_{0,2}$. The values of σ are indicated in the figure. $R_0 = 20$ nm and $D_0 = 50$ nm.

For a homogeneous gel,

$$S_{\rm homo} = \frac{4\pi}{3}\nu_{0,\rm homo}D_0^3$$

Substituting $\nu_0 \approx 1/a^3N^{3/2}$ and requiring $S_{\rm inh} = S_{\rm homo}$, we obtain the following equation for the length of subchains of an equivalent gel $N_{\rm homo}$:

$$\frac{D_0^3}{\sqrt{N_{\rm homo}}} = \frac{D_0^3 - R_0^3}{\sqrt{N_2}} + \frac{R_0^3}{\sqrt{N_1}} \tag{16}$$

The free energy of an equivalent gel in the same approximation as we made for an inhomogeneous gels reads[10]

$$\frac{F_{\rm homo}}{k_BT} = \frac{3}{2}\alpha^2 + \frac{N_{\rm homo}}{\sigma}\ln\frac{n_{0,\rm homo}a^3}{\alpha^3} \tag{17}$$

and the equilibrium swelling ratio $\alpha_{\rm homo}$ is

$$\alpha_{\rm homo} = \sqrt{\frac{N_{\rm homo}}{\sigma}} \tag{18}$$

In Figure 7, we plot the ratio of the macroscopic swelling ratio α of an inhomogeneous gel to the swelling ratio $\alpha_{\rm homo}$ of the equivalent homogeneous gel. The x-axis is $n_{0,1}/n_{0,2}$. First, note that $\alpha/\alpha_{\rm homo} < 1$; i.e., the inhomogeneous gel is less swollen than an equivalent homogeneous gel. The higher the gel charge, the lower the swelling degree of the gel in comparison to its homogeneous analogue.

The reason for this effect is simple: some counterions are entrapped by the regions with high polymer charge density; therefore, they are osmotically passive, and do not contribute to the full extent to the exerting osmotic pressure. This proves our initial assumption of the existence of osmotically active and osmotically passive counterions in inhomogeneous polyelectrolyte gels.

From Figure 7, it can be seen that, as expected, the greater the inhomogeneity in the distribution of charges in the gel (roughly defined as $n_{0,1}/n_{0,2}$), the greater the depression of the gel swelling ratio in comparison with the homogeneous gel (i.e., the greater the fraction of osmotically passive counterions). This effect is due to the greater depth of entrapping potential wells, so that a smaller part of counterions can escape from the core into the shell (see also Figure 5). This leads to the decrease of the osmotic pressure and the gel swelling ratio with respect to that of a homogeneous gel.

We have also studied the same effects for the case $R_0 = 20$ nm and $D_0 = 100$ nm. The main differences with respect to the case $R_0 = 20$ nm and $D_0 = 50$ nm are as follows: the counterion distribution is weaker pronounced, and the value of $\beta Q/Q_1$ is very close to unity in the whole range of $n_{0,1}/n_{0,2}$. This is caused by higher shell thickness and charge, which makes the uneven counterion distribution unfavorable. Accordingly, the value of $\alpha/\alpha_{\rm homo}$ is also closer to unity. Physically, in this situation, the influence of the shell is dominant, and the behavior of the gel is very close to that for a homogeneous shell system.

The results obtained can be used for a qualitative explanation of the experimental results described in the Introduction. Indeed, the decrease of the fraction of osmotically active counterions for the gels prepared in the presence of a large amount of solvent[3] can be associated with the increase of the degree of inhomogeneity of such gels. The results of Phillipova et al.[4] presented in Figure 1 are also apparently due to the "crowding" of osmotically passive counterions around the charged rods (Figure 2), although some modifications of the theory presented above are needed to describe this case (because the gel in Phillipova et al. is an uncharged one, and the charges are introduced by the embedded polyelectrolyte macromolecules.)

We would like to add that by calling some of the ions osmotically passive we do not mean that they do not create any osmotic pressure at all. Indeed, these ions create an osmotic pressure in the dense core area of the gel, thus preventing it from complete collapse. However, their contribution to the average osmotic pressure, which governs the behavior of the bulk gel sample, is small. This allows the usage of the term "osmotically passive ions". Alternatively, the term "osmotically hidden ions", suggested to us by a referee, could be also used to describe this type of counterions.

4. Conclusions

We have shown that the degree of swelling of inhomogeneous polyelectrolyte gels decreases in comparison with their homogeneous counterparts. The reason for this effect is the distribution of the electric potential inside inhomogeneous gels which leads to effective traps for the counterions. The trapped counterions become osmotically passive, and they do not contribute to the exerting osmotic pressure which is the main cause of gel swelling.

It should be emphasized that in this paper we are speaking primarily about the "trapping" which is in addition to normal Onsager−Manning condensation. The counterions condensed via Onsager−Manning mechanism are, of course, osmotically passive as well.

We believe that the concept of osmotically passive counterions formulated in the present paper may be useful for some other problems of physical chemistry of polyelectrolytes.

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