

Influence of the Counterion Size on Swelling and Collapse of Polyelectrolyte Gel

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Abstract—A theory that predicts the effect of the counterion size on the swelling and collapse of a weakly charged polyelectrolyte gel was developed. In addition to excluded-volume interactions between monomer units of the gel, the theory involves the counterion–monomer unit and counterion–counterion interactions in terms of the virial approximation. The character of interactions between different units in the system varies from repulsion to attraction depending on the type of solvent, counterion, and dielectric permittivity of the solvent. For solvents with a low permittivity, the effect of condensation of counterions resulting in the formation of ion pairs is taken into account.

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INTRODUCTION

Polymer gels that have the unique ability to vary their dimensions by factors of ten with a small change in the external conditions (temperature, solvent composition, pH of medium, electric or magnetic field, etc.) find application in various areas, such as medicine, industry, and agriculture. The potential and range of their application is very broad they can be used as both extremely responsive sensors and superabsorbents capable of absorbing and retaining a vast amount of various liquids.

A prerequisite for the experimental investigation of the collapse of a polyelectrolyte gel is a theoretical study by Dusek and Patterson [1] in which the feasibility of phase transitions was predicted. The point of departure was undoubtedly a study by Tanaka [2] who first observed the collapse of a polyelectrolyte gel. This author examined a polyacrylamide gel in a solvent composed of water and acetone. As the acetone concentration increased (or temperature decreased), the gel began to contract. Two different types of transition into the collapsed state were observed, continuous when the gel volume changed gradually and discrete when volume varied in an abrupt manner. Later, it was found that the type of transition depends on the degree of ionization of the gel, and the abrupt change in volume of the sample is due to the presence of the exerting osmotic pressure of free counterions. The electrostatic nature of swelling of polyelectrolyte gels was exemplified by the collapse due to a change in the salt concentration in the solution [4].

The discovery of the collapse of a polyelectrolyte gel was followed by a series of theoretical studies dealing with this problem. In particular, the collapse of neu-

tral networks was examined and it was shown that the character of the transition depends on chain rigidity: the transition is discrete for rigid chains and continuous for flexible chains [5]. The theory of swelling and collapse of a polyampholyte gel [6], gel collapse under mechanical stress [6, 7], swelling in a mixed solvent [6, 8] and a polymer melt [6, 9, 10], and interaction of polymer gels with surfactants [6, 11, 12] was developed. Phase transitions in a polyampholyte gel [13], gel collapse under the action of an external force [14], and gel interaction with surfactants [15, 16] were also studied experimentally.

In many theoretical studies, counterions are considered point entities. Nonetheless, experiments on various polymer systems involve counterions that are comparable with or exceed the size of a monomer unit. Such are tetraalkylammonium ions [17], aminomethylnaphthalene and aminomethylanthracene [18], and various amphiphilic ions [19]. The size and type of counterions have a substantial effect on the behavior of many polymer systems: e.g., the titration of polymeric acids [20, 21], the structure of polyelectrolyte brushes [22], the adsorption kinetics of a diblock copolymer on a hydrophobic surface [23], polyelectrolyte interaction with an amphiphilic compound, the viscosity of aqueous suspensions of ionic polymer latexes [24], etc. In some experimental studies [25–28], the influence of the type of counterion on the swelling and collapse of a polyelectrolyte gel was examined. In particular, Starodoubtsev et al. [25] investigated the specifics of the formation of ion pairs with counterions of different chemical structures. It was found that, the stronger the tendency toward the formation of ion pairs, the better the quality of the solvent in which the system collapses. These results agree well with theoretical predictions for poly-

electrolyte solutions [29] and a weakly charged polymer gel [30]. Boyd and Bunzl [31] studied volume changes that accompany the selective binding of ions in ion-exchange reactions between aqueous electrolyte mixtures and a polyelectrolyte gel based on polystyrenesulfonic acid. The counterions were tetraalkylammonium ions, which have a greater size than the gel monomer unit.

A number of theoretical studies have been reported in which the influence of the size of counterions on various processes in polymer systems is taken into account. For example, the selective interaction of a polyelectrolyte gel with counterions of different sizes was studied in [32, 33] with allowance for electrostatic forces alone. Jiang et al. [34] examined the interaction of counterions with linear polyelectrolyte macromolecules. An electrostress diffusion coupling model was formulated in [35] to describe the deformation dynamics of a polyelectrolyte gel with different counterions in the presence of an external electric field. However, as far as we know, many problems relating to the effect of short-range interaction of counterions with chains and with one another on the phase behavior of polyelectrolyte systems still remain an open question.

In this study, we extended the theory of swelling and collapse of weakly charged polyelectrolyte gels to the case of counterions of a finite size that experience both counterion-counterion and counterion-network unit interactions. The possibility of ion-pair formation is also taken into account in this case.

MODEL

We consider a weakly charged polymer network with counterions that occur in excess solvent. Let us assume that the polymer network is ideal, i.e., all subchains are identical and are composed of N units. The total number of monomer units is N_p , and the proportion of charged units is f . Thus, the number of univalent counterions in the gel, N_c , is defined from the condition of macroscopic electroneutrality of the system as $N_c = fN_p$. The monomer units and counterion are modeled by hard spheres with radii r_p and r_c , respectively. It is assumed that their ratio $b = r_c/r_p$ can vary from zero (point counterions) to a certain, relatively large value (bulky counterions). Let β be the fraction of counterions that form ion pairs with charged monomer units. We take the ion pair to be a sphere with a volume equal to the total volume of the monomer unit and the counterion and with a radius defined by $r_{ip} = (r_p^3 + r_c^3)^{1/3}$. It is assumed that the network is formed in a θ solvent, in which the statistics of subchains is Gaussian [5]. Then, the volume fraction of the polymer in the given state is defined by the ratio $\Phi_0 \approx N^{-1/2}$. A change in the gel volume depending on solvent quality is characterized by the swelling ratio α

$$\alpha^3 = \frac{V}{V_0} = \frac{\Phi_0}{\Phi}$$

Here, V , Φ , V_0 , and Φ_0 are the volume and the volume fraction of network units in the and initial final states, respectively.

The free energy of gel can be expressed as the sum of four terms corresponding to translational motion of counterions, F_{trans} ; elasticity of subchains, F_{el} ; excluded-volume interactions between monomer units and counterions, F_{vol} ; and electrostatic term relating to ion-pair formation, F_{ip} as follows:

$$F = F_{\text{trans}} + F_{\text{el}} + F_{\text{vol}} + F_{\text{ip}}$$

The free energy of the translational motion of counterions is defined by the standard expression [36]

$$F_{\text{trans}} = kTN_c(1 - \beta)\ln(\Phi_c(1 - \beta)),$$

where the volume fraction of counterions is related to the volume fractions of gel monomer units by $\Phi_c = f\Phi b^3$, k is the Boltzmann constant, and T is the absolute temperature.

The free energy term due to subchain elasticity is defined in the Flory approximation [36] as

$$F_{\text{el}} = \frac{3}{2}kTv\alpha^2$$

(the total number of subchains in gel is $v = N_p/N$, and the logarithmic term may be ignored).

To calculate the free energy of excluded-volume interactions, we will use the virial approximation. Let us assume that there are three types of particles in the system: monomer units, counterions, and ion pairs. The symbols n_p , n_c , and n_{ip} denote the concentrations of monomer units that are not involved in ion pairs, free counterions, and ion pairs, respectively. Then the free energy with allowance for two- and three-body interactions, will be written as

$$\begin{aligned} \frac{F_{\text{vol}}}{kTV} = & B_{pp}n_p^2 + B_{cc}n_c^2 + B_{ip}n_{ip}^2 + 2B_{pc}n_p n_c \\ & + 2B_{pip}n_p n_{ip} + 2B_{cip}n_c n_{ip} + C_{3p}n_p^3 + 3C_{2p1c}n_p^2 n_c \\ & + 3C_{2c1p}n_p n_c^2 + C_{3c}n_c^3 + C_{3ip}n_{ip}^3 + 3C_{2p1ip}n_p n_{ip}^2 \\ & + 3C_{2ip1p}n_p n_{ip}^2 + 3C_{2ip1c}n_c n_{ip}^2 + 3C_{2c1ip}n_c^2 n_{ip} \\ & + 6C_{1p1c1ip}n_p n_c n_{ip}. \end{aligned}$$

The subscripts p , c , and ip at the virial coefficients denote the monomer unit, counterion, and ion pair, respectively. For example, B_{pc} is the second virial coefficient, which describes monomer unit-counterion interaction, C_{2ip1p} is the third virial coefficient, which describes the three-body interaction between two ion

pairs and a monomer unit, etc. The calculation of the virial coefficients is detailed in the appendix.

The concentration of monomer units that are not involved in ion pairs is related to the concentration of all network units via the expression $n_p = (1 - \beta f)n$. The concentration of free counterions is given as $n_c = f(1 - \beta)n$, and that of ion pairs is expressed as $n_{ip} = \beta f n$. The concentration n is related to the concentration of network units in the initial state, n_0 , by the expression

$$n = \frac{n_0}{\alpha^3} \approx \frac{1}{v_0 N^{1/2} \alpha^3}, \quad v_0 = \frac{4}{3} \pi r_p^3$$

Thus, the contribution of excluded-volume interactions to the total free energy of the system can be described as

$$\frac{F_{vol}}{N_p kT} = B n_0 \alpha^{-3} + C n_0^2 \alpha^{-6},$$

where

$$B = B_{pp}(1 - \beta f)^2 + 2B_{pc}(1 - \beta f)(1 - \beta)f + B_{cc}f^2(1 - \beta)^2 + 2B_{pip}(1 - \beta f)\beta f + 2B_{cip}(1 - \beta)f^2\beta + B_{ip}\beta^2 f^2$$

and

$$C = C_{3p}(1 - \beta f)^3 + 3C_{2p1c}(1 - \beta f)^2(1 - \beta)f + 3C_{2p1ip}(1 - \beta f)^2\beta f + 3C_{1p2c}(1 - \beta f)(1 - \beta)^2 f^2 + 6C_{1p1cip}(1 - \beta f)(1 - \beta)f^2\beta + 3C_{1p2ip}(1 - \beta f)\beta^2 f^2 + C_{3c}(1 - \beta)^3 f^3 + 3C_{2c1ip}(1 - \beta)^2 f^3\beta + 3C_{1c2ip}(1 - \beta)f^3\beta^2 + C_{3ip}\beta^3 f^3.$$

The free energy term due to the formation of ion pairs was calculated in the same manner as in [30]. The energy of the Coulomb interaction between the charged network unit and the counterion in an ion pair is

$$E = -\frac{e^2}{\epsilon_d r_p (1 + b)}$$

Here, ϵ_d is the dielectric permittivity of the solvent and e is the electron charge. The number of ways L of selecting $\beta N_c \gg 1$ counterions to form ion pairs out of their total number $N_c \gg 1$ is determined by the binomial coefficient

$$L = \frac{N_c!}{(N_c \beta)!(N_c(1 - \beta))!} \approx \frac{N_c^{N_c}}{(N_c \beta)^{N_c \beta} (N_c(1 - \beta))^{N_c(1 - \beta)}}.$$

Consequently, the free energy of βN_c ion pairs is

$$\frac{F_{ip}}{kT} = \frac{N_c \beta E}{kT} - \ln L = N_c(1 - \beta) \ln(1 - \beta) + N_c \beta \ln \beta - N_c \frac{u_0 \beta}{(1 + b)}$$

$$u_0 = \frac{e^2}{\epsilon_d r_p kT},$$

and the total free energy of the system can be expressed as

$$\begin{aligned} \frac{F}{N_p kT} &= f(1 - \beta) \ln(fb^3 \Phi_0 \alpha^{-3}(1 - \beta)) \\ &+ B n_0 \alpha^{-3} + C n_0^2 \alpha^{-6} + \frac{3\alpha^2}{2N} + f(1 - \beta) \ln(1 - \beta) \\ &+ f\beta \ln \beta - \frac{f u_0 \beta}{1 + b}. \end{aligned}$$

MAIN RESULTS

In order to find the equilibrium swelling ratio and the amount of ion pairs formed, it is necessary to calculate the free energy minimum determined by setting the corresponding partial derivatives equal zero,

$$\frac{\partial F}{\partial \alpha} = 0, \quad \frac{\partial F}{\partial \beta} = 0.$$

This system was solved numerically at $f = 0.08$, $N = 100$, $\Phi_0 = 0.1$, and different values of relative temperature $t = (T - \theta)/\theta$ over the range of -0.9 to $+0.6$. Here, θ is the temperature at which the second virial coefficient for monomer unit interaction B_{pp} becomes zero (see Appendix). A decrease in the relative temperature corresponds to a decline in solvent quality. We revealed the dependence of the gel swelling ratio and the fraction of counterions that form ion pairs on the relative temperature at different values of u_0 . This parameter characterizes the dielectric permittivity of solvent in a gel. At $u_0 = 1$, the permittivity is high ($\epsilon_d \approx 80$, a value that approximately corresponds to water); in the case of organic solvents, ϵ_d may be an order of magnitude lower.

Let us first examine the behavior of the gel with different potentials of interaction between particles at a high permittivity ($u_0 = 1$). Then the amount of ion pairs

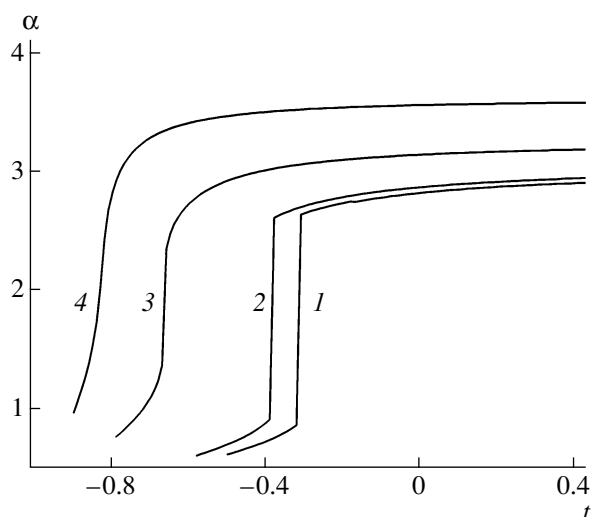


Fig. 1. Dependence of the swelling ratio α of polyelectrolyte gel on the relative temperature t for $b =$ (1) 0, (2) 1, (3) 3, and (4) 5 at $u_0 = 1$ and $\epsilon_{cc} = \epsilon_{cip} = \epsilon_{pc} = \epsilon_{pip} = \epsilon_{ipip} = 0$.

in the swollen gel is small and has no substantial effect on the behavior of the system. The gel swelling ratio is determined exceptionally by the osmotic pressure of counterions and excluded-volume interactions.

Assume that short-range attraction is possible between monomer units only and counterion-counterion and counterion-monomer unit interactions are repulsive because of the excluded-volume effect. The dependence of the network swelling ratio on relative temperature is shown for this case in Fig. 1. Different curves correspond to different values of b , the value of $b = 0$ corresponds to the gel with point (ideal) counterions; the higher the value of b , the greater the counterion size. An increase in the size of the counterion leads to an increase in the gel swelling ratio. This change is associated with the enhancement of excluded-volume interactions, which (together with the thermal motion of counterions) facilitate an increase in the gel volume. The temperature of transition from the swollen to the collapsed state becomes substantially lower in this case; i.e., the solvent must be significantly poorer for gel units (relative to the case of point counterions) in order to mitigate the pushing excluded-volume interactions. A change in the size of counterions alters not only the swelling ratio, but also the type of transition from the swollen to the collapsed state. This transition is a first-order phase transition for a gel with small counterions and a continuous process for the gel with large counterions. This crossover from one type of transition to another is due to the fact that the change in the size of counterions increases the contribution of excluded-volume interactions and, starting from a certain value, these interactions make a prevalent contribution to osmotic pressure; i.e., the behavior of the system becomes similar to that of neutral gels. It is well known

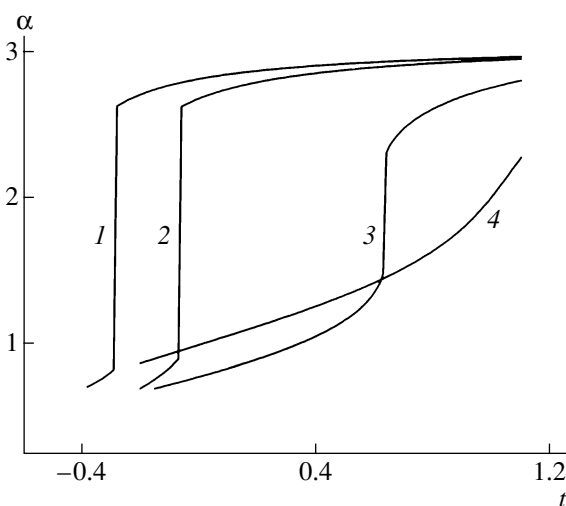


Fig. 2. Dependence of the swelling ratio α of polyelectrolyte gel on the relative temperature t for $b =$ (1) 0, (2) 1, (3) 3, and (4) 5 at $u_0 = 1$ and $\epsilon_{cc} = \epsilon_{cip} = \epsilon_{ipip} = \epsilon_{pc} = \epsilon_{pip} = 3\epsilon_{pp} = 3k\theta \ln(8/7)$.

[36] that the swelling and collapse of neutral gels occur in the continuous mode.

Let us assume now that there is short-range attraction in the system between all types of particles (counterions, monomer units, and ion pairs) and the interaction between monomer units varies from repulsion to attraction. Such a situation is possible when counterions have a complex chemical structure in which hydrophobic groups are present along with charged groups. To theoretically simulate these conditions, it is necessary to select such values of the energy parameters ϵ_{ij} that the corresponding second virial coefficients will be negative. The simplest choice is when all ϵ_{ij} parameters (except one) are equal to one another, $\epsilon_{cc} = \epsilon_{cip} = \epsilon_{ipip} = \epsilon_{pc} = \epsilon_{pip} = 3\epsilon_{pp} = 3k\theta \ln(8/7)$. The temperature dependence of the swelling ratio is shown in Fig. 2. Intuitively, it is guessed that the presence of additional attraction in the system must stimulate the collapse of the gel. Indeed, as the counterion size increases, the collapse becomes feasible even under the conditions when the solvent is good for network units. In other words, the attraction of counterions to one another and to network units induces the transition to the collapsed state. The increase in the size of counterions smoothes the transition and decreases the gel swelling ratio. Note that a decrease in the gel swelling ratio as a result of attraction between counterions was experimentally observed in a study [37] with hydrophobic tetraalkylammonium ions as counterions.

Let us now consider the case of low permittivity (organic solvents) and select $u_0 = 25$. In this case, the amount of ion pairs is relatively large (Figs. 3, 4) and their presence has a substantial effect on the behavior of the system.

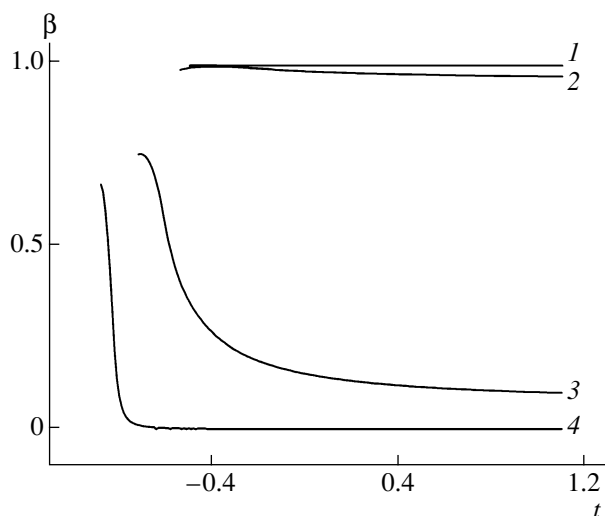


Fig. 3. Dependence of the proportion of counterions that form ion pairs, β , on the relative temperature t for $b = (1) 0, (2) 1, (3) 3,$ and $(4) 5$ at $u_0 = 25$ and $\epsilon_{cc} = \epsilon_{cip} = \epsilon_{pc} = \epsilon_{pip} = \epsilon_{ipip} = 0$.

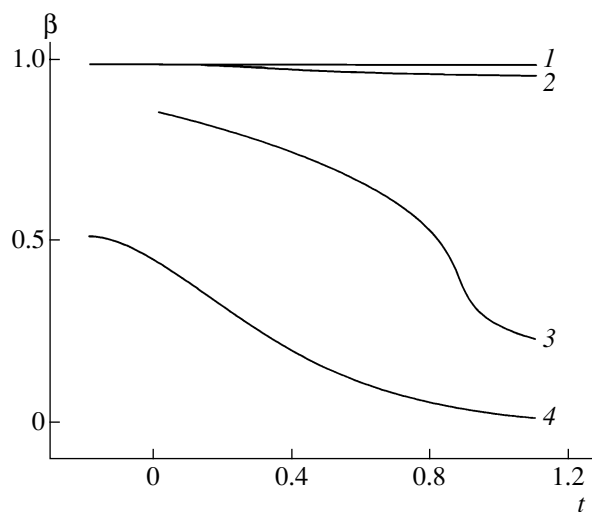


Fig. 4. Dependence of the proportion of counterions that form ion pairs, β , on the relative temperature t for $b = (1) 0, (2) 1, (3) 3,$ and $(4) 5$ at $u_0 = 25$ and $\epsilon_{cc} = \epsilon_{cip} = \epsilon_{ipip} = \epsilon_{pc} = \epsilon_{pip} = 3\epsilon_{pp} = 3k\theta\ln(8/7)$.

We assume that interactions between all types of particles in the system (except the monomer–monomer interaction) are reduced to repulsion due to excluded volume. The dependence of the proportion of counterions involved in ion pairs on the relative temperature is shown in Fig. 3. Almost 100% of point counterions and counterions that are comparable in size with the monomer unit ($b = 1$) form ion pairs. In this state, the counterions lose their mobility and their contribution to the osmotic pressure becomes zero. The gel behaves as virtually neutral in this case (Fig. 5, $b = 0$ and $b = 1$ curves). The fraction of ion pairs in the gel with bulky counterions ($b = 3$ or 5) is strongly dependent on temperature: at high temperatures (swollen state), a relatively small amount of counterions take part in the formation of ion pairs, but their proportion in the collapsed gel increases considerably (Fig. 3). The dependence of the swelling ratio of the gel on the counterion size is practically the same as in the case of high permittivity (Fig. 1). Note that the transition becomes smoother with an increase in the counterion size at $u_0 = 1$, whereas the opposite trend is observed at $u_0 = 25$; the larger the counterions, the more abrupt the transition to the collapsed state (Fig. 5). The latter effect is explained in terms of increase in the amount of osmotically active counterions with an increase in b ; the greater the number of free counterions, the more dramatic will be the transition.

Assume that there is short-range attraction between all types of particles in a low-permittivity solvent as well, and interaction of network units with one another varies from repulsion to attraction. It is obvious that the presence of the additional attraction of counterions to network monomer units increases the fraction of ion pairs (Fig. 4). Unlike the cases considered above, it is

difficult to unequivocally define the dependence of the gel swelling ratio on the counterion size in the given case (Fig. 6), since there are many factors that have an effect on the system and the significance of each of the factors depends on the size of counterions. For example, the existence of attraction by no means affects the behavior of the gel with point counterions ($b = 0$). However, for a gel with counterions that have a size comparable to that of the monomer unit ($b = 1$), both attraction between particles and the presence of a large amount of ion pairs are significant; for this reason, the collapse

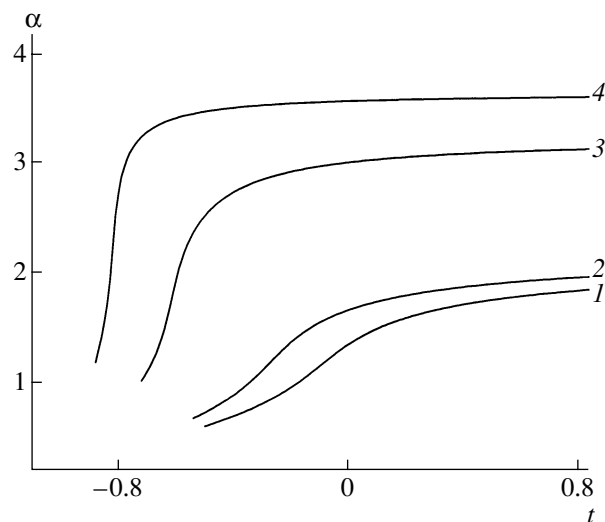


Fig. 5. Dependence of the swelling ratio α of polyelectrolyte gel on the relative temperature t for $b = (1) 0, (2) 1, (3) 3,$ and $(4) 5$ at $u_0 = 25$ and $\epsilon_{cc} = \epsilon_{cip} = \epsilon_{pc} = \epsilon_{pip} = \epsilon_{ipip} = 0$.

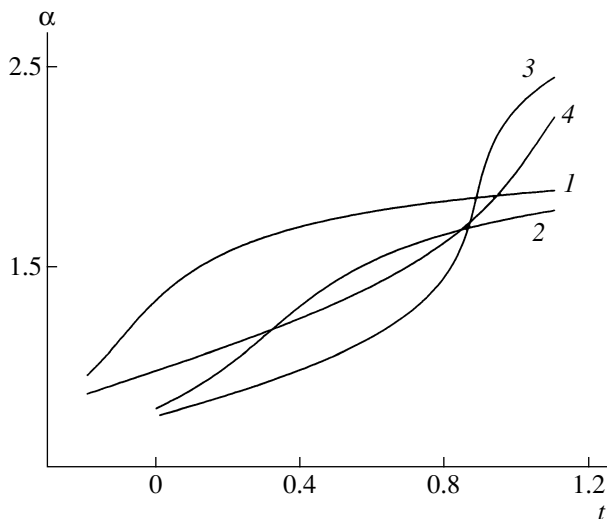


Fig. 6. Dependence of the swelling ratio α of polyelectrolyte gel on the relative temperature t for $b = (1) 0, (2) 1, (3) 3, \text{ and } (4) 5$ at $u_0 = 25$ and $\epsilon_{cc} = \epsilon_{cip} = \epsilon_{pip} = \epsilon_{pc} = \epsilon_{pip} = 3\epsilon_{pp} = 3k\theta \ln(8/7)$.

curve is close to that for a neutral gel. The swelling ratios for gels with different bulky counterions ($b = 3$ and 5) at a high temperature slightly differ because the two factors counterbalance one another. On the one hand, the larger the counterion, the smaller is the number of ion pairs formed and the higher the osmotic pressure of free counter ions. On the other hand, the effect of swelling due to the translational motion of counterions is compensated by the effect of attraction of counterions to one another and to chain units. Therefore, the difference in the swelling ratio between gels with the counterions sizes of $r_c = 3r_p$ and $5r_p$ is small.

CONCLUSIONS

It has been shown that the size of the counterion of a polyelectrolyte gel has a substantial effect on the swelling ratio and the character of transition to the collapsed state. In the polyelectrolyte mode (high solvent permittivity), an increase in the counterion size makes the transition from the swollen to the collapsed state smoother, regardless of the character of interaction of counterions with one another and with network units. In this case, the gel swelling ratio in a good solvent increases with an increase in the size of counterions if excluded-volume interactions alone exist in the system and decreases if short-range forces of attraction of counterions to one another and to gel units operate. In the case when the formation of ion pairs is favored (low solvent permittivity), an increase in the counterion size facilitates a decrease in the fraction of ion pairs and an increase in the gel swelling ratio in a good solvent.

The second and third virial coefficients B_{ij} and C_{ijk} for a multicomponent system are expressed via the potentials of pair interaction between particles $U_{ij}(r)$ in the following manners [37]

$$B_{ij} = \frac{1}{2} \int dV \left(1 - \exp\left(-\frac{U_{ij}(r_{ij})}{kT}\right) \right)$$

$$C_{ijk} = \frac{1}{6} \int dV_i dV_j \left(1 - \exp\left(-\frac{U_{ij}(r_{ij})}{kT}\right) \right) \times \left(1 - \exp\left(-\frac{U_{jk}(r_{jk})}{kT}\right) \right) \left(1 - \exp\left(-\frac{U_{ik}(r_{ik})}{kT}\right) \right).$$

Let us denote by B_{pp} the second virial coefficient of interaction of monomer units with one another. We will assume that the interaction potential U_{pp} is approximated by the stepwise function

$$U_{pp}(r) = \begin{cases} \infty, & r < 2r_p \\ -\epsilon_{pp}, & 2r_p < r < 4r_p, \quad \epsilon_{pp} > 0 \\ 0, & r > 4r_p. \end{cases}$$

Then $\frac{B_{pp}}{v_0} = 4 + 28 \left(1 - \exp\left(\frac{\epsilon_{pp}}{kT}\right) \right)$ and the θ temperature is defined by the equation $B_{pp} = 0$, which corresponds to $\epsilon_{pp}/k\theta = \ln(8/7)$.

The second virial coefficients that describe interactions between other particles are calculated in the same manner. The potentials of interaction between the particles and the corresponding values of the second virial coefficients are given below:

$$U_{pc}(r) = \begin{cases} \infty, & r < r_p + r_c \\ -\epsilon_{pc}, & r_p + r_c < r < 2(r_p + r_c), \quad \epsilon_{pc} > 0 \\ 0, & r > 2(r_p + r_c) \end{cases}$$

$$\frac{B_{pc}}{v_0} = \frac{1}{2}(1+b)^3 + \frac{7}{2}(1+b)^3 \left(1 - \exp\left(\frac{\epsilon_{pc}}{kT}\right) \right)$$

$$U_{cc}(r) = \begin{cases} \infty, & r < 2r_c \\ -\epsilon_{cc}, & 2r_c < r < 4r_c, \quad \epsilon_{cc} > 0 \\ 0, & r > 4r_c \end{cases}$$

$$\frac{B_{cc}}{v_0} = 4b^3 + 28b^3 \left(1 - \exp\left(\frac{\epsilon_{cc}}{kT}\right) \right)$$

$$U_{pip}(r) = \begin{cases} \infty, & r < r_p + r_{ip} \\ -\varepsilon_{pip}, & r_p + r_{ip} < r < 2(r_p + r_{ip}), \quad \varepsilon_{pip} > 0 \\ 0, & r > 2(r_p + r_{ip}) \end{cases}$$

$$\frac{B_{pip}}{v_0} = \frac{1}{2}(1+g)^3 + \frac{7}{2}(1+g)^3 \left(1 - \exp\left(\frac{\varepsilon_{pip}}{kT}\right)\right)$$

$$U_{cip}(r) = \begin{cases} \infty, & r < r_{ip} + r_c \\ -\varepsilon_{cip}, & r_{ip} + r_c < r < 2(r_{ip} + r_c), \quad \varepsilon_{cip} > 0 \\ 0, & r > 2(r_{ip} + r_c) \end{cases}$$

$$\frac{B_{cip}}{v_0} = \frac{1}{2}(g+b)^3 + \frac{7}{2}(g+b)^3 \left(1 - \exp\left(\frac{\varepsilon_{cip}}{kT}\right)\right)$$

$$U_{iip}(r) = \begin{cases} \infty, & r < 2r_{ip} \\ -\varepsilon_{iip}, & 2r_{ip} < r < 4r_{ip}, \quad \varepsilon_{iip} > 0 \\ 0, & r > 4r_{ip} \end{cases}$$

$$\frac{B_{iip}}{v_0} = 4(1+b^3) + 28(1+b^3) \left(1 - \exp\left(\frac{\varepsilon_{iip}}{kT}\right)\right),$$

where $g = r_{ip}/r_p$. If $\varepsilon_{ij} = 0$, the interaction of two particles reduces solely to repulsion due to excluded volume. If $\varepsilon_{ij} > 0$, short-range attraction between the particles is possible.

We will assume that the third virial coefficients slightly depend on temperature and set $\varepsilon_{ij} = 0$ in the pair interaction potential. The third virial coefficients for this model [37] are given below

$$\frac{C_{3p}}{v_0^2} = 5, \quad \frac{C_{3c}}{v_0^2} = 5b^6$$

$$\frac{C_{2p1c}}{v_0^2} = \frac{1}{6}(1 + 6b + 15b^2 + 8b^3)$$

$$\frac{C_{2c1p}}{v_0^2} = \frac{1}{6}(b^6 + 6b^5 + 15b^4 + 8b^3)$$

$$\frac{C_{2p1ip}}{v_0^2} = \frac{1}{6}(1 + 6g + 15g^2 + 8g^3)$$

$$\frac{C_{2c1ip}}{v_0^2} = \frac{1}{6}(b^6 + 6b^5g + 15b^4g^2 + 8g^3b^3)$$

$$\frac{C_{3ip}}{v_0^2} = 5g^6$$

$$\frac{C_{1p2ip}}{v_0^2} = \frac{1}{6}(g^6 + 6g^5 + 16g^4 + 8g^3)$$

$$\frac{C_{1c2ip}}{v_0^2} = \frac{1}{6}(g^6 + 6g^5b + 15g^4b^2 + 8g^3b^3)$$

$$\frac{C_{1p1c1ip}}{v_0^2} = \frac{1}{6}(b^3 + g^3 + 3g^2b + 3gb^2 + 3bg^3 + 9g^2b^2 + 3gb^3 + 3b^2g^3 + 3b^3g^2 + b^3g^3)$$

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