

Effect of Monovalent–Divalent Cation Exchange on the Swelling of Polyacrylate Hydrogels in Physiological Salt Solutions

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The volume transition induced by monovalent–divalent cation exchange of fully neutralized polyacrylate hydrogels was investigated in aqueous NaCl solutions. The variation of the osmotic swelling pressure, shear modulus, and mixing pressure was measured when Na⁺ ions were substituted by divalent or trivalent cations. Alkali metal salts move freely throughout the entire network, and alkaline earth metal salts (CaCl₂, SrCl₂) promote aggregation of polyacrylate chains, but these aggregates are relatively weak. Transition metal salts (CoCl₂, NiCl₂) form stronger interchain associates. Rare earth cations (La³⁺ and Ce³⁺) bind practically irreversibly to the polymer. Experimental data indicate that transition metal cations modify both the elastic and mixing components of the free energy, while alkaline earth metal cations affect primarily the mixing term. The behavior of freely swollen gels was compared with similar gels subjected to uniaxial compression. In uniaxially compressed gels, volume transition occurs at lower cation concentrations than in the corresponding undeformed gels. The shift of the transition point increases with the deformation ratio and is larger for Co²⁺ than for Ca²⁺.

Introduction

It is important to understand the osmotic and structural changes of polymer gels induced by addition of salts with respect to many physical and chemical processes in biological systems. It has been demonstrated that monovalent–divalent cation exchange plays a significant role in physiological processes such as nerve excitation and muscle contraction.^{1–3} Therefore, investigating the volume transition of synthetic polyelectrolyte gel model systems is expected to lead to a better understanding of these biological phenomena and their underlying molecular mechanisms.

The swelling behavior of charged polymer gels was described by Flory⁴ and Katchalsky.⁵ In many cases, salts can drastically change the physical properties of dissolved macromolecules.^{6,7} In gels, salt addition may cause a volume transition.^{8–11} These effects are usually explained by changes of the water structure induced by ion hydration.¹²

In a previous paper,¹¹ we reported swelling measurements on polyacrylate hydrogels in solutions of alkali metal and alkaline earth metal salts. In these experiments the concentrations of biologically relevant cations (Ca²⁺, Na⁺, K⁺) were varied in the physiological range. It was demonstrated that (1) in the presence of alkaline earth metal ions (Ca²⁺, Sr²⁺, Ba²⁺) gels exhibit a sudden and reversible volume change and (2) the magnitude of the volume change is governed by the ratio of divalent cations to monovalent cations.

Many previous studies have considered the effects of different factors such as electrolyte concentration, solvent

quality, and external mechanical and electric fields on the thermodynamic properties of swollen polyelectrolyte networks.^{4,5,13–18} The present work examines how electrolyte composition and mechanical deformation affect the equilibrium swelling degree and volume transition of polyacrylate hydrogels. The shear modulus and the osmotic swelling pressure are measured as a function of the ionic content and composition, and deformation ratio. New experimental results are reported for both isotropically and anisotropically deformed polyacrylate gels immersed in aqueous salt solutions containing monovalent, divalent, and trivalent cations.

We address the following specific questions: Is the volume transition induced by monovalent–divalent cation exchange in fully neutralized sodium polyacrylate gels affected by the type of divalent cation? Does the reversibility of the volume transition depend on the type and ion valence of the cations? How are the components of the network free energy modified by different divalent cations? Does the formation of a metal–polyion complex affect the static elastic properties of these gels? Does the deformation of the gel influence the volume transition of polyacrylate hydrogels?

Theory

Isotropic Swelling of Polyelectrolyte Gels. In agreement with previous experimental evidence,^{16–21} we adopt the assumption that the total free energy of a polyelectrolyte gel can be expressed as the sum of three terms

$$\Delta F_{\text{tot}} = \Delta F_{\text{el}} + \Delta F_{\text{mix}} + \Delta F_{\text{ion}} \quad (1)$$

where ΔF_{el} is the free energy of the elastic deformation of

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the gel, ΔF_{mix} is the free energy of mixing of polymer segments and solvent molecules, and ΔF_{ion} is the ionic contribution arising from the difference in concentrations of mobile ions in the gel and in the liquid phase outside the gel.

It should be noted that in eq 1 electrostatic interactions due to the presence of charges on the network chains are not considered. It was pointed out by Khoklov et al.²² that the electrostatic term (Coulomb interactions within the gel) is much smaller than the free energy due to the entropy of mobile ions.

The equilibrium condition of the freely swollen network is determined by the minimization of the total free energy. This implies that (1) the osmotic pressure inside the gel Π_{gel} is equal to the osmotic pressure of the surrounding solution Π_{sol}

$$\Pi_{\text{gel}} = \Pi_{\text{sol}} \quad (2)$$

and (2) the chemical potential of each component is the same inside and outside the gel

$$\partial \Delta F_{\text{gel}} / \partial n_{i,\text{gel}} = \partial \Delta F_{\text{sol}} / \partial n_{i,\text{sol}} \quad (3)$$

where ΔF_{gel} and ΔF_{sol} is the free energy of the gel and the solution, respectively, and $n_{i,\text{gel}}$ and $n_{i,\text{sol}}$ are the number of moles of the i th component of solvent mixture or salt solution inside the gel and the surrounding solution.

The osmotic swelling pressure ω of a polyelectrolyte gel swollen in the solution of a monovalent salt is given as

$$\omega = \Pi_{\text{mix}} + \Pi_{\text{el}} + \Pi_{\text{ion}} = -(RT/V_1)[\ln(1 - \varphi) + \varphi + \chi\varphi^2] - RTA\nu\varphi^{1/3} + RT(i\varphi/V_m + 2c_{\text{gel}} - 2c_{\text{sol}}) \quad (4)$$

where φ is the volume fraction of the polymer, χ is the Flory–Huggins interaction parameter (in general it depends on the polymer concentration, i.e., $\chi = \chi_0 + \chi_1\varphi + \dots$), V_1 is the molar volume of the solvent, A is a constant of the order of unity, ν is the concentration of network chains, i is the fraction of the charged monomers, V_m is the molar volume of the monomer, c_{gel} and c_{sol} is the concentration of added salt in the gel and in the equilibrium solution, respectively. R is the gas constant and T is the absolute temperature. According to the Donnan model, the equation describing the distribution of salt ions between the gel and the surrounding solution is⁴

$$c_{\text{gel}}(c_{\text{gel}} + i\varphi/V_m) = c_{\text{sol}}^2 \quad (5)$$

Equation 5 assumes that the activity coefficient of the ions in the gel is the same as that in the solution. It should be noted, however, that counterion condensation results in lowering the effective charge of the polymer chains, and reducing the osmotic activity coefficient of the salt ions in the gel.^{23,24} Counterion condensation occurs when the Coulombic interaction energy becomes comparable to the thermal energy; i.e., the charge density exceeds a critical threshold value

$$\alpha = d/\lambda_B \quad (6)$$

where d is the distance between neighboring charges and λ_B is the Bjerrum length ($=7 \text{ \AA}$ in water at $25 \text{ }^\circ\text{C}$).

It should be noted that the experimental results discussed in the present paper are obtained at relatively high charge densities where a certain fraction of the counterions is condensed on the polyelectrolyte chains.

Anisotropic Swelling. When the gel is deformed, eq 4 needs to be modified. Let us consider a gel which has a fixed length in one direction and is allowed to swell in the perpendicular directions. In this case, we have

$$\alpha_{\parallel} = \alpha_x = L/L_0, \quad \alpha_{\perp} = \alpha_y = \alpha_z, \quad \text{and } \alpha_{\parallel}\alpha_{\perp}^2 = \varphi^{-1} \quad (7)$$

where α_{\parallel} and α_{\perp} are the deformation ratios in parallel and perpendicular directions, respectively, L is the length of the deformed gel, and L_0 is that of the undeformed specimen.

The elastic free energy of the swollen deformed gel is given by²⁵

$$\Delta F_{\text{el}} = (ART\nu/2)[\alpha_{\parallel}^2 + 2/(\varphi\alpha_{\parallel}) - 3] \quad (8)$$

and the swelling pressure of a uniaxially deformed gel is

$$\omega = -(RT/V_1)[\ln(1 - \varphi) + \varphi + \chi\varphi^2] - RTA\nu\varphi^{1/3}\alpha_{\parallel}^{-1} + RT(i\varphi/V_m + 2c_{\text{gel}} - 2c_{\text{sol}}) \quad (9)$$

In the case of the freely swollen undeformed network, $\alpha_{\parallel} = 1$, and eq 9 reduces to eq 4.

Experimental Section

Gel Preparation. Sodium polyacrylate gels were made by free-radical copolymerization of partially neutralized acrylic acid and N,N' -methylenebis(acrylamide) cross-linker in aqueous solution according to a procedure described by Sugatani et al.²⁶ The monomer concentration was 30% (w/w), and 35% of the monomers were neutralized by sodium hydroxide before polymerization. Dissolved oxygen was removed by bubbling nitrogen through the solution. Then ammonium persulfate (0.5 g/L) was added to initiate the polymerization reaction. Gelation was carried out at $80 \text{ }^\circ\text{C}$.

Gel beads were made by polymerization in silicone oil (viscosity: 1000 cPs), that was previously degassed with nitrogen. Spherical droplets (diameter $< 1 \text{ mm}$) of the mixture were injected into the silicone oil. After gelation, gel samples were completely neutralized and washed in deionized water to remove all extractable materials (e.g., sol fraction). Water was renewed every day for 2 weeks.

For the mechanical measurements, cylindrical gel specimens (1 cm height, 1 cm diameter) were made in a special mold using the same cross-linking procedure. Gel cylinders were neutralized and washed for several weeks with deionized water before the experiments.

Osmotic Deswelling Measurements. Osmotic deswelling of polyacrylate gels was induced by aqueous solutions of poly(vinylpyrrolidone) (PVP, molecular weight: 29 kDa). The osmotic pressure of the PVP is known from independent measurements.^{27,28} The swollen network was separated from the solution by a semipermeable membrane (dialysis bag), which prevented the penetration of the polymer molecules

into the gel. At equilibrium, the swelling pressure of the gel inside the dialysis bag is equal to the osmotic pressure of the PVP solution outside. The size and the weight of the gel samples were measured when equilibrium was attained. The reversibility of the deswelling process was checked by transferring the deswollen gels into PVP solutions having different osmotic pressures. No significant difference was found between swelling degrees obtained by decreasing or increasing osmotic pressures.

When the gel beads were equilibrated with salt solutions, it was assumed that the salt concentration in the liquid phase outside the gel sample was unchanged (infinite bath).

Elastic Modulus Measurements. Uniaxial compression measurements were performed on gel cylinders in equilibrium with salt solutions using a TA.XT2I HR texture analyzer (Stable Micro Systems). This apparatus measures the deformation (± 0.001 mm) as a function of the applied force (± 0.01 N). Measurements were performed at deformation ratios $0.7 < \alpha_{||} < 1$. Typical sample sizes were as follows: height 0.5–2 cm; diameter 0.5–2 cm. The elastic (shear) modulus, G , was calculated from the nominal stress, σ (force per unit undeformed cross-section), using the equation^{25,29}

$$\sigma = G(\alpha_{||} - \alpha_{||}^{-2}) \quad (10)$$

The same apparatus was used to perform swelling measurements on uniaxially deformed gels. Gel cylinders were compressed between two parallel flat plates, the distance of separation of which was adjusted to impose the desired uniaxial deformation on the sample. During the experiment gel samples were immersed in salt solutions. The time needed to attain equilibrium was about 2–3 weeks depending on the size of the cylinder. The absence of volume change and barrel distortion during these measurements was checked.

Both swelling and mechanical measurements were carried out at 25 ± 0.1 °C.

Results and Discussion

Figure 1 shows the variation of the swelling degree ($1/\varphi$) of sodium polyacrylate hydrogels in different salt solutions as a function of the salt concentration, c_{salt} . The first data points on the y axis correspond to the degree of swelling in 40 mM NaCl solution. In general, salt addition leads to contraction of the gel because ions screen repulsive interactions between charged monomer units. The behavior of these gels exhibit substantial differences in aqueous solutions of 1:1 salt (NaCl), 2:1 salts (CaCl_2 , SrCl_2 , NiCl_2 , CoCl_2), and 3:1 salts (CeCl_3 , LaCl_3). In NaCl solution the variation of the swelling degree is weak. In the presence of divalent cations, however, at a “critical concentration” (or critical ratio of divalent to monovalent cations) a sudden volume change occurs. In solutions of 3:1 salts, the transition point is shifted toward lower cation concentrations.

Figure 2 compares the water uptake of polyacrylate gel beads deswollen in different salt solutions. (To ensure a fair comparison between the data, prior to the swelling experiment identical gel beads were equilibrated with salt solutions containing 40 mM NaCl and 2 mM of the corresponding 2:1 or 3:1 salt. Then the beads were transferred into large

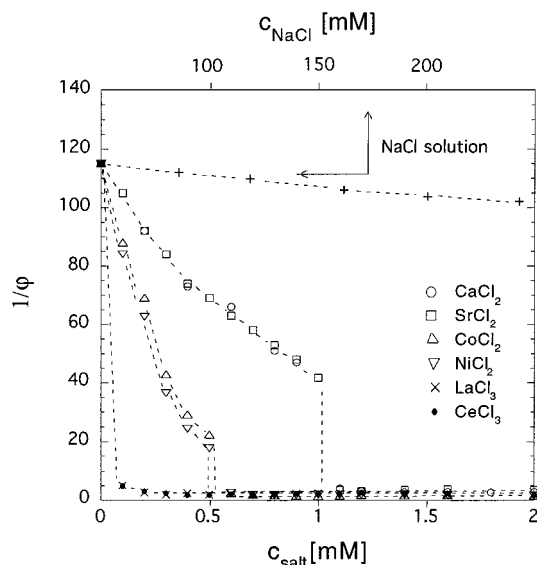


Figure 1. Variation of the degree of swelling ($1/\varphi$) of sodium polyacrylate hydrogels as a function of salt concentration of the surrounding solution.

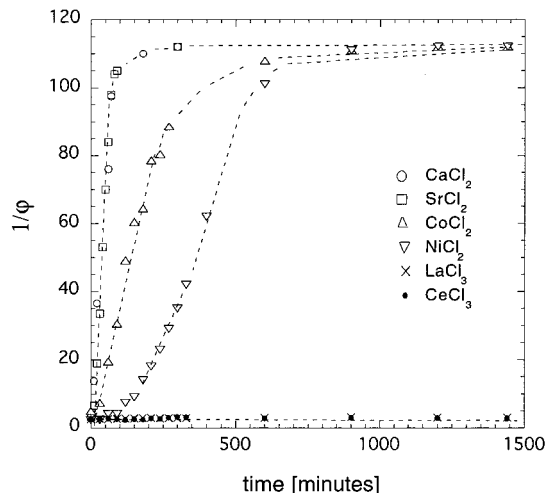


Figure 2. Kinetics of swelling of polyacrylate hydrogels deswollen in different salt solutions.

amount of 40 mM NaCl solution.) There are notable differences among the swelling rates: the water uptake of gels deswollen in solutions of alkaline earth metal salts (CaCl_2 , SrCl_2) is the fastest, followed by gels containing transition metal cations (Co^{2+} , Ni^{2+}). In the case of trivalent cations no appreciable increase in the swelling degree was observed even after 3–4 weeks. On the basis of the data displayed in Figure 2, the relative “stability” of the collapsed state increases in the order $\text{La}^{3+} \approx \text{Ce}^{3+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Ca}^{2+} \approx \text{Sr}^{2+}$.

Volume transition results from the interplay of two main effects: attractive interactions between polymer segments that tend to shrink the gel and repulsion between similarly charged groups (either charged units of the polymer or mobile ions). Therefore, any change in the mixing and elastic interactions, and in the degree of ionization of the network chains should be reflected by a change in the corresponding free energy. There is, however, no well-established relationship between network free energy and the ionic composition of the surrounding solution.

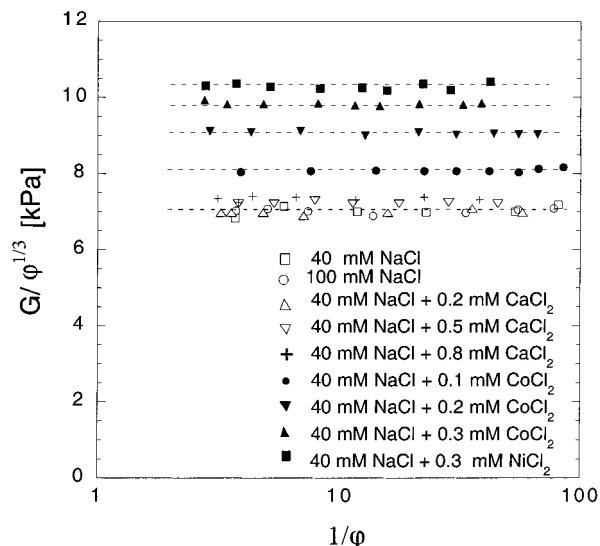


Figure 3. Variation of $G/\phi^{1/3}$ as a function of the swelling degree ($1/\phi$) for polyacrylate hydrogels in different salt solutions.

To reveal the effect of added salts we determined the terms of eq 4 separately. We start with the elastic modulus, G , which is directly related to Π_{el} through the relation^{25,30}

$$G = -\Pi_{el} = G_0\phi^{1/3} \quad (11)$$

where $G_0 = RTAv$.

In Figure 3 is shown the dependence of $G/\phi^{1/3}$ on $1/\phi$ for polyacrylate hydrogels in different salt solutions.

The experimental data indicate that the concentration dependence of the shear modulus can be fairly well described by eq 11 throughout the whole concentration range. (It should be mentioned, however, that in pure water at high swelling degrees ($1/\phi > 100$) significant deviation from the Gaussian network behavior has been observed,¹¹ presumably due to finite extensibility of the network chains.)²⁵ It is apparent that in NaCl solutions, and in solutions of NaCl and CaCl_2 , all data points scatter around the same horizontal straight line; i.e., G_0 is practically independent of the salt concentration and the ionic composition of the solution. Alkali metal and alkaline earth metal ions cause gel contraction, but they do not form additional cross-links. When CaCl_2 is replaced by CoCl_2 , the value of $G/\phi^{1/3}$ becomes higher and increases with increasing salt concentration. A plausible explanation of the increase of $G/\phi^{1/3}$ is complex formation between the transition metal ions and the polyanion. The data shown in Figure 3 suggest that transition metal ions (Co^{2+} , Ni^{2+}) act as cross-linker and contribute to the shear modulus of the gel. Complex formation is, however, reversible; i.e., by decreasing cation concentration, $G/\phi^{1/3}$ decreases.

It is expected that specific interactions between cations and carboxylic groups affect the mixing term of the free energy. The mixing pressure is given by

$$\Pi_{\text{mix}} = \omega + G - \Pi_{\text{ion}} = -\left(\frac{RT}{V_1}\right) [\ln(1-\phi) + \phi + \chi_0\phi^2 + \chi_1\phi^3] \quad (12)$$

where χ_0 and χ_1 are constants. Π_{mix} as a function of ϕ is shown in Figure 4 for polyacrylate gels swollen in salt solutions. It can be seen that both quality and concentration

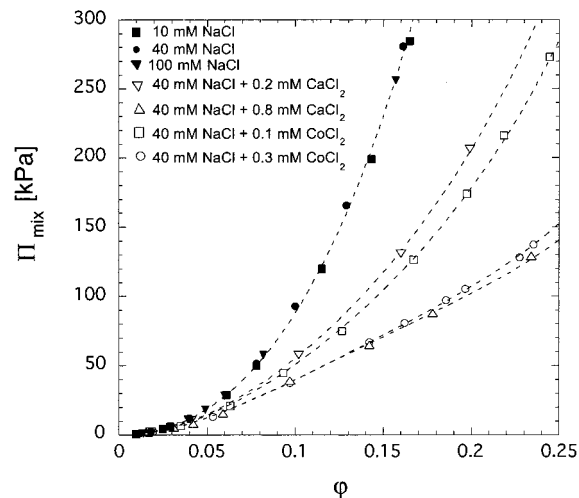


Figure 4. Mixing pressure, Π_{mix} , vs polymer volume fraction, ϕ , plots for polyacrylate hydrogels in different salt solutions. The dashed lines show the fits of eq 12 to the experimental data.

Table 1. Values of the Flory–Huggins Interaction Parameter for Polyacrylate Gels in Salt Solutions

salt solution	χ_0	χ_1
10 mM NaCl	0.452 ± 0.001	0.21 ± 0.01
40 mM NaCl	0.448 ± 0.001	0.21 ± 0.01
100 mM NaCl	0.451 ± 0.002	0.20 ± 0.01
40 mM NaCl + 0.2 mM CaCl_2	0.450 ± 0.001	0.45 ± 0.01
40 mM NaCl + 0.5 mM CaCl_2	0.453 ± 0.001	0.50 ± 0.01
40 mM NaCl + 0.8 mM CaCl_2	0.454 ± 0.001	0.53 ± 0.01
40 mM NaCl + 0.1 mM CoCl_2	0.452 ± 0.001	0.47 ± 0.01
40 mM NaCl + 0.2 mM CoCl_2	0.454 ± 0.002	0.50 ± 0.01
40 mM NaCl + 0.3 mM CoCl_2	0.455 ± 0.001	0.52 ± 0.01

of counterions affect Π_{mix} . There are distinct differences between the behavior of gels in the presence of monovalent and divalent cations. In the former case Π_{mix} is higher and practically independent of the NaCl concentration. This finding implies that there are no strong specific interactions between Na^+ and the polyanion. The corresponding Π_{mix} vs ϕ data obtained for gels containing divalent cations lie below this curve. It is apparent that Π_{mix} decreases with increasing concentration of divalent counterions and depends on the chemical type of the cation. At identical salt concentrations the effect of Co^{2+} significantly exceeds that of Ca^{2+} . The values of χ_0 and χ_1 deduced from the least-squares fits of eq 12 to the data are listed in Table 1.

The data presented so far suggest that both alkaline earth metal ions and transition metal ions cause gel contraction when they are added to sodium polyacrylate hydrogels swollen in aqueous NaCl solution. To estimate the effect of deformation on the volume transition induced by monovalent–divalent cation exchange, we compared the swelling behavior of freely swollen and uniaxially compressed polyacrylate hydrogels in CaCl_2 and CoCl_2 solutions. These salts were added to gels equilibrated with 40 mM NaCl solution. The results are shown in Figures 5 and 6, respectively. It can be seen that in the deformed gels volume transition occurs at lower concentrations of the divalent cations than in the corresponding freely swollen networks.

From eq 9, we can calculate the spinodal of the volume transition at which the gel becomes unstable and exhibits

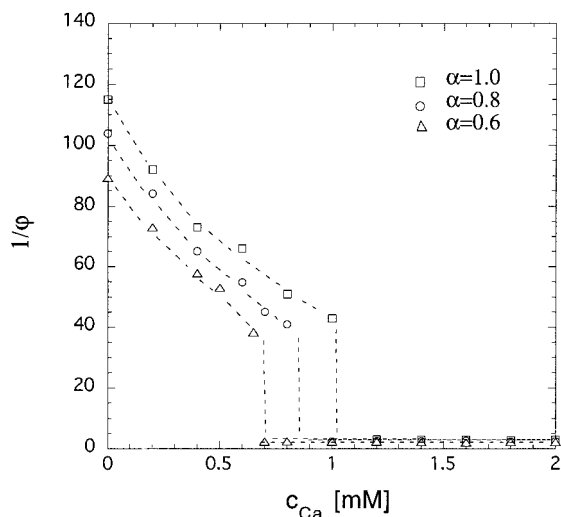


Figure 5. Variation of the degree of swelling ($1/\varphi$) of uniaxially deformed polyacrylate hydrogels as a function of the concentration of CaCl_2 in the surrounding solution.

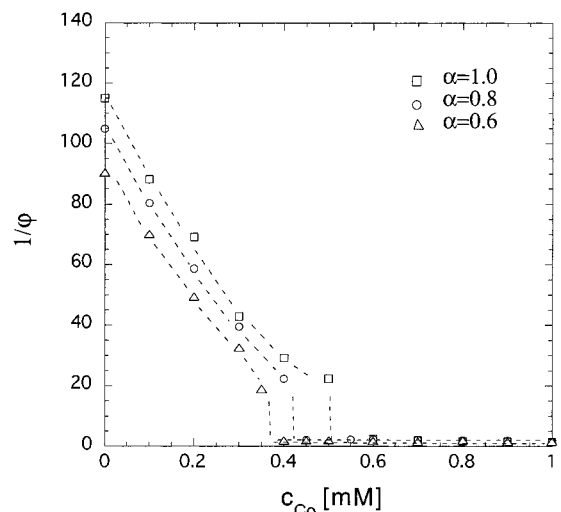


Figure 6. Variation of the degree of swelling ($1/\varphi$) of uniaxially deformed polyacrylate hydrogels as a function of the concentration of CoCl_2 in the surrounding solution.

volume change by expelling solvent molecules. The spinodal is defined by the conditions $\partial\Delta F_{\text{tot}}/\partial\varphi = 0$ (swelling equilibrium), and $\partial^2\Delta F_{\text{tot}}/\partial\varphi^2 = 0$. The latter condition implies that the osmotic compression modulus vanishes, i.e., $K_{\text{os}} = \varphi^2\partial^2\Delta F_{\text{tot}}/\partial\varphi^2 = 0$. This yields

$$\chi_{\text{sp}} = -\frac{AvV_1}{6\varphi^{5/3}\alpha_{\parallel}} + \frac{1}{2(1-\varphi)} + \frac{iV_1}{2\varphi V_{\text{m}}} \quad (13)$$

According to eq 13, volume transition occurs at smaller χ when α_{\parallel} decreases, or when the cross-link density of the gel increases. Both predictions are consistent with the experimental findings displayed in Figures 5 and 6.

Conclusions

Addition of divalent or trivalent counterions leads to volume transition in fully neutralized sodium polyacrylate gels swollen in NaCl solution. This volume transition is governed by the interactions between the polyion and the counterions. The counterions investigated in this work exhibit

different behaviors: alkali metal ions can move freely all over the entire network, and alkaline earth metal ions promote aggregation of polymer molecules, but these aggregates are relatively weak. Transition metal ions form stronger (but not irreversible) bridges between the network chains. There appears a continuous transition between the latter two types of cations. Three valence cations (La^{3+} and Ce^{3+}) bind practically irreversibly to the polyanion.

Alkali metal and alkaline earth metal cations do not affect considerably the static elastic properties of polyacrylate hydrogels. The reduction of the swelling degree with increasing concentration of alkaline earth metal salts is primarily due to modification of the mixing free energy. Experimental data indicate that addition of CaCl_2 has little effect on χ_0 , but changes χ_1 . Transition metal cations form much stronger complexes with the polyanion, which act as additional cross-links as verified by elastic modulus measurements. In these gels cations affect both elastic and mixing free energy terms.

Volume transition in uniaxially compressed gels occurs at lower concentration of the divalent cations than in the corresponding isotropic gels. The shift of the transition point increases with the extent of deformation, and depends on the chemical quality of the cation.

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