Effect of electrostatic interactions on phase transition in the swollen polymeric network

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An earlier relation describing swelling equilibria in polyelectrolyte networks is analysed from the viewpoint of the effect of electrostatic interactions on the existence of phase transition in polyelectrolyte gels. While the increase in the number of charges on the chain initiates the transition, both the increasing concentration of the low-molecular weight electrolyte and the decreasing flexibility of the chain (increasing length of the statistical segment) suppress this phenomenon. Swelling experimental data obtained on polyacrylamide (PAAm) gels may be described semiquantitatively assuming the existence of ~1 mol— charges on the PAAm chain.

INTRODUCTION

The theory of swelling equilibrium predicts that under suitable conditions two polymeric phases may exist in a polymeric network swollen to equilibrium. These phases differ in the conformation of chains and concentration of segments[1,2]; a small change in the polymer–solvent interaction (given by a change in temperature[3] or by the composition of the solvent[4]) then leads to a pronounced change (collapse) in the degree of swelling of the gel. Recent swelling experiments on polyacrylamide gels (PAAm) in an acetone–water mixture[4] led to a collapse in networks with a long curing time (or ageing); ageing played a decisive role in the existence of transition. The original explanation suggested by Tanaka[4] assumed a large increase in the network density v with the curing time. An investigation into the mechanical behaviour of these gels[5], however, led to the conclusion that the network density of gels remains constant with ageing, and the swelling collapse was related to the formation of a more pronounced heterogeneous structure presumably formed during the curing time. The most recent experiments on PAAm gels[6,7] demonstrated the necessity for the presence of electrostatic interactions (probably owing to the hydrolysis of PAAm chains) for the occurrence of the collapse. Potentiometric titration[8] has indeed revealed charged acid groups in solutions of linear PAAm of ~1%. So far, however, the effect of electrostatic interactions has not been considered in comparing the theory and experimental data on PAAm gels.

In our preceding paper[9] we included the effect of electrostatic interactions of charges on the chain, thus modifying the kinetic theory of rubber elasticity, and derived relations for deformational, swelling and potentiometric equilibria in polyelectrolyte gels. The theory was verified experimentally on the deformational, swelling and potentiometric behaviour of ionized gels of polymethacrylic acid[10] and their copolymers with 2-hydroxyethyl methacrylate[11]. A good fit between the theory and experiment was found in the range of low ionizations and low contents of methacrylic acid in copolymers.

Using an earlier relation for the swelling equilibrium[9], this study presents a quantitative evaluation of the effect of electrostatic interaction on the possibility of occurrence of phase transition in polyelectrolyte gels.

THEORY

Swelling equilibrium

A charged chain was described[9] using the model of a random coil with statistical segments; the distance between the segments is determined by an appropriate distribution function. This function also determines the distance probability between any two charges on the chain. Interaction between charges on the chain is given by the Debye–Hückel theory, while interaction between charges on various chains is neglected. The swelling equilibrium in the network is determined by the relation:

$$P = -\left(\frac{\partial \Delta F}{\partial V}\right)_{T,n_j} = \sum_{i=1}^{4} -\left(\frac{\partial \Delta F}{\partial V}\right)_{T_i n_j} = \sum_{i=1}^{4} \Phi_i \qquad (1)$$

where P is the swelling pressure, ΔF is a change in free energy determined by a change in the sample volume V during swelling, T is the temperature, n_j is the number of mols of ions of the j-th type in the gel, and $\Phi_i = -(\partial \Delta F_i/\partial V)_{T,n_j}$.

The contribution Φ_1 corresponds to the mixing of polymeric segments with the solvent (Flory–Huggins equation)

$$\Phi_1 = -(RT/V_1)[\ln(1-\varphi_2) + \varphi_2 + \chi\varphi_2^2] \qquad (2)$$

where V_1 is the molar volume of the solvent, R is the gas constant, φ_2 is the volume fraction of the polymer in the swollen gel and χ is the interaction parameter.

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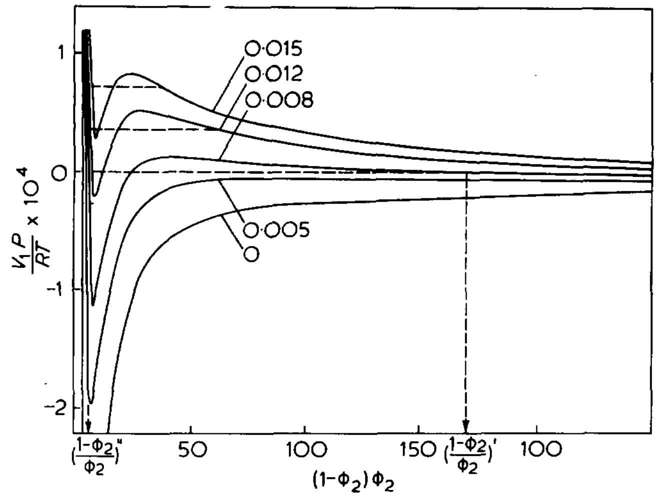

Figure 1 Dependence of reduced swelling pressure PV_1/RT from equation 1 on $(1-\phi_2)/\phi_2$ for $\chi = \chi_c = 0.570$ in equation 2, $\underline{c} = 0$, $s = 0.5$. Numbers at curves indicate the number charge fraction on the chain, i. For $i = 0.08$, equation 9 is satisfied for free swelling, and two phases, ϕ_2'' and ϕ_2' coexist in the gel

The contribution Φ_2 corresponds to the difference between the osmotic pressure in the gel and in solution (mixing of ions with the solvent)

$$\Phi_2 = (RT/M_0)\left\{i\rho\varphi_2 - 2f\underline{c}M_0\left[\left(1+\frac{i\rho\varphi_2}{M_0 f\underline{c}}\right)^{1/2} - 1\right]\right\} \quad (3)$$

where M_0 is the molecular weight of the monomeric unit, i is the ratio of the number of charges to the number of monomeric units (with respect to the low values of $i \sim 0.01$ used throughout this this study, we assume the osmotic coefficient to be 1 (see ref. 9), ρ is the density of the dry gel, and $\underline{c}$,f respectively are the concentrations of co-ions and their activity coefficient (for f we use [10] $f = 0.66 - 0.13 \log \underline{c}$ but the highest admissible value is $f = 1$).

The contribution Φ_3 has been calculated from the change in the configurational free energy with swelling. Owing to the high values of swelling, the finite extensibility of chains had to be considered, and Φ_3 has been divided into the Gaussian, Φ_3^G, and non-Gaussian, Φ_3^{NG}, contributions:

$$\Phi_3 = \Phi_3^G + \Phi_3^{NG} = -v_d RT(\langle\alpha_0^2\rangle\varphi_2^{1/3} - \varphi_2/2)$$
$$-v_d RT\left(\frac{3}{5}\langle\alpha_0^2\rangle^2\varphi_2^{-1/3}n^{-1} + \frac{99}{175}\langle\alpha_0^2\rangle^3\varphi_2^{-1}n^{-2} + \right.$$
$$\left.\frac{513}{875}\langle\alpha_0^2\rangle^4\varphi_2^{-5/3}n^{-3} + \ldots\right) \quad (4)$$

where v_d is the molar concentration of chains related to the dry volume, $\langle\alpha_0^2\rangle$ is the dilatation factor of the dry state ($\langle\alpha_0^2\rangle = (v^0)^{2/3}$, where v^0 is the volume fraction of the polymer at network formation), and n is the number of statistical segments in the chain (expressed through the number of monomeric units in the statistical segment s).

The last contribution Φ_4 is determined from the change in the free energy of electrostatic interaction with swelling

$$\Phi_4 = \frac{v_d N_A Z^2 i^2 e^2 \varphi_2^{4/3}}{3D(\overline{h_0^2}\langle\alpha_0^2\rangle)^{1/2}}\left[\frac{2.5\bar{A}}{1+\bar{A}} - \ln(1+\bar{A})\right] \quad (5)$$

where $\bar{A} = 6h/x\overline{h_0^2} = \left[\frac{9\langle\alpha_0^2\rangle\varphi_2^{-2/3}DkTM_0}{\pi N_A e^2 h_0^2(2M_0\underline{c} + i\rho\varphi_2)}\right]^{1/2}$

and h and $(\overline{h_0^2})$ are the chain end distances in the deformed and reference states, x is the inverse of the Debye radius of the ion atmosphere, D is the dielectric constant of the medium, k is the Boltzmann constant, N_A is the Avogadro number, Z is the degree of polymerization of the chain and e is the unit charge (further details see ref. 9). The swelling equilibrium for free swelling is given by

$$\Phi_1 + \Phi_2 + \Phi_3^G + \Phi_3^{NG} + \Phi_4 = 0 \quad (6)$$

Phase transition in the gel at free swelling

A characteristic manifestation of the existence of two gel phases and hence of the collapse of the swollen network consists in the van der Waals loop which appears in the dependence of the swelling pressure P (or of the chemical potential of the solvent $\mu_1 = -PV_1$) on φ_2 (or $(1-\varphi_2)/\varphi_2$, *Figure 1*[1,2,4]). The stability of phases requires $P \geqslant 0$ and the stability of the gel along the loop P vs. φ_2. The composition of gel phases (values of φ_2' and φ_2'') is given by the condition of equality of the chemical potentials of the solvent ($\mu_1' = \mu_1''$) and polymer ($\mu_2' = \mu_2''$) in both phases. For free swelling it holds that

$$\mu_1' = \mu_1'' = 0; \quad (7)$$

from the equality of the chemical potentials of polymers in both phases we can write (by using the Gibbs–Duhem equation)

$$\mu_2' - \mu_2'' = \int_{x_1'}^{x_1''}(\mathrm{d}\mu_2)_{T,p,x_2} = rV_1\int_{\varphi_2'}^{\varphi_2''}\frac{1-\varphi_2}{\varphi_2}\left(\frac{\mathrm{d}P}{\mathrm{d}\varphi_2}\right)_{T,p,x_2}\mathrm{d}\varphi_2$$
$$= rV_1\int_{\varphi_2'}^{\varphi_2''}P\varphi_2^{-2}\mathrm{d}\varphi_2 = 0 \quad (8)$$

where x_1 and x_2 are the numbers of moles of the solvent and polymer respectively, p is the external pressure and r is the number of equivalent segments of the macromolecule (the validity of equation 7 was used in equation 8, i.e. $P(\varphi_2') = P(\varphi_2'') = 0$). Equation 8 shows that Maxwell's construction (in order to guarantee stability of the gel in free swelling and to determine the composition of phases φ_2' and φ_2'') can be performed on the dependence $P\varphi_2^{-2}$ or $\mu_1\varphi_2^{-2}$) on φ_2. Equation 8 also demonstrates that Maxwell's construction can also be carried out on the plot of the dependence of P on $(1-\varphi_2)/\varphi_2$, because it holds that

$$\int_{\varphi_2'}^{\varphi_2''}\frac{1-\varphi_2}{\varphi_2}\left(\frac{\mathrm{d}P}{\mathrm{d}\varphi_2}\right)_{T,p,x_2}\mathrm{d}\varphi_2 = \oint_k \frac{1-\varphi_2}{\varphi_2}\mathrm{d}P = -\oint_k P\mathrm{d}\left(\frac{1-\varphi_2}{\varphi_2}\right) = 0 \quad (9)$$

where the closed curve k is determined by the dependence of P on $(1-\varphi_2)/\varphi_2$ between φ_2' and φ_2'' and by the straight line $P = 0$ between φ_2'' and φ_2'. In the case of swelling at constant swelling pressure $P_0 > 0$, Maxwell's construction is performed on the line P_0 (*Figure 1*).

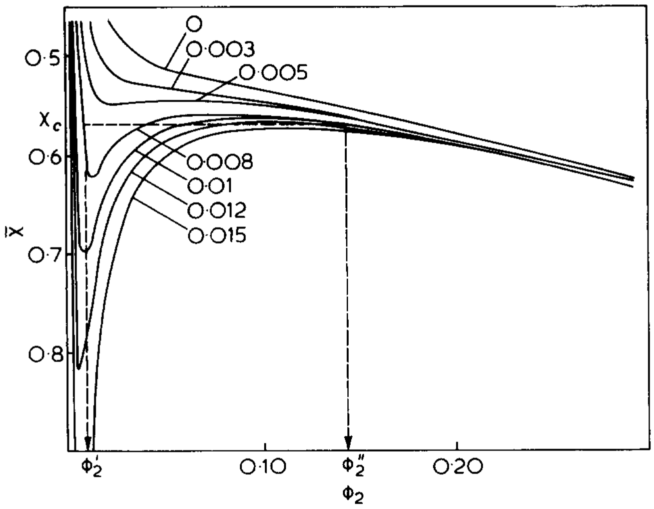

Figure 2 Concentration dependence of $\bar{\chi}$ for free swelling in water (equation 6) for $\underline{c} = 0$ and $s = 0.5$. Numbers at curves denote the charge fraction on the chain, i. For $i = 0.08$, the critical value χ_c = 0.57 was determined using equation 11 (Maxwell's construction)

As has been discussed earlier[1,2], the phase transition in the gel may occur in a poor solvent, i.e. the critical value of the interaction parameter at which the collapse takes place is $\chi_c > 0.5$. This corresponds to the collapse of PAAm gels, experimentally observed in free swelling during a change in the composition of the swelling mixture acetone–water. A change in the composition of the mixture corresponds in the first approximation to a change in the effective value of the parameter χ; with increasing acetone content, χ increases and the collapse occurs at ~40% acetone in water, which corresponds[5] to $\chi_c \sim 0.57$. A change in χ may be experimentally achieved also by a change in temperature (usually, χ for a poor solvent decreases with increasing temperature).

For free swelling of the network, equation 6 allows us to calculate curves describing the equilibrium composition of gels (characterized by φ_2) as a function of $\bar{\chi}$ (if only a single one further parameter changes, e.g. i, *Figure 2*[1,2,7]). $\bar{\chi}$ used instead of χ indicates that equation 6 has been used. Qualitatively, the shape of the curves P vs. $(1-\varphi_2)/\varphi_2$ corresponds to the shape of $\bar{\chi}$ vs. φ_2 (see *Figures 1* and *2*); it is shown below that the performance of Maxwell's construction in the dependence of P on $(1-\varphi_2)/\varphi_2$ (or $P\varphi_2^{-2}$ on φ_2) corresponds quantitatively to the construction in the dependence of $\bar{\chi}$ on φ_2 at the critical value χ_c. The dependence of the swelling pressure P for a constant $\chi = \chi_c$ in equation 2 on φ_2 may be expressed using the dependence of $\bar{\chi}$ on φ_2 by substracting equation 6 (with $\bar{\chi}$ in equation 2) from equation 1 (with χ_c in equation 2), which gives, eventually,

$$P = \frac{RT}{V_1}(\bar{\chi} - \chi_c)\varphi_2^2 \cdot \qquad (10)$$

Equation 10 shows that if the van der Waals loop exists in the $P\varphi_2^{-2}$ vs. φ_2 dependence, it also exists in the $\bar{\chi}$ on φ_2 dependence, see refs. 1, 2, 7, and its occurrence in $\bar{\chi}$ indicates the possibility of collapse of the swollen network. Substitution of equation 10 into equation 8 gives the condition

$$rRT\int_{\varphi_2'}^{\varphi_2''}(\bar{\chi} - \chi_c)d\varphi_2 = 0 \qquad (11)$$

which means that Maxwell's construction carried out on the $\bar{\chi}$ vs. φ_2 dependence determines the critical value χ_c, and hence also the composition of both phases (φ_2' and φ_2'', *Figure 2*). By this procedure, equation 7 is also satisfied. In the case of swelling at constant swelling pressure $P_0 > 0$, it is necessary to determine the dependence of $\bar{\chi}$ on φ_2 when 0 is replaced by P_0 on the right-hand side of equation 6.

Phase transition in the swollen gel[1,2] can also be predicted in the case of a network without charges (in equation 6 $\Phi_2 = \Phi_3^{NG} = \Phi_4 = 0$). The existence of this phenomenon depends markedly on the dilution at network formation (v^0) and on the network density (v_d or v_dV_1); a high value of v_d is required at a low value of the volume fraction of the polymer at network formation, v^0. For a PAAm network prepared at $v^0 = 0.04$ (corresponding to the preparation of PAAm gels[4]), the existence of a collapse and thus also the occurrence of the van der Waals loop in the dependence of $\bar{\chi}$ on v_2 requires $v_dV_1 \geqslant 0.9$, which corresponds for $V_1 = 33.6$ cm^3 mol^{-1} (40% mixture of acetone in water[5]) to an experimentally inaccessible value $v_d \geqslant 0.025$ mol cm^{-3}.

EFFECT OF THE CHARGE CONCENTRATION ON THE CHAIN, SALT CONCENTRATION AND CHAIN FLEXIBILITY ON PHASE TRANSITION AT FREE SWELLING

The dependence of $\bar{\chi}$ on φ_2 was analysed for a set of input parameters corresponding to a partly hydrolysed and neutralized PAAm network swollen in water: $M_0 = 71$ g mol^{-1}, $V_1 = 18.1$ cm^3 mol^{-1}, $\rho = 1.3$ g cm^{-3}, $T = 298$ K, $v^0 = 0.04$, $D = 80$ and $v_d = 0.00005$ mol cm^{-3} (corresponding to mechanical experiments[5]). The number fraction of charges on the chain i, concentration of co-ions in the gel $\underline{c}$ and a number of monomeric units in the statistical segment s were used as variable parameters.

Effect of charge concentration on the chain

Figures 1 and *2* show that even if in the nonionized network ($\underline{c} = 0$ and $s = 0.5$, i.e. negligible effect of Φ_3^{NG}) no phase transition takes place, the increasing fraction of charges on the chain, i, induces this effect. Approximately 0.5% of charges on the overall number of monomeric units on the chain are sufficient to induce the transition (for the given assembly of input parameters), and the collapse occurs for the critical value $\chi_c = 0.545$ (*Figures 2* and *3*). These 0.5% ionized groups exhibit the same qualitative effect on the occurrence of the phase transition as a ~1000 × rise in network density for the nonionized network. With increasing charge fraction on the chain in the case of free swelling, the beginning of the transition is shifted towards higher degrees of swelling and higher critical values of χ_c (*Figures 2* and *3*); the increase in the molar volume of the solvent V_1 is reflected in an increased χ_c. The intensity of the collapse $\Delta(= \varphi_2'' - \varphi_2')$ also increases with increasing i (*Figure 3*). It has been found experimentally[4,5,7] that the increasing curing time makes the collapse more pronounced and displaces its beginning towards higher degrees of swelling and higher acetone concentrations in the mixture. The fit between the theory and experiment may be achieved by assuming that the number of hydrolysed groups on the PAAm chain increases with the curing time.

Also the dependence of φ_2 on the fraction of charges on the chain i is nonmonotonic for appropriate constant

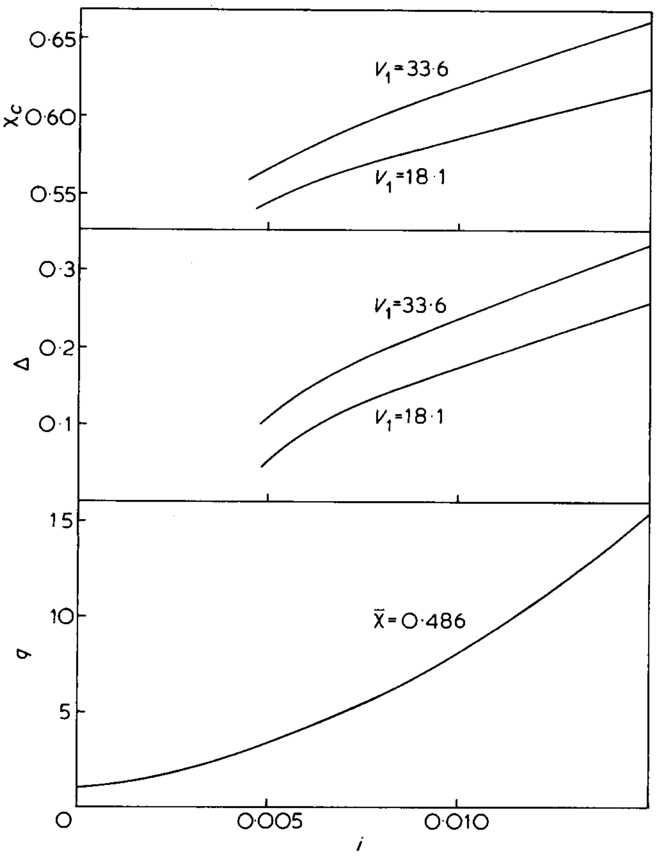

Figure 3 Dependence of the critical value of the interaction parameter χ_c, intensity of collapse Δ and change in the degree of swelling in water, q, on the number charge fraction on the chain, i

values of the parameter $\bar{\chi}$ (in equation 6) and indicates phase transition in the gel at free swelling (*Figure 4*). This plot is attractive from the experimental point of view, because the change in i may be regulated by a change in pH of the solvent (up to the complete ionization of hydroxylic groups on the chain). Experimentally, the collapse of PAAm gels was observed[6] as function of pH in a 50% mixture of acetone in water (the corresponding $\bar{\chi} = 0.595$[5]). Experimental data[6] agree semiquantitatively with the dependence shown in *Figure 4* for $\bar{\chi} = 0.595$. *Figure 4* demonstrates that the quality of the solvent (i.e. $\bar{\chi}$) affects pronouncedly both the intensity of the collapse Δ and the critical charge concentration on the chain at which the collapse takes place.

The change in the degree of swelling of the PAAm network at free swelling in water $q = \varphi_2(i=0)/\varphi_2(i)$ depending on the charge fraction i is shown in *Figure 3* for a constant $\bar{\chi} = 0.486$ (corresponds to the experimental value of the system PAAm-water[5]) in equation 6. The value φ_2 $(i=0) = 0.03$ corresponds to the swelling of the network cured for 3 h (see ref 7). The experimentally found increase in q up to $q = 10$ (for the curing time $t = 60$ days[7]) requires an increase in the number of charges on the PAAm chain up to $i \sim 0.012$.

Increasing crosslinking density (the other parameters being constant) reduces the positive effect of electrostatic interactions on the existence of phase transition (a times 10 rise in ν_d displaces the critical value of i for the occurrence of transition by 4 to 5 times). In this case the effect of ν_d is the reverse compared with nonionized networks.

Effect of salt concentration and chain flexibility

The effect of concentration of the low-molecular weight univalent electrolyte (concentration of co-ions in the gel characterized by $\underline{c}$) on the $\bar{\chi}$ vs. φ_2 dependence for $i = 0.012$ and $s = 0.5$ is shown in *Figure 5*. It is clear that electrolyte concentration suppresses phase transition in the bel; both the critical value of χ_c and the intensity of the collapse decrease with increasing $\underline{c}$ (collapse disappears for $\underline{c} \geqslant 5.10^{-3}$ mol l^{-1}, *Figure 6*). The χ_c and Δ values given in *Figure 6* are based on the assumption that the concentration of co-ions is the same in both gel phases. A quantitative analysis of equation (6) demonstrates that

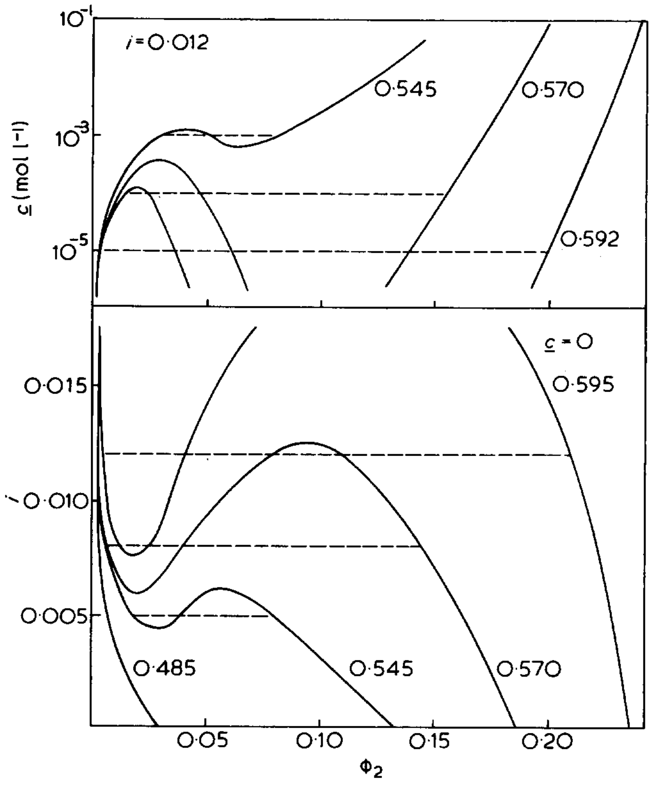

Figure 4 Concentration dependence of the charge fraction on the chain i ($\underline{c}$ = 0) and concentration of co-ions in the gel $\underline{c}$ (i = 0.012) at free swelling. Numbers at curves denote a constant value of $\bar{\chi}$ in equation 6

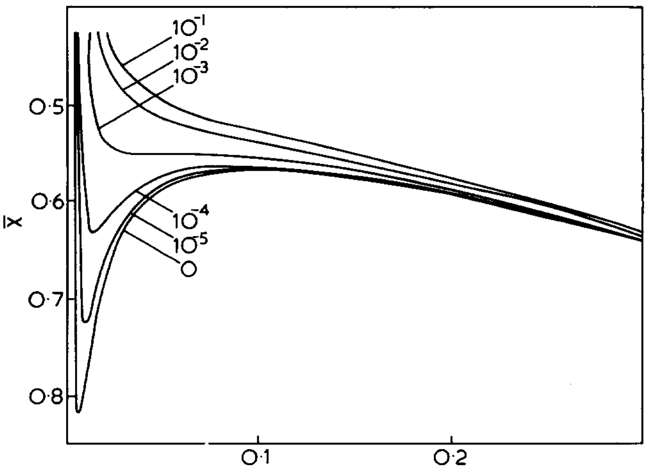

Figure 5 Concentration dependence of $\bar{\chi}$ for free swelling in a uni-univalent electrolyte for i = 0.012 and s = 0.5. Numbers at curves denote the concentration of co-ions in the gel, $\underline{c}$

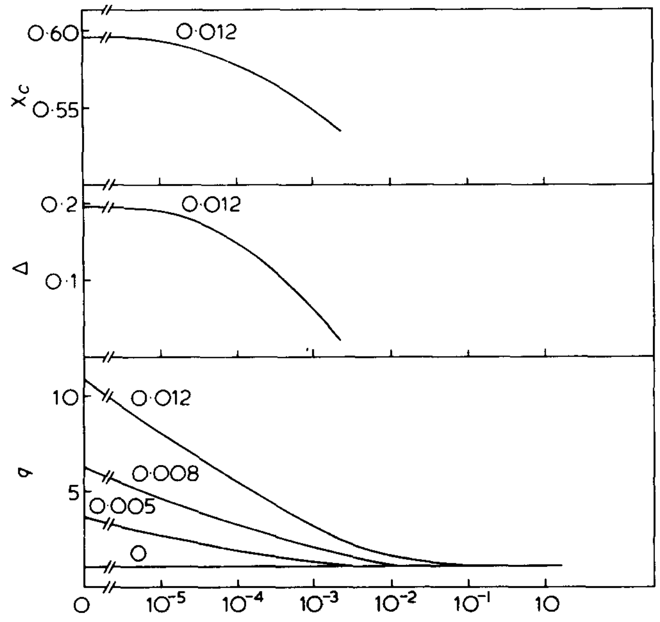

Figure 6 Dependence of the critical value χ_c, intensity of collapse Δ and change in the degree of swelling q on the concentration of co-ions in the gel, $\underline{c}$. Numbers at curves denote the charge fraction on the chain, i

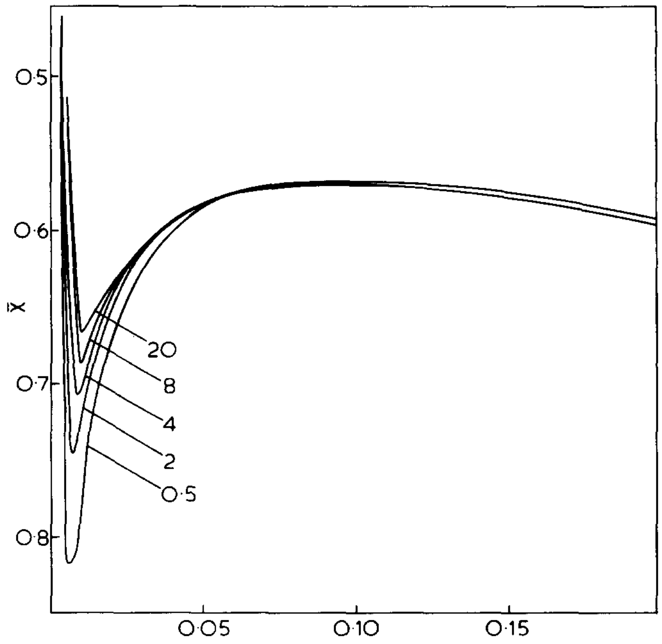

Figure 7 Concentration dependence of $\bar{\chi}$ for i = 0.012 and $\underline{c}$ = 0. Numbers at curves denote the number of monomers in the statistical segment s

with increasing $\underline{c}$ there is a marked decrease especially in the osmotic contribution Φ_2 (positive within the whole range of φ_2); the absolute magnitude of the electrostatic contribution Φ_4 (negative) also decreases.

The experimentally more attractive dependence of φ_2 on the concentration of co-ions in the gel, $\underline{c}$ can be seen in *Figure 4*; this dependence too is nonmonotonic for adequate values of the constant parameter $\bar{\chi}$ in equation (6) and indicates the possibility of phase transition in the gel at free swelling. Also in this case the quality of the solvent affects pronouncedly both the intensity of the collapse Δ and the critical concentration $\underline{c}$ at which the transition takes place.

The increasing concentration $\underline{c}$ causes a considerable decrease in swelling $q=\varphi_2(i=0,\underline{c})/\varphi_2(i,\underline{c})$ (*Figure 6*, the φ_2 values were calculated for a constant $\bar{\chi}=0.486$ in equation 6) of ionized gels; with decreasing number of charges on the PAAm chain, this effect disappears as expected. *Figure 6* is in good agreement with swelling experiments on PAAm gels having various curing times and swollen in aqueous solutions of NaCl (see ref 7). The comparison shows that time of cure $t=30$ days corresponds to ~0.8% charges and $t=60$ days corresponds to ~1.2% charges on the PAAm chain (the same conclusion follows from the analysis of the dependence of q on i, *Figure 3*).

The chain flexibility characterized by the number of monomeric units in the statistical segment s is also reflected in the magnitude of phase transition in the network (*Figure 7*). At a constant charge fraction $i=0.012$ and $\underline{c}=0$, the intensity of the collapse decreases with decreasing flexibility and its beginning is shifted towards lower degrees of swelling of the gel and lower χ_c values. From the experimental point of view, the change in chain flexibility may be due only to a change in the type of monomer, because our earlier results show[11] that in the range $i \sim 0.01$ considered in this study the charge concentration has no influence on the parameter s.

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