Concentration redistribution of low-molecular-weight salts of metals in the presence of a strongly swelling polyelectrolyte hydrogel

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This paper deals with the behaviour of a superswelling hydrogel based on sodium polyacrylate crosslinked with the allyl ester of carboxymethyl cellulose in solutions of salts of mono- and polyvalent metals. The effect of cooperative sorption of polyvalent ions by the hydrogel was detected. An expression describing the concentration redistribution in the system hydrogel–univalent salt solution was obtained.

(Keywords: hydrogel; metal salts; sodium polyacrylate; concentration redistribution; cooperative phenomena)

INTRODUCTION

Superswelling hydrogels exhibit a combination of unique physico-chemical properties, thus permitting their wide-ranging, and often exceptional, possibilities in practical applications (high and fine technologies, biotechnologies, ecology, medicine, etc.). Gel properties may be programmed by the choice of the main polymer that forms the framework and of the either low-[1,2] or high-[3] molecular-weight crosslinking agent. In the present paper superswelling gels based on a copolymer of acrylamide and acrylic acid crosslinked by carboxymethyl cellulose (CMC) are considered.

The behaviour of these gels in solutions of low-molecular-weight salts of mono- and polyvalent metals was investigated. A concentration redistribution of low-molecular-weight salt in the system hydrogel–solution was detected. The theoretical possibility of this kind of effect has already been reported[4], but this phenomenon has not been systematically investigated.

EXPERIMENTAL RESULTS

A hydrogel based on sodium polyacrylate was chosen for investigations. This weakly crosslinked network was obtained by the free-radical polymerization of acrylamide in aqueous solution promoted by a Co III redox system. Water-soluble allyl carboxymethyl cellulose with a degree of substitution in allyl groups of 0.4 was used as a crosslinking agent. After synthesis, polymer samples were washed in water and subjected to hydrolysis in a 0.1 M solution of NaOH. The degree of equilibrium swelling of the gel freed by washing from excess alkali was 1000 g/g. In order to obtain a dry polymer, the hydrolysed gel was treated with excess ethanol, vacuum dried over P_2O_5 and disintegrated in a ball mill. The fraction of dry polymer with particle size 63 μm was detected.

The kinetics of gel formation are characterized by the fact that a branching reaction seems to be absent as a separate elementary reaction. The allyl groups of CMC play the role of comonomers through which linear chains of the acrylamide–acrylic acid copolymer simply 'grow', including these groups as hetero units. There are many of them on one rigid CMC molecule, and, as a result, a network is formed. The crosslinking agents, being rigid, play the role of 'spreaders', which greatly increase the hydrogel strength in the swollen state. This gel retains its shape in the swollen state and when pressed with the hands does not release water.

Salt concentration in solution was measured on a 'Specord' spectrophotometer in the case of coloured salts ($CuSO_4$, $NiSO_4$, $CoSO_4$, $K_3[Fe(CN)_6]$) or by titration for the $Na_2S_2O_3$ salt.

The following measurement procedure was used. The dry powder feed of hydrogel was brought to the degree of swelling of ~300† using distilled water. Then a solution of low-molecular-weight salt was added, the mixture was stirred and was left to stand for 15–20 min. After the equilibrium state was attained, the volume occupied by the contracted gel was measured. Subsequently a few millilitres of the solution over the gel was collected and its concentration c' was determined.

The results are shown on the plots of the dependence of salt concentration after interaction with the hydrogel c'/c_{polym} on the initial salt concentration c_0/c_{polym} (*Figure 1*) in a double-logarithmic scale, c_{polym} being the concentration of COO^- groups. Concentrations were calculated in moles per litre total volume of the gel + salt solution. The bisectrix $c' = c_0$ indicating the absence of both sorption and desorption is shown by the broken line A (*Figure 1*).

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† This degree was chosen, first, because of the high sorption capacity at this degree of swelling and, secondly, because of the high rate of processes and rapid attainment of equilibrium[3]

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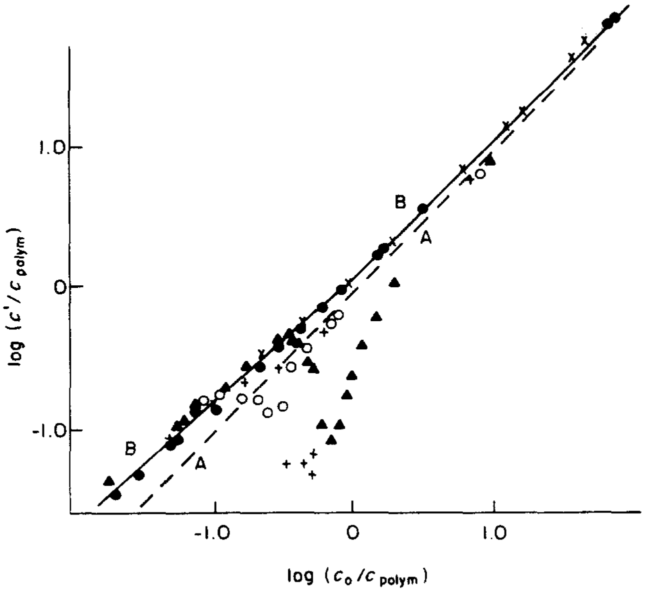

Figure 1 Salt concentration after the interaction with the hydrogel c'/c_{polym} vs. initial salt concentration c_0/c_{polym} for $Na_2S_2O_3$ (×), $K_3[Fe(CN)_6]$ (●), $CuSO_4$ (▲), $NiSO_4$ (+) and $CoSO_4$ (○). The broken line A ($c'=c_0$) indicates the absence of sorption as well as desorption in the system hydrogel–solution. Full curve B corresponds to the theoretical curve (equation (4))

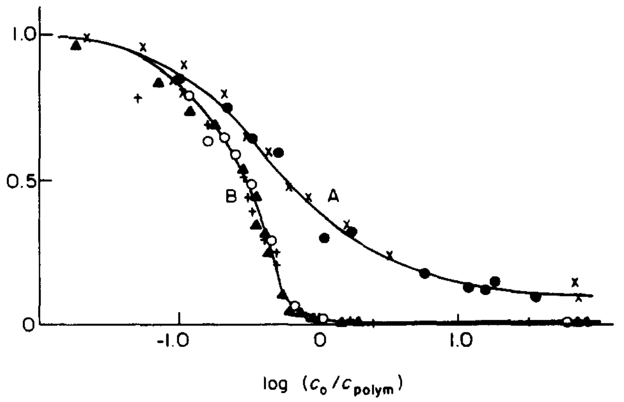

Figure 2 Degree of hydrogel contraction α vs. initial salt concentration c_0/c_{polym} for $Na_2S_2O_3$ and $K_3[Fe(CN)_6]$ (curve A), and $CuSO_4$, $NiSO_4$ and $CoSO_4$ (curve B)

It is clear that, for the salts of the monovalent metals investigated, all points fall above the bisectrix, i.e. salt concentration in solution increases after the interaction with the hydrogel. For solutions of salts of polyvalent metals at low metal concentrations $c_0<c_{\mathrm{polym}}$, the salt solution is concentrated outside the hydrogel. With increasing initial salt concentration, at $c_0\approx c_{\mathrm{polym}}$, the concentration of solution outside the gel decreases sharply. When the salt concentration is increased further, $c_0\gg c_{\mathrm{polym}}$, asymptotic approximation to the straight line $c_0=c'$ takes place.

Figure 2 shows the dependence of the degree of hydrogel contraction ($\alpha=V/V_0$, V being the volume occupied by the hydrogel after the interaction with low-molecular-weight salt solution and V_0 the volume of a sample that is swollen in water at the equilibrium degree of swelling) on initial salt concentration c_0/c_{polym}. For solutions of both $K_3[Fe(CN)_6]$ and $Na_2S_2O_3$ (*Figure 2*, curve A), starting from $c_0/c_{\mathrm{polym}}\sim 3$ the curve of the dependence $\alpha(c_0/c_{\mathrm{polym}})$ attains a limiting value, i.e. further increase in salt concentration does not lead to a decrease in size of the hydrogel sample. The value of $\alpha_{\mathrm{lim}}\approx 0.1$ corresponds (at the equilibrium degree of hydrogel swelling in water of 10^3) to the value of the degree of swelling of an uncharged polyacrylamide network ($\approx 10^2$), which is in agreement with the conclusions in ref. 5.

For solutions of polyvalent metal salts, similar general relationships are manifested more specifically: The hydrogel sample begins to contract relatively markedly at salt concentrations one order of magnitude less than those of monovalent salts. The achievement of α_{lim} occurs in a more narrow range of initial concentrations of polyvalent metal salts. In this case we have $\alpha_{\mathrm{lim}}\approx 0.01$ and less, which corresponds to hydrogel contraction almost to a 'dry' unswollen state and is due to heterovalent crosslinking of hydrogel substance by metal ions.

THEORY AND DISCUSSION

Let us obtain an expression that gives a quantitative description of the concentration redistribution in the system hydrogel–univalent salt solution. We consider a sample of polyelectrolyte hydrogel immersed in a solution of a simple 1:1 electrolyte (to be specific, we consider a network of sodium polyacrylate in a solution of Na^+A^- salt, A^- being a simple anion, e.g. Cl, etc.). Let us analyse the distribution of mobile Na^+ and A^- ions in the system hydrogel–salt solution (*Figure 3*).

As a result of thermal motion, counterions leave the surface layer of the hydrogel. In the steady state this diffusion flow is counterbalanced by the forces of electrostatic attraction of free counterions to the charged backbone of the network. Hence, an electric double layer is formed on the interface. In the equilibrium state the flows of co- and counterions are equal. If the ionogenic groups of the hydrogel are distributed uniformly throughout the network, Donnan's approach can be applied, and it is not necessary to solve diffusion balance equations. When the distance from the sample surface equals approximately several Debye radii, the condition of quasi-neutrality begins to be obeyed. It can be written in the following form:

$$\begin{gathered} n_1^{\mathrm{II}}=n_2^{\mathrm{II}} \\ n_1^{\mathrm{I}}=n_2^{\mathrm{I}}+N_0 \end{gathered} \tag{1}$$

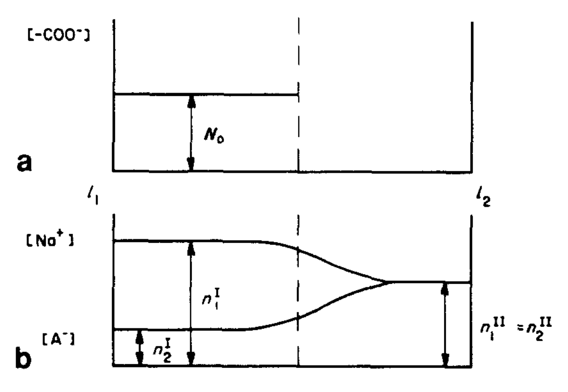

Figure 3 Qualitative shapes of profiles of concentration distributions of (a) COO^- ions and (b) Na^+ and A^- ions, established in the system gel–solution of a univalent salt in the equilibrium state

n_1 and n_2 being the concentrations of mobile positive and negative ions, respectively; superscripts I and II correspond to the asymptotic concentration values in regions I and II shown in *Figure 3*; and N_0 is the concentration of ionogenic groups in the hydrogel.

The relationship of the equality of chemical potentials on both sides of the hydrogel–solution interface can be given as:

$$n_1^{\mathrm{I}} n_2^{\mathrm{I}} = n_1^{\mathrm{II}} n_2^{\mathrm{II}} \tag{2}$$

Equations (1) and (2) should be supplemented with the conditions of the maintenance of the total number of ions:

$$\begin{aligned} n_1^{\mathrm{I}} l_1 + n_1^{\mathrm{II}} l_2 &= c_0(l_1 + l_2) + N_0 l_1 \\ n_2^{\mathrm{I}} l_1 + n_2^{\mathrm{II}} l_2 &= c_0(l_1 + l_2) \end{aligned} \tag{3}$$

l_1 being the extension of the hydrogel sample and l_2 the extension of the surrounding solution. The obtained equations (1)–(3) completely describe the concentration distribution in the system hydrogel–monovalent salt solution.

The solution of this system of equations gives an expression for the connection between the salt concentration c' and the initial salt concentration c_0:

$$\frac{c'}{c_{\mathrm{polym}}} = \frac{(1-w)(2c_0/c_{\mathrm{polym}}+1) + [(1-w)^2 + 4w^2(c_0/c_{\mathrm{polym}}+1)c_0/c_{\mathrm{polym}}]^{1/2}}{2(2w-1)} \tag{4}$$

where $w = l_1(l_1 + l_2)$ is the volume fraction occupied by the sample in the hydrogel–solution system.

The results obtained are in good agreement with the experimental data (*Figure 1*, theoretical curve B). The values of the parameter w for each concentration c_0 were established from the experimental dependence of the degree of hydrogel contraction α on the initial salt concentration c_0 (*Figure 2*).

Figure 1 shows that the redistribution of concentrations of monovalent salts in the hydrogel–solution system is described by equation (4) over the entire concentration range investigated.

The concentration redistribution of bivalent metals is satisfactorily described by equation (4) only at low initial salt concentrations $c_0 < c_{\mathrm{polym}}$. In this case bonding of the hydrogel by polyvalent metals does not occur and, correspondingly, hydrogel collapse is slight. When the initial salt concentration increases to $c_0 \sim c_{\mathrm{polym}}$, the concentration of polyvalent ions inside the hydrogel increases drastically. This increase may be due to the appearance of a cooperative effect because of an avalanche-line increase in the number of multicharged metal ions bonding the gel. In other words, if the number of 'salt bridges' in the hydrogel exceeds a certain critical value, further formation of these bridges stimulates a still greater increase of their number.

CONCLUSIONS

Experimental results are obtained characterizing the behaviour of the system superswelling hydrogel–solution of a low-molecular-weight salt of mono- and polyvalent metals over a wide salt concentration range.

An expression for the quantitative description of the concentration redistribution in the system hydrogel–monovalent salt solution was obtained. This expression is in satisfactory agreement with the experimental data for the case when bonding of the hydrogel by metal ions does not occur.

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