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Influence of a Salt on Some Properties of Hydrophilic Methacrylate Hydrogels

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ABSTRACT: Poly(2-hydroxyethyl methacrylate) (PHEMA) and poly[*N*,*N*-dimethyl-*N*-[(methacryloyloxy)-ethyl]-*N*-(3-sulfopropyl)ammonium betaine] (PSPE) hydrogels have been prepared by means of γ-irradiation. The variation of the swelling and mechanical properties of these gels with the concentration of potassium thiocyanate in the swelling medium has been examined. Comparison of these properties in terms of the nature of the hydrophilic group has been made. The results have been analyzed and quantified via the application of the Donnan-type equilibrium theory in conjunction with the equilibrium thermodynamics of ternary systems solvent/polymer/solvent. In this manner, relevant water/polymer, salt/water, and salt/polymer interaction parameters have been obtained. The thermodynamic analysis shows the importance of the zwitterionic group in PSPE with regard to the swelling behavior of PSPE hydrogels in comparison with PHEMA hydrogels in aqueous salt solutions.

Introduction

The influence of the presence of salts in the swelling medium of a hydrogel is of importance in agricultural and biomedical applications, viz. water reservoirs in agriculture and hydrogels as implants for drug release applications.[1] In principle, changes in swelling behavior due to the presence of a salt can affect the mechanical properties of the material (see ref 2 in which the changes in mechanical properties have been attributed to the plasticizing effect of water) as well as the "tortuosity" of the matrix which gives rise to different diffusion coefficients of drug release.[3,4]

Hydrophilic polymers can be categorized into two types with regard to their behavior in aqueous salt solutions: (a) undissociable polymers in water and (b) dissociated polymers in water. Considering polymers of type a, the presence of salt ions may enhance polymer/water mixing conditions (salting-in) or may impair them (salting-out). Partial effects such as electrostatic ones, water structuring due to microsolutes (salts can be structure makers or structure breakers), association of the hydrophobic sites of the macromolecule, and formation of complexes between polymer and ions contribute to the overall effect.[5] Polymers of type b (i.e., acid derivatives) exhibit the so-called polyelectrolyte behavior characterized by a marked deswelling in salt solution.[6,7]

Recent results on the aqueous salt solution behavior of a new type of vinyl polymers which include a zwitterion in the side chain [poly(sulfobetaines)] suggest the new category of hydrophilic polymers. These polymers are mainly characterized by their antipolyelectrolyte behavior conferred by the zwitterionic group. Thus, the presence of salt ions produces the breaking of intrachain and intragroup association of the poly(sulfobetaines) and gives rise to chain expansion.[8-10] Furthermore, Salamone et al.[11,12] have observed a large increase in swelling of vinylimidazolium sulfobetaine hydrogels in an aqueous salt medium (1 mol dm^{-3} NaCl solutions). However, relevant studies on the salt concentration dependence of the equilibrium swelling, influence of swelling on mechanical properties, and concentration dependence of the partitioning coefficient C_p for hydrogels based on this type of polymers have not yet been undertaken.

This paper is aimed at establishing the dependences mentioned in the last paragraph for hydrogels based on the monomer *N*,*N*-dimethyl-*N*-[(methacryloyloxy)ethyl]-*N*-(3-sulfopropyl)ammonium betaine (SPE). The salt used in this work was KCNS. The selection of it was dictated by the earlier observations by Monroy Soto and Galin[9] and Schulz et al.[10] The former found from critical salt concentration measurements that the sequences of increasing solubility power for cations (chlorides) and anions (sodium salts) for PSPE were

cations

$$\mathrm{Li^+ < H^+ < Ca^{2+}, NH_4^+ < K^+ < Ba^{2+} < Na^+ < Mg^{2+} < N^+(CH_3)_4}$$

anions

$$\mathrm{OH^-, F^- \ll Cl^- < Br^- < I^- < CNS^- < ClO_4^- < B^-(C_6H_5)_4}$$

Moreover, the critical salt concentrations reported showed that the most important role was played by the anion. Furthermore, Schulz et al.[10] found a cloud point curve independent of polymer concentration for a system water/KCNS/linear PSPE. According to all these observations, the swelling properties of PSPE hydrogels in KCNS solutions should depend mainly on salt concentration.

For the sake of completeness, the results found will be compared to the behavior exhibited by poly(2-hydroxyethyl methacrylate) (PHEMA) hydrogels in KCNS solutions. Both monomers, SPE and HEMA, are methacrylates and have the same number of methylene groups before the hydrophilic group but are dissimilar in the nature of the latter, which is a sulfobetaine for PSPE and a hydroxyl group for PHEMA. A few workers have studied the influence of salt and salt concentration on the swelling properties of PHEMA.[5,13] From these studies, it is apparent that (i) the decisive role is played by the anion, particularly at low salt concentrations; (ii) the anions can be classified into two categories, salting-in and salting-

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out anions (the latter are preferentially sorbed in the gel phase); (iii) salting-out and salting-in effects decrease with increasing salt concentrations; and (iv) the anion CNS$^-$ shows the highest positive sorption among the anions studied at low concentrations.

Experimental Procedures

Materials. SPE (Rasching Co.), EDMA (Aldrich Chemical Co.), HEMA (Ubichem Ltd., 99.7 wt % pure; EDMA content, 0.08 wt %), and potassium thiocyanate (KCNS) (Aldrich, analytical grade) were used as received. Doubly distilled deionized water was used for polymerization, swelling, and stress-strain experiments.

Polymerization. Aqueous solutions of SPE (500 g dm^{-3}) and EDMA (0.5 wt %) were prepared gravimetrically, outgassed with gaseous nitrogen, and irradiated with γ-irradiation from a 9000-Ci ^{60}Co source. The γ-irradiation dose was 1 Mrad, the dose rate being 0.01 Mrad h^{-1} as determined by Fricke dosimetry. During the outgassing stage a slight phase separation was observed, which was due to partial miscibility of EDMA. This phase separation disappeared after the polymerization was complete and clear flexible rods of hydrogel were finally obtained. PHEMA hydrogels were prepared similarly. The resultant hydrogel rods were swollen to equilibrium for 2 months. During this time the unreacted monomer was removed by changing the swelling media once a day. Parallel to this swelling conditioning to equilibrium of the hydrogels, preweighed dry fragments of them were Soxhlet extracted for 24 h in hot water. A sol fraction of 10 wt % was obtained by these means, which indicates that a 90 wt % conversion was attained. With regard to PHEMA hydrogels, 100% conversion was obtained since no sol fraction was detected.

After swelling equilibrium was reached, the rods were inserted in metal tubes of appropriate thickness and diameter and the protruding end was cut with a scalpel to produce thin disks (diameter $\approx$11 mm and thickness $\approx$2 mm) for measurement of swelling and cylindrical pellets (diameter $\approx$11 mm and thickness $\approx$11 mm) for measurements of compression modulus.

Swelling in KCNS Solutions. Dry xerogels were preconditioned in water to avoid a swelling shock which could produce the breaking of the gel. This conditioning stage was followed by immersion of the hydrogels in the KCNS solutions of appropriate concentrations (0 < [KCNS] < 1.7 mol dm^{-3}) for 144 h. The total degree of equilibrium swelling (W), the degree of swelling in terms of content of water alone W_1, the mole fractions of water in the gel (X_1) and in external solution (X_1^*) at equilibrium, and the partitioning coefficients (C_p and C_p') between salt inside and outside the gel were determined. The definitions of these quantities and the mode of evaluating them are given in Appendix A.

Volumetric Swelling. The volume fraction of polymer within a hydrogel ϕ_2 is given by

$$\phi_2 = (D_0/D)^3 \tag{1}$$

where D_0 and D are the diameters of dry and swollen disks respectively. D_0 was measured at 293 K with a micrometer. Values of D were obtained for every KCNS concentration. A Minolta X300 35-mm camera fitted with a Tamron 90-mm f/2.5 lens was used in the photographic procedure, details of which have been given previously.[14]

Compression Measurements. Elastic moduli of the hydrogels were determined by stress (compression)-strain experiments. Full experimental details of the assembly used as well as the relevant equations and plots are given elsewhere.[15]

Results and Discussion

Swelling Behavior. Figure 1 shows the change of W and W_1 with concentration of KCNS ([KCNS]) for hydrogels based on PSPE and PHEMA. With regard to the former, the main swelling features are (i) W increases sharply at low salt concentrations and becomes constant thereafter at a high value of 0.91 and (ii) W_1 experiences the same sharp change as W at low [KCNS] (0 < [KCNS] < 0.15 mol dm^{-3}) but decreases smoothly for [KCNS] > 0.15 mol dm^{-3}. PHEMA, on the other hand (Figure 1c,d), exhibits a somewhat different swelling behavior: (i) W displays an increasing tendency over the entire concentration range. This change is more pronounced for 0 < [KCNS] < 0.6 mol dm^{-3}. (ii) W_1 increases for 0 < [KCNS] < 0.6 mol dm^{-3} and thereafter reaches a constant value of 0.58. It is apparent therefore that the presence of the zwitterionic group in SPE promotes W and W_1 compared with PHEMA.

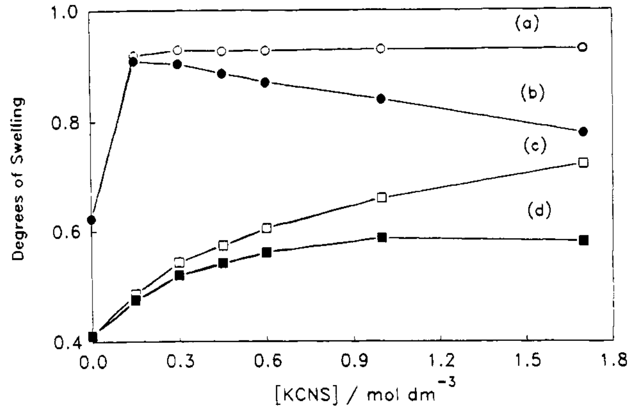

Figure 1. Degree of equilibrium swelling W [(a) PSPE hydrogels and (c) PHEMA hydrogels] and hydrogel water content W_1 [(b) PSPE hydrogels and (d) PHEMA hydrogels] as a function of KCNS molar concentration.

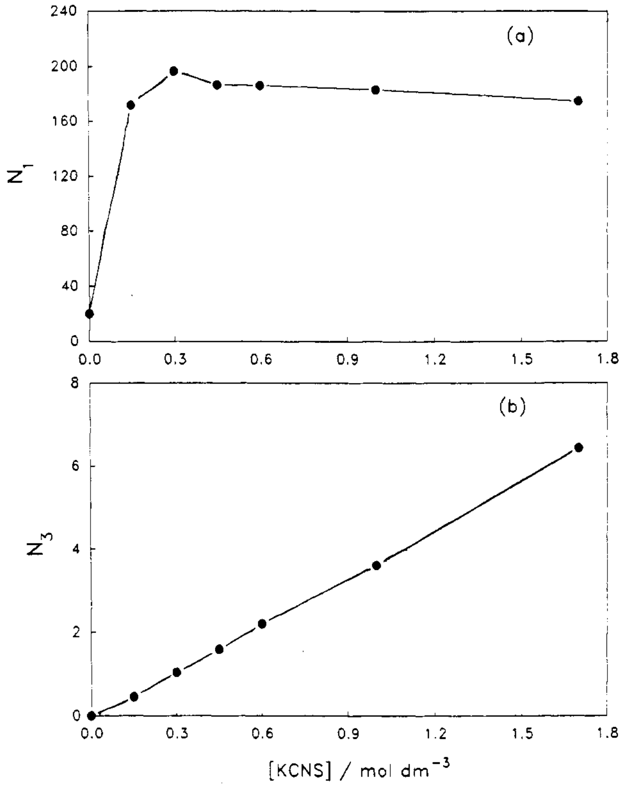

Figure 2. Change of (a) the number of water molecules per monomeric unit (N_1) and (b) the number of salt molecules per monomeric unit (N_3) with [KCNS] for PSPE hydrogels.

The calculation of the number of water molecules per monomeric unit N_1 and the number of salt molecules per monomeric unit N_3 affords valuable information with regard to the swelling behavior at the molecular level. The variation of N_1 and N_3 with [KCNS] for PSPE is given in Figure 2. N_1 increases very sharply in the concentration range 0–0.30 mol dm^{-3} and decreases for 0.30 < [KCNS] < 1.7 mol dm^{-3}. The maximum N_1 value attained is 196 at [KCNS] = 0.3 mol dm^{-3}. For [KCNS] = 1.7 mol dm^{-3},

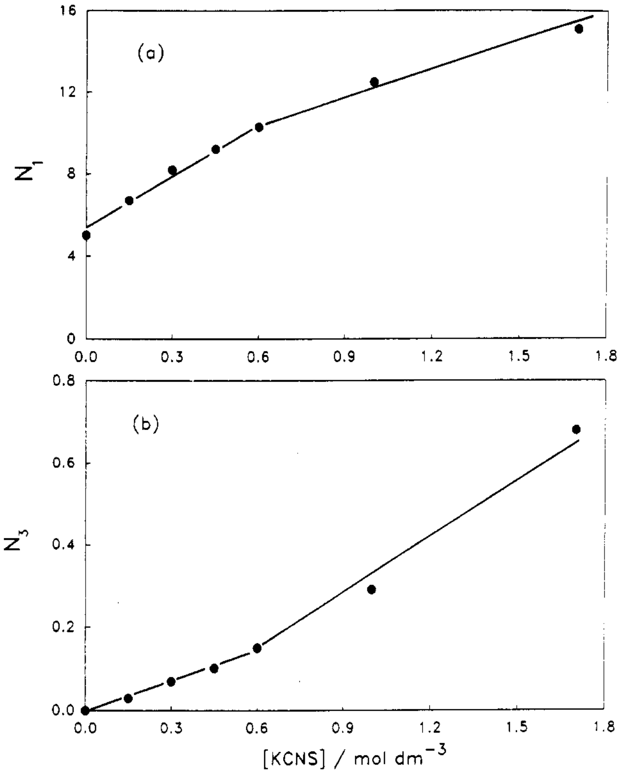

Figure 3. Change of (a) the number of water molecules per monomeric unit (N_1) and (b) the number of salt molecules per monomeric unit (N_3) with [KCNS] for PHEMA hydrogels.

this value becomes 175. On the other hand, N_3 shows an overall increasing tendency, which contrasts with the observations given before on N_1. It becomes apparent from these findings that the swelling properties of PSPE in KCNS solution must be divided into two regions as a function of KCNS concentration. In the first one (0 < [KCNS] < 0.30 mol dm^{-3}), the presence of salt promotes the water uptake. It should be noted that the maximum N_1 value is obtained for $N_3 = 1$. This indicates each zwitterionic group is coupled to one KCNS molecule giving rise to the ingress in the hydrogel of a high concentration of water molecules which solvate mobile and immobile ions. In the high KCNS concentration region, 0.30 < [KCNS] < 1.70 mol dm^{-3}, the network does not undergo any further increasing swelling. The N_1 and N_3 values for this concentration range show clearly that the constant swelling is to be ascribed to the replacement of water molecules by KCNS molecules.

The corresponding N_1 and N_3 values obtained for PHEMA as a function of KCNS concentration are represented in Figure 3. The N_1,[KCNS] and N_3,[KCNS] experimental pairs have been grouped into two regimes to highlight the different swelling behavior at low and high KCNS concentrations. Thus, in the region 0 < [KCNS] < 0.6 mol dm^{-3}, the slope dN_1/d[KCNS] is 11.4 dm^3 mol^{-1}, whereas dN_3[KCNS] is 2.4 dm^3 mol^{-1}. This shows unambiguously that at low KCNS concentrations the entrance of water into the hydrogel is favored with respect to the entrance of salt. At high KCNS concentrations ([KCNS] > 0.6 mol dm^{-3}), dN_1/d[KCNS] = 4.4 dm^3 mol^{-1} and dN_3/d[KCNS] = 4.7 dm^3 mol^{-1}. Accordingly, at these concentrations the entrances of water and salt are equally favored. It is also relevant to note that the largest values of N_3 (0.68) and N_1 (15) within the range of salt concentration used occur at [KCNS] = 1.7 mol dm^{-3}.

With regard to the partitioning coefficient Figure 4 shows that C_p exhibits a KCNS concentration dependence for both PSPE and PHEMA. This dependence is, however, enormously influenced by the presence of the zwitterionic group. Thus, for PSPE C_p increases for 0 < [KCNS] < 0.45 mol dm^{-3} and remains constant and equal to unity thereafter, whereas for PHEMA there exists a minimum of C_p at [KCNS] approximately equal to 0.5 mol dm^{-3}.

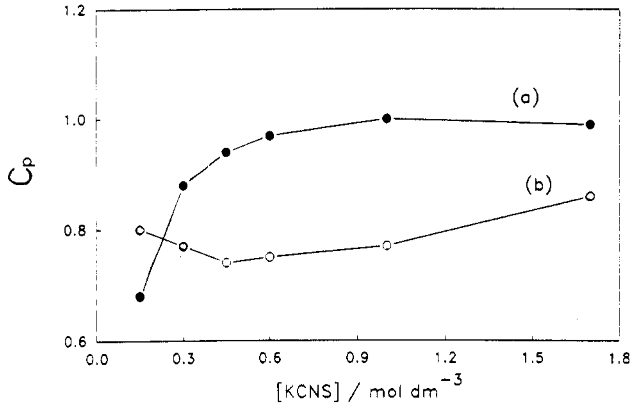

Figure 4. Partitioning coefficient C_p as a function of molar concentration of KCNS for (a) PSPE and (b) PHEMA.

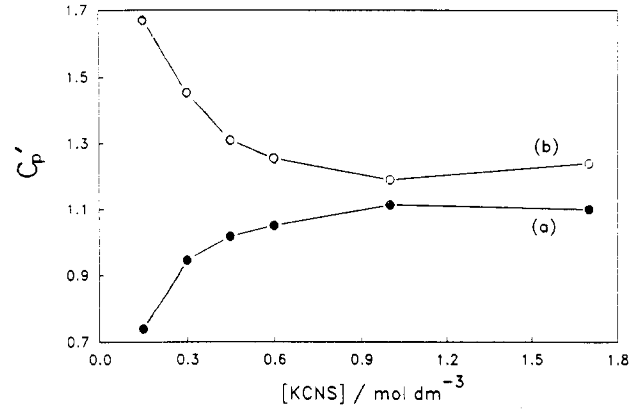

Figure 5. Partitioning coefficient C_p' as a function of molar concentration of KCNS for (a) PSPE and (b) PHEMA.

It is possible to define the partition coefficient in an alternative manner, i.e., as C_p' (see Appendix A). Accordingly, the corresponding variation of C_p' with salt concentration is also presented here (Figure 5) for comparison. It is seen that the plots for PSPE are similar for both modes of expressing the partition coefficient. However, for PHEMA (Figure 5b) there is the important difference that $C_p' > C_p$ at each salt concentration. Reference to the definitions of C_p and C_p' shows that C_p tends to C_p' the smaller the polymer content of swollen gel, which is the situation for the more highly swellable PSPE.

For the sake of clarity, the gravimetric swelling results given will be discussed separately in more detail for each type of hydrogel. Regarding first PSPE hydrogels, Figure 2 in conjunction with Figure 4a indicates that C_p depends on the number of dissociated sulfobetaine groups within the hydrogel. This is more apparent in the low salt concentration region, where C_p undergoes the most dramatic changes with concentration. Thus, for the lowest salt concentration used [KCNS] = 0.15 mol dm^{-3}, the values of N_3 and C_p are 0.4 and 0.68, respectively, whereas for [KCNS] = 0.30 mol dm^{-3}, $N_3 = 1$ and $C_p = 0.88$. At higher salt concentrations ([KCNS] > 0.3 mol dm^{-3}), C_p is approximately constant and equal to unity and N_3 varies from 1.7 at [KCNS] = 0.45 mol dm^{-3} to 6.3 at [KCNS] = 1.7 mol dm^{-3}. These findings can be explained by

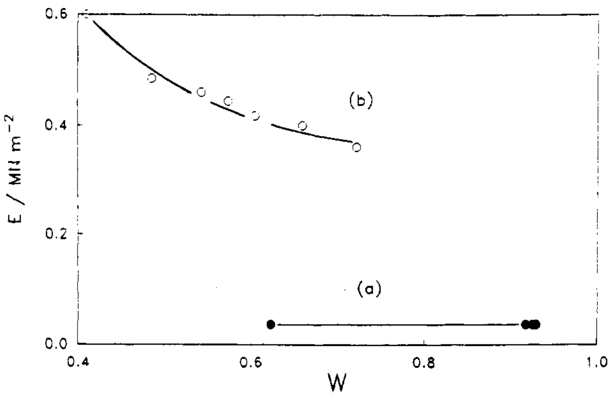

Figure 6. Young's modulus E (MN m^{-2}) as a function of the equilibrium degree of swelling W for (a) PSPE hydrogels and (b) PHEMA hydrogels.

considering that the swelling behavior is governed by two opposite thermodynamic forces: (i) on the one hand, the osmotic pressure π due to the different chemical potential inside and outside the hydrogel as a consequence of the existence of a concentration gradient and (ii) on the other hand, the repulsive force F_r between charged neighboring zwitterionic groups. The first force is a positive swelling one, whereas the second one is negative. Consequently, the swelling data suggest that at the lowest salt concentration, 0.15 mol dm^{-3}, the repulsive force F_r prevails over π, whereas at [KCNS] = 0.3 mol dm^{-3}, $\pi > F_r$ and for higher KCNS concentrations, the swelling is only controlled by π.

The swelling behavior associated with PHEMA hydrogels can be explained by taking into consideration the earlier work by Dusek et al.,[5] who concluded that the decisive role in swelling is played by the anions. At low KCNS concentrations (0 < [KCNS] < 0.6 mol dm^{-3}), CNS$^-$ anions are adsorbed onto the polymer molecules, charging them negatively. Repulsions between like-like charges produce chain expansion and an increase in water uptake which was described above. Further effects of this partial negative charge of the polymer are (i) reduction of the hydrophobic character of the polymer chain, (ii) reduction of the association of hydrophobic groups, and (iii) electrostatic attraction of cations and their hydration layers. The overall effect is therefore an increase in water content (Figure 1d) and a decrease of C_p (Figure 4b). At higher KCNS concentrations ([KCNS] > 0.6 mol dm^{-3}), additional effects must be considered:[5] (i) ion interactions (formation of crystalline hydrates, ion pairs, ion association, or complex ions); (ii) dependence of the ion interactions on the composition and properties of the solvent, viz. polymer/water ratio; (iii) ion/polymer interactions which must increase; and (iv) the water structuring effect, which becomes less important. As mentioned above, $dN_1/d[\mathrm{KCNS}]$ is lower in this region than in the lower salt concentration range and similar to $dN_3/d[\mathrm{KCNS}]$. These results indicate that the number of ion/polymer interactions is growing and there is a simultaneous increase in the ion/ion interactions, which gives rise to a reduction of space between ions for water molecules. Consequently, C_p increases.

Network Parameters. In principle, changes in the mechanical properties of the hydrogels must be expected due to the modification of the swelling behavior, through addition of salt to the swelling medium. The variation of the compression stress-strain Young's moduli E as a function of the overall degree of swelling W is given in Figure 6a for PSPE and Figure 6b for PHEMA hydrogels. As can be observed PSPE hydrogels exhibit E values independent of W. In contrast, E decreases with W (Figure 6b) for PHEMA hydrogels. These dependences can be scaled according to the equations

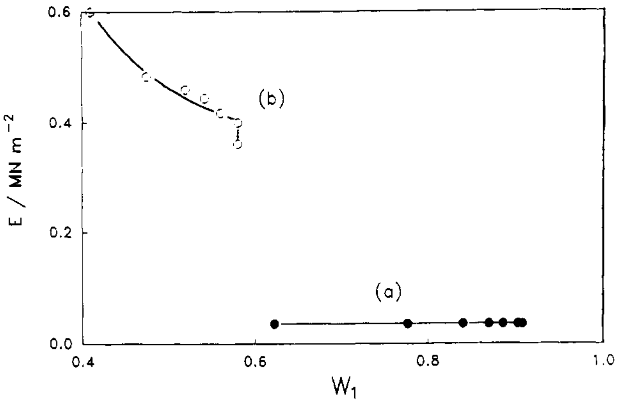

Figure 7. Young's modulus E (MN m^{-2}) as a function of the water content W_1 for (a) PSPE hydrogels and (b) PHEMA hydrogels.

$$\text{PSPE} \quad E = 0.037W^{0} \tag{2}$$

$$\text{PHEMA} \quad E = 0.29W^{-0.74} \tag{3}$$

The changes in E found for these hydrogels could be due to both higher water uptake or the presence of salt. The representation of E as a function of water content W_1 allows one to elucidate between both contributions. Accordingly, Figure 7 shows that E does not depend on W_1 for PSPE hydrogels, whereas for PHEMA hydrogels the following observations can be made: (i) for $0.41 < W_1 < 0.58$, E decreases with W_1 according to the equation

$$\text{PHEMA} \quad E = 0.25W_1^{-0.91} \tag{4}$$

and (ii) for $W_1 = 0.58$ there exist two E values. The higher one (E = 0.40 MN m^{-2}) corresponds to W = 0.66 ([KCNS] = 1 mol dm^{-3}), whereas the second one (E = 0.36 MN m^{-2}) is associated with W = 0.723 ([KCNS] = 1.7 mol dm^{-3}). Consequently, PSPE hydrogels exhibit mechanical properties insensitive to water content and/or salt content as a probable consequence of physical cross-linking brought about by the hydration spheres around the opened zwitterionic groups. On the contrary, for PHEMA hydrogels both species, water and KCNS molecules, plasticize the network, giving rise to lower Young's moduli.

Interaction Parameters. Several specific interactions take place in the ternary system water (1)/polymer (2)/salt (3), viz. water/water, salt/salt, polymer/polymer, water/polymer (1/2), salt/water (3/1), and salt/polymer (3/2). Each of these interactions is characterized by an interaction parameter χ_{ij}. The overall interaction parameter χ_T, which comprises all those above mentioned, can be obtained experimentally via[16]

$$\phi_2^{\,2}(\chi_T - 0.5) + V[\nu_e\phi_2^{\,1/3} - (\nu_e/2)\phi_2] = 0 \tag{5}$$

In eq 5, ϕ_2 is the volume fraction of polymer defined under Experimental Procedures, V is the molar volume of solvent ($V = V_1X_1 + V_3(1 - X_1)$, where V_1 is the molar volume of water (18 × 10^{-3} dm^3 mol^{-1}), V_3 is the molar volume of salt (51.54 × 10^{-3} dm^3 mol^{-1}), X_1 is the mole fraction of water inside the gel, and ν_e is the effective cross-linking density (moles of cross-links per unit volume of xerogel (mol dm^{-3})). It should be pointed out that the application of this equation is bound to the acceptance that the entropy of mixing is given entirely by the configurational entropy; this assumption implies that other contributions to the

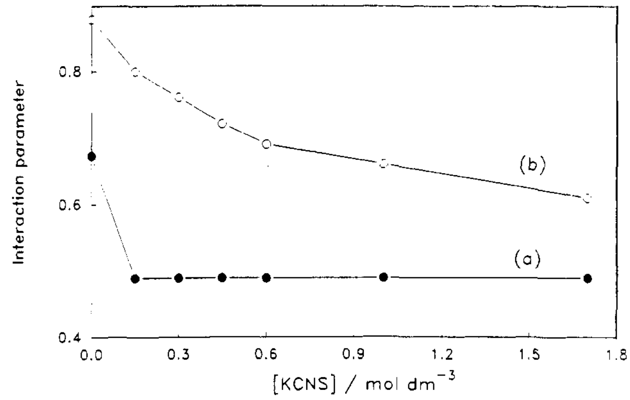

Figure 8. Overall interaction parameter χ_T as a function of molar concentration of KCNS for (a) PSPE and (b) PHEMA.

entropy derived from specific interactions between neighboring components are neglected. Compression stress–strain measurements in conjunction with the values of the volume fractions of polymer in water ϕ_2 determined as described under Experimental Procedures afforded the following cross-linking densities for PSPE[17] and PHEMA hydrogels at 293 K: ν_e(PSPE) = 8.6 × 10^{-3} mol dm^{-3} and ν_e(PHEMA) = 0.101 mol dm^{-3}.

The results obtained for the overall interaction parameter χ_T are given in Figure 8. It is noteworthy from this figure that (i) χ_T for PSPE decreases from 0.673 at [KCNS] = 0 mol dm^{-3} to a constant value of 0.49 independent of salt concentration and (ii) χ_T for PHEMA decreases gradually from 0.88 in pure water to 0.62 at [KCNS] = 1.7 mol dm^{-3}. These results indicate that, although the presence of salt enhances the swellability of PSPE hydrogels in aqueous solutions, water must be considered a poor solvent for PSPE. This finding, furthermore, is consonant to those reported by Monroy Soto and Galin[8] on the χ_T value for linear PSPE in NaCl solutions. With reference to PHEMA hydrogels, it is apparent that the presence of the salt KCNS promotes the swellability of this gel, but χ_T is still greater than 0.5. Therefore, the hydrophobic interactions remain predominant in this system.

The application of the Donnan-type equilibrium theory in conjunction with the equilibrium thermodynamics of ternary systems[16] allows one to separate χ_T into some of its contributions. According to the Donnan-type equilibrium theory, the chemical potential of water outside the gel $(\Delta\mu_1)^*$ is equal to the chemical potential of water inside the gel $\Delta\mu_1$ at swelling equilibrium. $(\Delta\mu_1)^*$ is given by

$$(\Delta\mu_1)^* = RT \ln X_1^* \gamma_1^* \tag{6}$$

where X_1^* is the mole fraction of water outside the gel and γ_1^* is the activity coefficient of water in the external solution. $\Delta\mu_1$, on the other hand, can be divided into two contributions, viz. a mixing contribution $(\Delta\mu_1)_m$ and a contribution $(\Delta\mu_1)_{el}$ due to the elastic deformation of the network.

$$\Delta\mu_1 = (\Delta\mu_1)_m + (\Delta\mu_1)_{el} \tag{7}$$

For the salt, $(\Delta\mu_3)^* = \Delta\mu_3$, where $(\Delta\mu_3)^*$ is the change in chemical potential on mixing salt and water with reference to the pure salt in its crystalline state at 298 K and $\Delta\mu_3$ is the change in chemical potential of salt inside the gel.

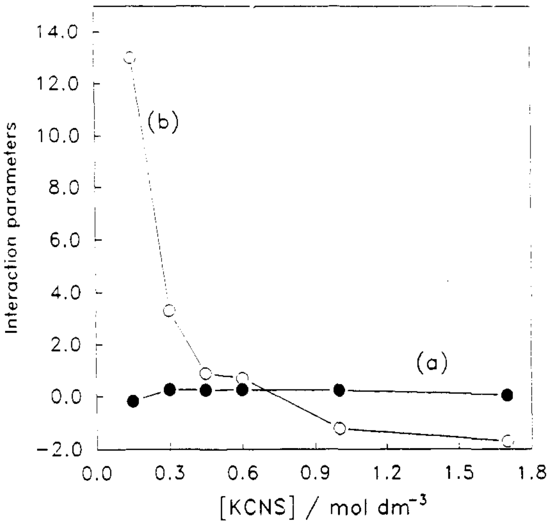

Figure 9. Variation of (a) the salt/water (χ_{31}) interaction parameter and (b) the salt/polymer (χ_{32}) interaction parameter with molar concentration of KCNS for PSPE hydrogels.

$$(\Delta\mu_3)^* = RT \ln X_3^* \gamma_3 \tag{8}$$

$$\Delta\mu_3 = (\Delta\mu_3)_m + (\Delta\mu_3)_{el} \tag{9}$$

In eq 8, X_3^* and γ_3^* are the mole fraction of salt and the activity coefficient of salt outside the gel, respectively.

$(\Delta\mu_i)_{el}$ (where i = 1) will be assumed to have the same form as $(\Delta\mu_i)_{el}$ (where i = 3):

$$(\Delta\mu_i)_{el} = RTV_i\nu_e[\phi_2^{1/3} - (\phi_2/2)] \tag{10}$$

In eq 10, R is the gas constant, T is the absolute temperature (293 K throughout this work), and V_i is the molar volume of water (i = 1) or salt (i = 3).

$(\Delta\mu_1)_m$ and $(\Delta\mu_3)_m$ are given by[16]

$$(\Delta\mu_1)_m = RT[\ln \phi_1 + (1 - \phi_1) - \phi_2(x_1/x_2) - \phi_3(x_1/x_3) + (\chi_{12}\phi_2 + \chi_{13}\phi_3)(\phi_2 + \phi_3) - \chi_{23}(x_1/x_2)\phi_2\phi_3] \tag{11}$$

$$(\Delta\mu_3)_m = RT[\ln \phi_3 + (1 - \phi_3) - \phi_1(x_3/x_1) - \phi_2(x_3/x_2) + (\chi_{31}\phi_1 + \chi_{32}\phi_2)(\phi_1 + \phi_2) - \chi_{12}(x_3/x_1)\phi_1\phi_2] \tag{12}$$

In these equations, ϕ_1, ϕ_2, and ϕ_3 are the volume fractions of water, polymer, and salt within the gel, respectively (see Appendix A), x_1, x_2, and x_3 represent the number of segments per molecule in the respective species, and χ_{ij} are the pair interaction parameters.

Under the experimental conditions used here, $x_2 = \infty$ (due to the network structure of the polymer). Furthermore, for simplicity x_1 is taken as unity. Accordingly, since

$$x_i/x_j = V_i/V_j \tag{13}$$

and V_3 is 51.54 10^{-3} dm^3 mol^{-1}, x_3 = 2.86. χ_{12} (the water/polymer interaction parameter) has been determined for both polymers by means of compression stress–strain measurements in conjunction with the volume fractions of polymer in water. For PSPE χ_{12} = 0.67 at 293 K,[17] and for PHEMA χ_{12} has been found here to be 0.88. Moreover, to circumvent the arithmetic problem resulting from the infinite value of x_2, χ_{23} has been converted into χ_{32} by means of

$$\chi_{ij} = \chi_{ji}(x_i/x_j) = \chi_{ji}(V_i/V_j) \tag{14}$$

Similarly, for convenience, χ_{31} will be used instead of χ_{13}. Consequently, it is possible to write for the two equilibria between water in external solution and gel and between

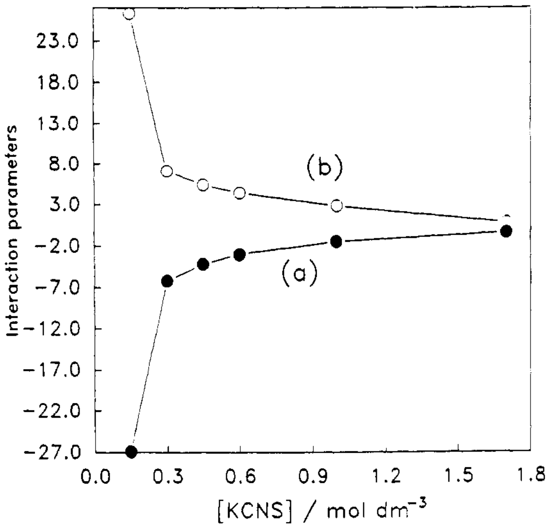

Figure 10. Variation of (a) the salt/water (χ_{31}) interaction parameter and (b) the salt/polymer (χ_{32}) interaction parameter with molar concentration of KCNS for PHEMA hydrogels.

salt in external solution and gel:

$$RT \ln X_1^*\gamma_1^* = RT\{\ln \phi_1 + (1 - \phi_1) - (\phi_3/2.86) + [\chi_{12}\phi_2 + (\chi_{31}/2.86)\phi_3](\phi_2 + \phi_3) - (\chi_{32}/2.86)\phi_2\phi_3\} + RTV_1\nu_e[\phi_2^{1/3} - (\phi_2/2)] \quad (15)$$

$$RT \ln X_3^*\gamma_3^* = RT\{\ln \phi_3 + (1 - \phi_3) - 2.86\phi_1 + [\chi_{31}\phi_1 + \chi_{32}\phi_2](\phi_1 + \phi_2) - 2.86\chi_{12}\phi_1\phi_2\} + RTV_3\nu_e[\phi_2^{1/3} - (\phi_2/2)] \quad (16)$$

Equations 15 and 16 can be recast as

$$\begin{vmatrix} A & B \\ D & E \end{vmatrix} \cdot \begin{vmatrix} \chi_{31} \\ \chi_{32} \end{vmatrix} = \begin{vmatrix} C \\ F \end{vmatrix} \quad (17)$$

where

$$A = (\phi_3/2.86)(\phi_2 + \phi_3) \quad (18)$$

$$B = -\phi_2\phi_3/2.86 \quad (19)$$

$$C = \ln X_1^*\gamma_1^* - \{\ln \phi_1 + (1 - \phi_1) - (\phi_3/2.86) + \chi_{12}\phi_2(\phi_2 + \phi_3)\} - V_1\nu_e[\phi_2^{1/3} - (\phi_2/2)] \quad (20)$$

$$D = \phi_1(\phi_1 + \phi_2) \quad (21)$$

$$E = \phi_2(\phi_1 + \phi_2) \quad (22)$$

$$F = \ln X_3^*\gamma_3^* - \{\ln \phi_3 + (1 - \phi_3) - 2.86\phi_3 - 2.86\chi_{12}\phi_1\phi_2\} - V_3\nu_e[\phi_2^{1/3} - (\phi_2/2)] \quad (23)$$

The calculations of γ_1^* and γ_3^* are given in full detail in Appendix B. χ_{31} and χ_{32} can be obtained by simply solving a system of two equations and two unknowns (eq 17).

The results obtained are given in Figures 9 and 10, where χ_{32} and χ_{31} are plotted as a function of [KCNS] for PSPE and PHEMA hydrogels, respectively. With regard to the former, it is relevant to note the following: (i) χ_{31} has a negative value (−0.16) at [KCNS] = 0.15 mol dm^{-3}. At higher KCNS concentrations, χ_{31} is positive and approximately equal to a constant value of 0.26 with the exception of [KCNS] = 1.7 mol dm^{-3}, for which χ_{31} = 0.06. (ii) χ_{32} shows a high positive value of 12.9 at [KCNS] = 0.15 mol dm^{-3} and undergoes a great decrease primarily in the concentration range 0.15 < [KCNS] < 0.30 mol dm^{-3}. Thereafter, the decrease is less pronounced, the lower value (−1.72) being obtained at the highest KCNS concentration. With reference to PHEMA hydrogels, the variation of χ_{31} as a function of KCNS concentration is, in qualitative terms, the mirror image of the variation of χ_{32} with [KCNS]. The former lies in the negative region, whereas the latter is in the positive one. Moreover, as for PSPE, the most abrupt changes are observed in the low KCNS concentration region. The greatest absolute values $|\chi_{31}|$ and $|\chi_{32}|$ (26.9 and 26.3, respectively) are obtained at [KCNS] = 0.15 mol dm^{-3} and the lowest (0.48 and 0.72) at [KCNS] = 1.7 mol dm^{-3}.

Correlation of N_1 and N_3 data given previously with these thermodynamic features affords further interesting observations. Thus, for PSPE hydrogels we find the following:

1. For [KCNS] = 0.30 mol dm^{-3}, N_3 = 1, that is, each sulfobetaine group is coupled to a KCNS molecule. However, under these conditions χ_{32} does not afford its highest value, but on the contrary remains bigger than 0.5, the threshold of spontaneous interaction.
2. For [KCNS] > 0.60 mol dm^{-3}, χ_{32} is lower than 0.5. Under these conditions N_3 > 2 and water molecules are being substituted by salt molecules.

Accordingly, the salt/polymer interaction is only a thermodynamically favorable process when each sulfobetaine group is surrounded by approximately three or more KCNS molecules. The sharp changes observed for χ_{32} at low KCNS concentrations are not accompanied by large changes in χ_{31}. This observation can be attributed to the high water content. Therefore, any change described earlier for the salt/polymer interaction involves simultaneously a small percentage of the total number of water molecules and χ_{31} remains constant.

For PHEMA hydrogels, the interaction salt/polymer is always greater than the threshold value of 0.5. N_3, moreover, is small, being always less than 1 over the entire concentration range. The observed decrease of χ_{32} determined here is consistent with the salting-in character of potassium thiocyanate. In view of the increasing interaction of salt with polymer, one would anticipate a decrease in interactions of salt with water. Reference to Figure 10 shows that this indeed is the case, viz. χ_{31} increases in magnitude with increasing [KCNS].

All the findings described above can be expressed quantitatively by determining the following relationship:

$$\chi_T - \chi_{32} - \chi_{12} = f(\chi_{31}) \quad (24)$$

The plots (not reproduced here) of the left-hand side of eq 24 vs χ_{31} are linear for both hydrogels and afford (i) for PHEMA, $f(\chi_{31}) = 0.93\chi_{31} - 1.373$ and (ii) for PSPE, $f(\chi_{31}) = 22\chi_{31} - 6$. As expected, the coefficient of χ_{31} for PSPE is much higher than the one for PHEMA due to the higher relevance of the salt/water interactions for the latter than for the former.

Conclusions

In conclusion it should be stated that this investigation was focused primarily on the effect of one specific salt of the salting-in type on the hydrogel of PSPE. The zwitterionic nature of this polymer has been shown to exert a pronounced influence on the swelling, partitioning thermodynamic, and elastic properties, as evidenced by results from parallel experiments on neutral PHEMA hydrogels. Exceptionally high swelling in water and the influence of salts on this are well recognized for polyelectrolyte gels, but it is important to reiterate here that PSPE is fundamentally different and should be regarded as an antipolyelectrolyte in its behavior. As far as the authors are aware, no comprehensive quantitative study has been reported before on cross-linked hydrogels of this type. One aspect that remains unresolved, however, is the extent to which the observed differences in properties of PSPE and PHEMA can be apportioned to the very marked difference between the values of ν_e of these two hydrogels (we are grateful to an anonymous referee for drawing this point to our attention). In principle, it would be possible to elucidate this problem by measuring the properties of these two hydrogels at equal effective cross-linking densities. The present preparative conditions were such as to afford equal values of the theoretical cross-linking density ν_t based on the content of EDMA in the feed mixture, but, as found also in other systems,[2,14,15,20] the value of ν_e cannot be predicted a priori. For the purpose in question it would be necessary to effect changes in ν_t for one of the systems, measure the value of ν_e for each of the resultant hydrogels, and interpolate to determine the value of ν_t required to yield the same value of ν_e as that possessed by the other system. Apart from the work involved, it is not beyond the bounds of possibility that such a situation may be unrealizable in practice. Effectively, the feasibility depends on the form of the interrelation between ν_t and ν_e for these particular hydrogels. For others, the interrelation can be either simple[2,14,20] or complex.[15] Moreover, copolymerization by γ-irradiation can often give rise to a finite value of ν_e even in the absence of EDMA, i.e., at $\nu_t = 0$.[2,14,15,20]

The present findings on PSPE suggest the further need to examine the importance of possible couplings of the sulfobetaine unit, viz. inter- and intrachain, interactions between nearest neighbors, etc. The expedient of introducing neutral spacers between SPE units should allow one to at least estimate the importance of nearest-neighbor interactions. The HEMA monomer unit is suitable for this purpose. Work on the preparation and properties of poly(SPE-*co*-HEMA) hydrogels of various compositions is currently in progress.

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Appendix A: Calculation of Gravimetric Swelling and Partitioning Parameter

The total degree of swelling was calculated from eq A.1 in which g_1 and g_3 are the masses of water and salt inside the swollen gel, respectively, and g is the total mass of gel:

$$W = (g_1 + g_3)/g \tag{A.1}$$

The degree of swelling on the basis of content of water alone (W_1) was calculated from eq A.2:

$$W_1 = g_1/g \tag{A.2}$$

The total mass of hydrogel (g) is given by eq A.3, in which g_2 is the mass of polymer:

$$g = g_1 + g_2 + g_3 \tag{A.3}$$

The initial weight of dry polymer (g_2) and the total degree of swelling at equilibrium were measured. Hence, the difference afforded ($g_1 + g_3$). To isolate the value of g_3 alone (and thereby subsequently g_1), the gel was dried under vacuum to a constant weight, giving this weight $g_2 + g_3$.

For the purpose of obtaining partitioning coefficients and activity coefficients, certain quantities relating to both the hydrogel and the external swelling medium are required. Thus, the mole fraction of water inside the gel X_1 is calculated from

$$X_1 = \frac{(g_1/M_1)}{[(g_1/M_1) + (g_2/M_2) + (g_3/M_3)]} \tag{A.4}$$

where M_1 (18 g mol^{-1}), M_2 (279 g mol^{-1}), and M_3 (97.2 g mol^{-1}) are the molar masses of water, monomer unit in PSPE, and KCNS, respectively.

The mole fraction of water in the external solution ($X_1{}^*$) at swelling equilibrium is given by

$$X_1{}^* = \frac{(g_1{}^*/M_1)}{[(g_1{}^*/M_1) + (g_3{}^*/M_3)]} \tag{A.5}$$

Determination of the masses $g_1{}^*$ and $g_3{}^*$ of water and salt, respectively, in the external solution at equilibrium requires the following procedure. Into an empty vessel, a known volume (V_a dm^3) of KCNS solution of molarity M_a (mol dm^{-3}) was added. Hence, the mass of salt in the initial swelling solution is $V_aM_aM_3$.

At swelling equilibrium, the swollen gel is removed and the external solution is weighed (M_b). Hence, $M_b = g_1{}^* + g_3{}^*$. By mass balance one has

$$(V_aM_aM_3) - g_3 = g_3{}^* \tag{A.6}$$

Consequently, $g_1{}^*$ is yielded as $g_1{}^* = M_b - g_3{}^*$.

The volume fractions are defined as

$$\phi_i = \frac{(g_i/\rho_i)}{\sum_i (g_i/\rho_i)} \tag{A.7}$$

where $i = 1$ (water), 2 (polymer), or 3 (salt). ρ_i is the density of water (1 kg dm^{-3}), polymer (1.1 kg dm^{-3} for both polymers), and salt (1.886 kg dm^{-3}).

The partitioning coefficient is defined as

$$C_p = m_3/m_3{}^* \tag{A.8}$$

where the concentration of salt in gel (no asterisk) and in swelling medium (with asterisk) are expressed in molalities (m):

$$C_p = \frac{g_3/(g_1 + g_2)}{g_3{}^*/g_1{}^*} \tag{A.9}$$

In eq A.9 the salt concentration in hydrogel is on the basis of moles of salt per kilogram of salt-free solvent, i.e., per kilogram of (polymer + water). If water alone is considered as solvent for the salt in the hydrogel, the partitioning coefficient is somewhat different and may be denoted as C_p':

$$C_p' = \frac{g_3/g_1}{g_3{}^*/g_1{}^*} \tag{A.10}$$

Appendix B: Water Activity Coefficients

The Gibbs–Duhem equation can be recast for a binary system as[19]

$$\left(\frac{\partial(\ln \gamma_1{}^*)}{\partial X_1{}^*}\right)_{(p,T)} = \frac{X_3{}^*}{X_1{}^*}\left(\frac{\partial(\ln \gamma_3{}^*)}{\partial X_3{}^*}\right)_{(p,T)} \tag{B.1}$$

where $\gamma_1{}^*$ and $\gamma_3{}^*$ are the activity coefficients of water and salt in the swelling medium, respectively. $X_3{}^*$ is the mole fraction of salt in the external solution, and $X_1{}^*$ has been defined in Appendix A. It is apparent from eq B.1 that if $\gamma_3{}^* = f(X_3{}^*)$ is known, $\gamma_1{}^* = f(X_1{}^*)$ can be calculated.

$\ln \gamma_3^* - \ln X_3^*$ data in the literature[18] for aqueous KCNS have been found to fit the following functions depending on the salt concentration range:

$$0.965 < X_3^* < 1 \qquad \ln \gamma_3^* = -0.107 \ln X_3^* - 0.939 \quad \text{(B.2)}$$

$$0.89 < X_3^* < 0.965 \qquad \ln \gamma_3^* = -0.0686 \ln X_3^* - 0.821 \quad \text{(B.3)}$$

Equations B.2, B.3, and B.1 in conjunction with the fact that $\gamma_1^* = 1$ when $X_1^* = 1$ provide the following $\ln \gamma_1^* - \ln X_1^*$ dependences:

$$0.965 < X_3^* < 1 \qquad \gamma_1^* = X_1^{*-0.107} \quad \text{(B.4)}$$

$$0.88 < X_3^* < 0.965 \qquad \gamma_1^* = X_1^{*-0.0686} \quad \text{(B.5)}$$

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