Influence of a Salt on the Properties of Hydrogels of 2-Hydroxyethyl Methacrylate with a Sulfobetaine Comonomer

Malcolm B. Huglin* and Jose M. Rego†

Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, U.K.

Received October 19, 1992; Revised Manuscript Received March 1, 1993

ABSTRACT: Copolymeric hydrogels of 2-hydroxyethyl methacrylate (HEMA) and *N,N*-dimethyl-*N*-[(methacryloyloxy)ethyl]-*N*-(3-sulfopropyl)ammonium betaine (SPE) 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. 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 nearest-neighbor interactions in SPE-based systems and indicates that copolymers prepared from SPE and HEMA represent an appropriate model system to study the above-mentioned interactions.

Introduction

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.[1] Polymers of type b (i.e., acid derivatives) exhibit the so-called polyelectrolyte behavior characterized by a marked deswelling in the salt solution.[2,3]

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 a 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.[1,4,5] In this connection, Salamone et al.[6,7] have observed a large increase in the swelling of vinylimidazolium sulfobetaine hydrogels in an aqueous salt medium (1 mol dm^{-3} NaCl solutions).

The dependence of salt concentration on the equilibrium swelling, the influence of swelling on mechanical properties, the concentration dependence of the partitioning coefficient of salt between hydrogel and external solutions, and thermodynamic properties in aqueous KCNS solutions of hydrogels prepared from *N,N*-dimethyl-*N*-[(methacryloyloxy)ethyl]-*N*-(3-sulfopropyl)ammonium betaine (SPE) were studied in a previous paper[8] in comparison with the corresponding properties obtained for 2-hydroxyethyl methacrylate (HEMA) hydrogels. The application of the polymer solution theory for ternary systems water/polymer/salt in conjunction with the Donnan-type equilibrium theory enabled the relevant water/polymer, salt/water, and salt/polymer interaction parameters for both polymeric hydrogels to be estimated. The following were apparent from this study: (i) The zwitterionic group in SPE exerts a pronounced influence on the swelling, partitioning, thermodynamic, and elastic properties of poly(SPE) hydrogels in aqueous KCNS. (ii) The salting-in effect associated with the salt KCNS is observed for both polymeric hydrogels, the salt KCNS producing a decrease of the overall interaction parameter χ_T from 0.673 ([KCNS] = 0 mol dm^{-3}) to 0.49 ([KCNS] > 0.15 mol dm^{-3}) for poly(SPE) gels and from 0.88 ([KCNS] = 0 mol dm^{-3}) to 0.62 ([KCNS] = 1.7 mol dm^{-3}) for poly(HEMA) hydrogels. (iii) There is a maximum of water molecules that poly(SPE) gels can retain from which water molecules are substituted by salt molecules (at [KCNS] = 0.15 mol dm^{-3}). This phenomenon is not observed in poly(HEMA) gels for which water and salt retention increase monotonically within the KCNS concentration range studied. (iv) The salt/water interaction parameter is approximately independent of salt concentration and equal to 0.25 for poly(SPE) gels, whereas the salt/polymer interaction parameter varies from very high positive values at low KCNS concentrations to negative values at KCNS concentrations higher than 0.6 mol dm^{-3}. In contrast, for poly(HEMA) gels the salt/water interactions are more favored than the salt/polymer ones over the entire range of concentration. (v) Poly(SPE) hydrogels show a marked antipolyelectrolyte effect, as can be concluded from the previous observations.

In the present paper attention is focused on the behavior of cross-linked poly(SPE–HEMA) swollen in aqueous KCNS. The relevance of nearest-neighbor interactions was noted previously[9] for these copolymeric hydrogels swollen in pure water. Specifically, a maximum in the water uptake obtained at copolymer compositions for which the like–unlike diads were calculated to predominate. Accordingly, water/SPE interactions are promoted when neutral spacers are interposed between two betaine monomer units. It would thus appear *a priori* that the swelling behavior of poly(SPE–HEMA) hydrogels in aqueous KCNS may well also be nonadditive, viz., not intermediate between that exhibited by the two homopolymeric hydrogels.

Conditions and Nomenclature

The preparation of copolymers via γ-irradiation and swelling and compression–strain measurements were made at 293 K.

Hydrogels are referred to according to the nature and composition of the dry unswollen xerogel. Since the

† Present address: DOW IBERICA S.A., Apartado 512, Bilbao, Vizcaya, Spain.

0024-9297/93/2226-3118$04.00/0

content of EDMA is very small and approximately constant, nomenclature is based on the two principal comonomers. It is convenient to abbreviate SPE and HEMA further to S and H, respectively, each followed by the appropriate mole fraction. For example, S0.0/H1.0 is the cross-linked homopolymer poly(HEMA) and S0.3/H0.7 is the cross-linked copolymer in which the mole fractions of SPE and HEMA are 0.3 and 0.7, respectively. Subscripts 1, 2, and 3 refer to the components SPE, HEMA, and EDMA, respectively, of the copolymer. Thus the mole fraction of SPE in a copolymer is F_1.

The swollen hydrogel is also multicomponent and, although adherence to the conventional subscripts 1, 2, and 3 is adopted too for a hydrogel, no confusion should arise because of the context. Subscripts 1 and 3 relate to water and KCNS, respectively, and subscript 2 refers to the polymeric (or copolymeric) component. For example, at swelling equilibrium the volume fraction of water in the hydrogel is ϕ_1, the thermodynamic interaction parameter between water and polymer is χ_{12}, and the mass of KCNS inside the hydrogel is g_3. Where one particular component of the swollen hydrogel is described with specific relation to one specific component of the copolymer, the abbreviations S and H (rather than 1 and 2) are used as superscripts for the latter to avoid confusion. Thus N_3^S means the number of moles of KCNS per monomer unit of SPE.

Experimental Procedure

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 Chemical Co., analytical grade) were used as received. Doubly distilled deionized water was used for polymerization, swelling, and stress–strain experiments.

Preparation of Hydrogels. Aqueous solutions of SPE, HEMA, and EDMA were prepared gravimetrically in previously siliconized glass tubes. Five mole fractions F_1 of SPE in the feed mixture were made up, viz., 0.15, 0.30, 0.45, 0.60, and 0.75. In every preparation, the EDMA concentration used was 0.5 wt % based on the total weight of the two principal monomers. Every feed composition required a different water content in order to compensate for two opposite effects: (i) when the water content is too high (>ca. 40 wt %), poly(HEMA) phase separates, and (ii) when the water content is too low (<ca. 50 wt %), SPE tends to gel.[1] The following volumes of water per gram of monomer mixture were found to be most convenient in order to compensate for the effects mentioned: 0.4, 0.5, 0.8, 1.0, and 1.2 cm^3 for F_1 = 0.15, 0.30, 0.45, 0.60, and 0.75, respectively. The reaction mixtures were 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. The resultant hydrogel rods were swollen to equilibrium for 2 months. During this time the unreacted monomer was removed by changing the swelling medium 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. After Soxhlet extraction, the gel fragments were dried in an oven at 348 K during 48 h followed by subsequent drying in a vacuum oven during another 48 h. The weights of the fragments prior to the Soxhlet extraction and after the extraction were found to be the same. Consequently, 100 wt % conversion was attained in all cases. The feed compositions, therefore, are equal to the overall copolymer compositions, denoted as the mole fraction F_1 of SPE in the copolymer. The copolymeric hydrogels will be denoted hereafter as S0.15/H0.85, S0.3/H0.7, S0.45/H0.55, S0.6/H0.4, and S0.75/H0.25 for F_1 = 0.15, 0.30, 0.45, 0.60, and 0.75 respectively. Hydrogels from poly(SPE) (S1.0/H0.0) and poly(HEMA) (S0.0/H1.0) cross-linked with 0.5 wt % EDMA were also prepared as described in ref 8. It is noted that, because of the different molar masses of SPE and HEMA, the constant EDMA concentration in the copolymers of 0.5 wt % does not correspond to a constant mole fraction of F_3 = 0.005 for EDMA; over the range of composition F_3 actually lies within the narrow interval 0.004–0.006.

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 ≈11 mm and thickness ≈2 mm) for measurement of the swelling and cylindrical pellets (diameter ≈11 mm and thickness ≈11 mm) for measurements of the compression modulus.

Swelling in KCNS Solutions. Dry xerogels were preconditioned in water in order 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 ($0 < [KCNS] \leq 1.7$ mol dm^{-3}) for 144 h. The total degree of equilibrium swelling (W), the degree of swelling in terms of the 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 total degree of swelling was calculated from eq 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 the gel. The degree of

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

swelling on the basis of the content of water alone (W_1) was calculated from eq 2. The total mass of the hydrogel (g) is given

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

by eq 3 in which g_2 is the mass of the polymer. The initial weight

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

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 (and thereby, subsequently, g_1), the gel was dried in vacuum to a constant weight, giving $g_2 + g_3$.

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:

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

where M_1 (18 g mol^{-1}), M_2 and M_3 (97.2 g mol^{-1}) are the molar masses of water, the reduced monomer unit in poly(SPE–HEMA) (this quantity is defined later in the paper), and KCNS, respectively.

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

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

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 a KCNS solution of molarity M_a (mol dm^{-3}) was added. Hence, the mass of salt in the initial swelling solution is $V_a M_a M_3$. At swelling equilibrium, the swollen gel is removed and the external solution is weighted (M_b). Hence, $M_b = g_1^* + g_3^*$. By mass balance one has

$$V_a M_a M_3 - g_3 = g_3^* \tag{6}$$

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

Finally, the partitioning coefficients C_p and C_p' are defined later in this paper.

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

$$\phi_2 = (D_0/D)^3 \tag{7}$$

where D_0 and D are the diameters of dry and swollen disks,

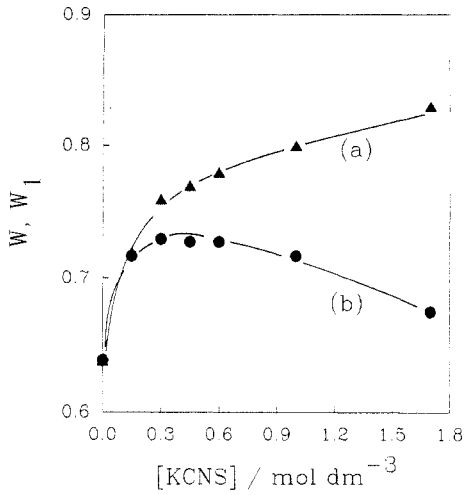

Figure 1. Dependence of (a) degree of equilibrium swelling W and (b) hydrogel water content W_1 on the concentration of KCNS for the hydrogel S0.15/H0.85.

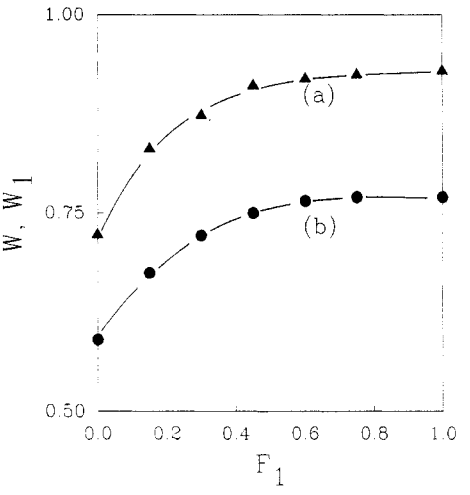

Figure 2. Dependence of (a) degree of equilibrium swelling W and (b) hydrogel water content W_1 on the copolymer composition for swelling in 1.7 mol dm^{-3} aqueous KCNS.

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.[10] The volume fractions of water, polymer, and salt are also calculated from gravimetric data as

$$\phi_i = \frac{(g_i/\rho_i)}{\sum_i (g_i/\rho_i)} \tag{8}$$

where i = 1 (water), 2 (copolymer), or 3 (salt). ρ_i are the densities of water (1 kg dm^{-3}), copolymer (1.1 kg dm^{-3} for all copolymers), and salt (1.886 kg dm^{-3}).

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.[11]

Results and Discussion

Swelling Behavior. Figure 1 shows the change of W and W_1 with the concentration of KCNS in the swelling medium for S0.15/H0.85. Changes of W and W_1 for hydrogels S0.3/H0.70, S0.45/H0.55, S0.6/H0.4, and S0.75/H0.25 have not been included, since they all exhibit the same qualitative behavior as hydrogel S0.15/H0.85, viz., (i) an increase in W, which becomes asymptotic at high concentrations of KCNS and (ii) a maximum in W_1 at [KCNS] = 0.15 mol dm^{-3} followed by a decrease in this quantity at higher concentrations of salt. It should also be noted that the profile of the variation of W and W_1 with the concentration of KCNS is similar to that obtained for SPE hydrogels,[8] which suggests that the swelling behavior of these copolymeric hydrogels is governed by the comonomer SPE. The variations of W and W_1 with copolymer composition F_1 are compared in Figure 2 for the highest concentration of KCNS. The selection of this specific concentration serves only comparative purposes. It is apparent from this figure that both W and W_1 increase with F_1, this increase being most marked at copolymer compositions F_1 lower than 0.3. From this composition onward W and W_1 increase very slowly.

A knowledge of the number of water molecules per monomeric unit N_1 and the number of salt molecules per monomeric unit N_3 provides information regarding the swelling behavior at the molecular level, as was demonstrated previously.[8] The relevant calculations are somewhat more difficult here, since the molar mass of the monomer unit is not an obvious magnitude in copolymeric systems. This problem has been circumvented by defining the monomeric units in these copolymers as being formed by both monomers in a quantity which is given by the copolymer mole composition F_1; that is:

$$M = M_S F_1 + M_H(1-F_1) \tag{9}$$

where M_S and M_H are the molar masses of SPE (279 g mol^{-1}) and HEMA (130 g mol^{-1}), respectively, and M is the molar mass of the *reduced* monomer (by this we understand a new monomer unit formed by corresponding mole fractions of the two comonomers). The calculated values of M for each copolymeric hydrogel studied here are 152.4, 174.7, 197.1, 219.4, and 241.8 g mol^{-1} for samples S0.15/H0.85, S0.3/H0.7, S0.45/H0.55, S0.6/H0.4, and S0.75/H0.25 respectively. Figure 3 shows the variation of N_3 (Figure 3a) and of N_1 (Figure 3b) with concentration of KCNS for all the copolymers. The values of N_1 and N_3 for the homopolymers are also included as a reference. The following features are apparent: (i) N_1 increases sharply for low concentrations of KCNS (between 0 and 0.15 mol dm^{-3}); after this sharp increase, N_1 remains almost constant ([KCNS] > 0.15 mol dm^{-3}); (ii) the variation of N_3 with [KCNS] is linear in the concentration range studied here; (iii) the slopes $dN_3/d[KCNS]$ increase with increasing copolymer composition F_1; (iv) at all concentrations of KCNS, the values of N_1 and N_3 for the copolymeric hydrogels lie between the two extremes represented by the homopolymeric gels S0.0/H1.0 and S1.0/H0.0.

In connection with the last observation, the values of N_1 and N_3 at [KCNS] = 0.6 mol dm^{-3} as a function of the copolymer composition are given in Figure 4. The slopes $dN_3/d[KCNS]$ have also been determined at each copolymer composition and are shown in Figure 5. These figures will enable one to elucidate whether the behavior associated with the swelling properties of the copolymeric hydrogels is additive or not. Additivity is taken to mean that the values of N_1 and N_3 fulfill the following conditions:

$$N_1 = F_1 N_1^S + (1-F_1)N_1^H = N_1^H + F_1 (N_1^S - N_1^H) \tag{10}$$

$$N_3 = F_1 N_3^S + (1-F_1)N_3^H = N_3^H + F_1 (N_3^S - N_3^H) \tag{11}$$

where N_3^S and N_3^H are the number of moles of KCNS per monomeric unit for S1.0/H0.0 and S0.0/H1.0, respectively, and N_1^S and N_1^H the number of moles of water per monomeric unit for S1.0/H0.0 and S0.0/H1.0, respectively.

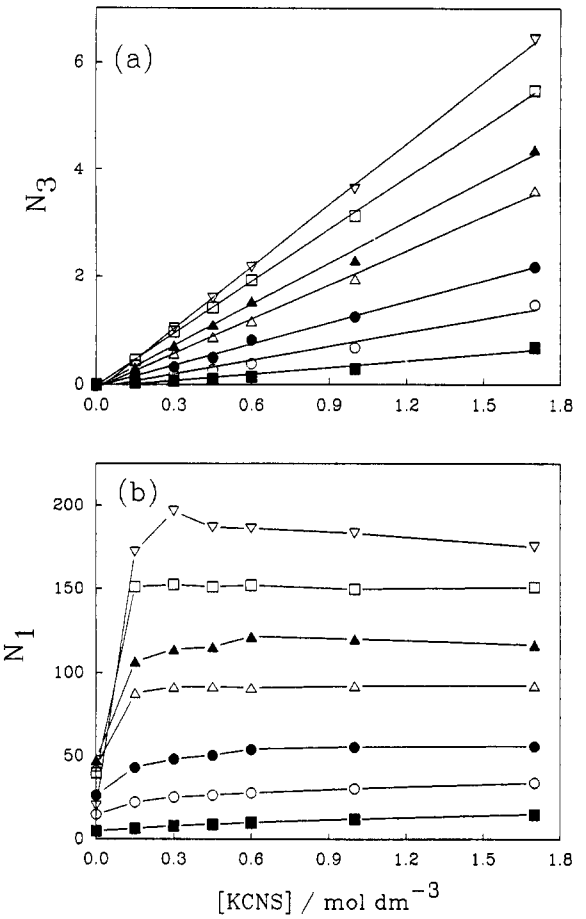

Figure 3. Change of (a) the number of salt molecules per monomeric unit (N_3) and (b) the number of water molecules per monomeric unit (N_1) with the concentration of KCNS for (■) S0.0/H1.0, (○) S0.15/H0.85, (●) S0.3/H0.7, (△) S0.45/H0.55, (▲) S0.6/H0.4, (□) S0.75/H0.25, and (▽) S1.0/H0.0.

Accordingly, the swelling behavior will be additive if the slopes of graphs of N_1 and N_3 vs F_1 have values approximately equal to (N_1^S-N_1^H) (=173) and (N_3^S-N_3^H) (=2.0), respectively, and the intercepts are N_1^H (=10.3) and N_3^H (=0.15). The values obtained for the slopes and intercepts for the variation of N_1 and N_3 with F_1 at [KCNS] = 0.6 mol dm^{-3} are as follows. (i) N_1 vs F_1: slope = 174 and intercept = 10. (ii) N_3 vs F_1: slope = 2 and intercept = 0.15. Consequently, since experimental values and those obtained on the basis of additivity are very close, it can be concluded that the swelling behavior of these copolymeric hydrogels in aqueous KCNS is a function of copolymer composition. This additive behavior seems to contradict the apparent qualitative swelling behavior controlled by SPE suggested by the variation of W and W_1 with the concentration of KCNS and F_1. It should be noted that the qualitative variations of N_1 and N_3 are also very similar to that found for the homopolymer S1.0/H0.0; viz., (i) N_1 exhibits a sharp increase at 0 < [KCNS] < 1.5 mol dm^{-3} and reaches a plateau (no further increase) at [KCNS] > 0.15 mol dm^{-3} and (ii) N_3 shows an increasing behavior at all concentrations of salt and for all copolymeric hydrogels. The additive behavior makes reference, therefore, to the quantitative values of N_1 and N_3.

With regard to the variation of dN_3/d[KCNS] with F_1, it is apparent from Figure 5 that this is a linear relationship, the slope being 3.69 dm^3 mol^{-1}. Physically, this quantity dN_3/d[KCNS] represents the rate of variation of the number of salt molecules per monomeric unit with the concentration of salt in the swelling medium for a

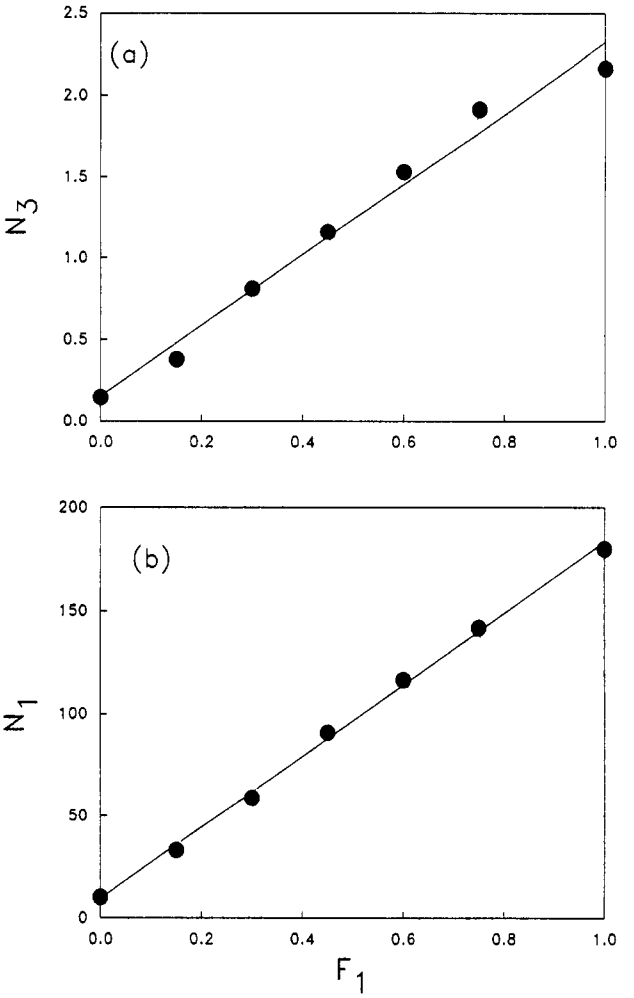

Figure 4. Change of (a) the number of salt molecules per monomeric unit (N_3) and (b) the number of water molecules per monomeric unit (N_1) with the composition of copolymer for swelling in 0.6 mol dm^{-3} aqueous KCNS.

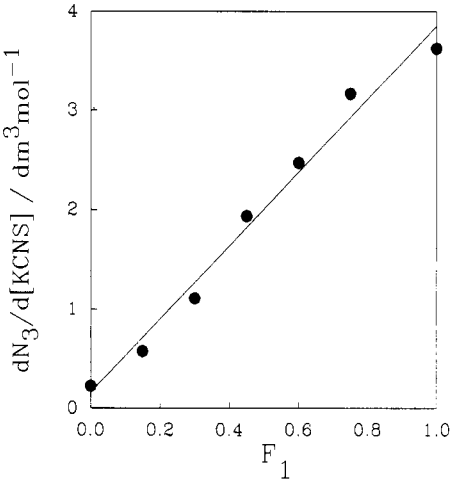

Figure 5. Variation of the slope dN_3/d[KCNS] with the copolymer composition.

copolymeric gel of given composition F_1. Accordingly, the linearity exhibited by the plot of dN_3/d[KCNS] vs F_1 denotes again an additive swelling behavior with respect to the salt uptake. This can be tested by differentiating eq 11 with respect to the concentration of salt:

$$\frac{dN_3}{d[KCNS]} = \frac{d(N_3^S - N_3^H)}{d[KCNS]} F_1 + \frac{dN_3^H}{d[KCNS]} \quad (12)$$

According to eq 12, therefore, the slope of the plot dN_3/

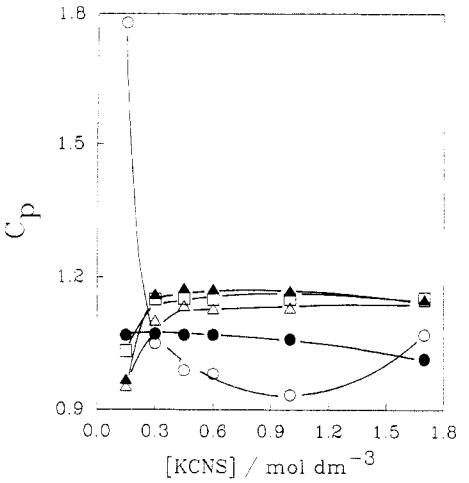

Figure 6. Partitioning coefficient C_p as a function of concentration of KCNS for (○) S0.15/H0.85, (●) S0.3/H0.7, (△) S0.45/H0.55, (▲) S0.6/H0.4, and (□) S0.75/H0.25.

d[KCNS] vs F_1 should be equal to $d(N_3^S-N_3^H)/d[KCNS]$. The values of this slope has been calculated to be 3.45 dm^3 mol^{-1}, which is close to the value 3.69 dm^3 mol^{-1} obtained experimentally from Figure 5. These calculations provide further proof of the additive swelling behavior shown by these copolymers.

The partition coefficient of one substance between two different phases provides information related to the affinity of this substance for each phase and consequently is a thermodynamic measure of the relative goodness of each medium to this substance. It should be recalled that the partition coefficient can be defined in two different modes C_p and C_p' both expressing the ratio of the molality of salt in the swollen gel to the molality of salt in the external solution at swelling equilibrium. The former molality is per kilogram of (water + polymer) for C_p, whereas for C_p' it is per kilogram of water alone.

$$C_p = \frac{g_3/(g_1+g_2)}{g_3^*/g_1^*} \tag{13}$$

$$C_p' = \frac{g_3/g_1}{g_3^*/g_1^*} \tag{14}$$

In eqs 13 and 14, g_1, g_2, and g_3 are the masses of water, polymer, and salt, respectively, as defined in the Experimental Section; quantities without an asterisk relate to weights within the swollen hydrogel and those with an asterisk to weights in the external swelling at equilibrium. These two definitions were employed previously[8] for hydrogels prepared from the homopolymers poly(SPE) and poly(HEMA). The following points were noted: (i) plots of C_p and C_p' vs [KCNS] for poly(SPE) are similar for both modes of expressing the partition coefficient, whereas for poly(HEMA) there is the important difference that $C_p' > C_p$ at each salt concentration; (ii) the definitions of C_p and C_p' show that C_p tends to C_p' the smaller the polymer content of swollen gel, which is the situation for the more highly swellable poly(SPE). For the sake of comparison only one definition is needed. The selection of this definition is dictated by the swelling behavior of the copolymeric hydrogels studied here; viz., they all exhibit higher swellability than poly(HEMA) hydrogels, and accordingly C_p appears to be more appropriate. Figure 6 shows the variation of C_p with the KCNS concentration for the different copolymeric hydrogels studied here. The curves corresponding to S0.0/H1.0 and S1.0/H0.0 are not included, since have already been discussed in detail.[8] However, for the sake of clarity a few comments on relevant aspects of the variation of C_p in aqueous KCNS associated with these two homopolymeric hydrogels must be made. Thus, it was found for poly(SPE) (S1.0/H0.0) that C_p varied from 0.68 at [KCNS] = 0.15 mol dm^{-3} to 0.88 at [KCNS] = 0.3 mol dm^{-3}. At higher salt concentrations ([KCNS] > 0.3 mol dm^{-3}), C_p is approximately constant and equal to unity. Hydrogels of poly(HEMA) (S0.0/H1.0) exhibit a minimum value of C_p (=0.74) at [KCNS] = 1.0 mol dm^{-3}. Furthermore, for this hydrogel C_p varies over a rather narrow interval with the concentration of KCNS, being 0.8 at [KCNS] = 0.15 mol dm^{-3} and 0.74 at [KCNS] = 1.0 mol dm^{-3} and between this latter value and 0.86 at [KCNS] = 1.7 mol dm^{-3}. Consequently, it is apparent from Figure 6 that the variation of C_p with concentration of KCNS for the copolymeric hydrogel S0.15/H0.85 resembles qualitatively the behavior observed for the homopolymeric hydrogel S0.0/H1.0, whereas the behavior of the other four hydrogels of higher content of SPE is similar to that of S1.0/H0.0. Quantitatively, however, S0.15/H0.85 is very different from S0.0/H1.0. Thus, for this copolymer C_p decreases from 1.78 at [KCNS] = 0.15 mol dm^{-3} to 1.07 at [KCNS] = 1.7 mol dm^{-3} and exhibits a minimum (=0.93) at [KCNS] = 1.0 mol dm^{-3}. Accordingly, the presence of a small proportion of SPE units in S0.15/H0.85 produces very important changes in the swelling behavior of HEMA-based hydrogels. With regard to the other copolymeric hydrogels, although their behavior is similar in profile to that of S1.0/H0.0, they all exhibit higher values of C_p than the latter homopolymers. Thus, the plateau of C_p appears at 1.06 for S0.3/H0.7, at 1.13 for S0.45/H0.55, at 1.17 for S0.6/H0.4, and at 1.15 for S0.75/H0.25. At this point, it is useful to give the factors that governed the swelling behavior of the homopolymeric gels S1.0/H0.0 and S0.0/H1.0, since the values of C_p obtained for the copolymers can be explained similarly. Considering S1.0/H0.0, the swelling behavior is governed by two opposite thermodynamic forces: (i) on the one hand, the osmotic pressure π due to the different chemical potentials 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 is negative. With regard to S0.0/H1.0, the variation of C_p with the concentration of KCNS was explained considering the earlier work on poly(HEMA) hydrogels by Dušek et al.,[12] who concluded that the anion CNS^- absorbs onto the polymer molecules, charging them negatively. At low salt concentrations, this absorption yields a high salt uptake which decreases at higher salt concentration due to repulsions between like–like molecules, which is accomplished by chain expansion and an increase in the water uptake. 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 variation of the partition coefficients for the copolymeric hydrogels studied here can be explained now on the basis of the considerations given above. Thus, for the gel S0.15/H0.85 the following apply: (i) At low KCNS concentrations C_p exhibits its highest value as a consequence of the solvation of the zwitterionic groups and the absorption of the anions CNS^- onto the HEMA segments. The value obtained for this copolymer differs greatly from that shown by the homopolymer S0.0/H1.0 due to the solvation of the zwitterionic groups which promotes salt uptake. (ii) At concentrations of KCNS higher than 0.15

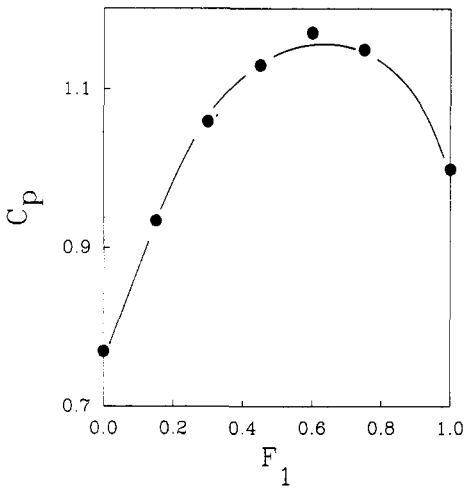

Figure 7. Partitioning coefficient C_p as a function of copolymer composition for swelling in 1.0 mol dm^{-3} aqueous KCNS.

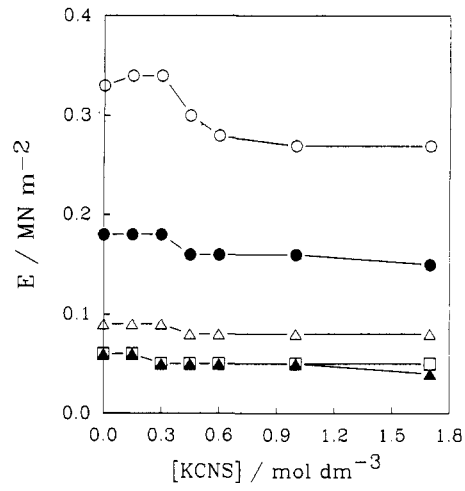

Figure 8. Variation of Young's modulus E with the concentration of KCNS for (○) S0.15/H0.85, (●) S0.3/H0.7, (△) S0.45/H0.55, (▲) S0.6/H0.4, and (□) S0.75/H0.25.

mol dm^{-3}, other effects such as repulsions between like–like molecules which is accomplished by chain expansion and an increase in the water uptake, reduction of the hydrophobic character of the polymer chain, reduction of the association of hydrophobic groups, and electrostatic attraction of cations and their hydration layers become dominant and C_p undergoes changes qualitatively similar to those observed for S0.0/H1.0. Quantitative differences are to be attributed to the presence of SPE units. On the other hand, the variation of the partition coefficient with the concentration of KCNS for copolymeric hydrogels of higher SPE content ($F_1 \geq 0.30$) is governed by the SPE units, as can be concluded from the profile of the curves C_p vs [KCNS] given in Figure 6. Accordingly, the results obtained must be explained in terms of osmotic pressure and repulsive forces between solvated SPE nearest neighbors as was done for SPE hydrogels (S1.0/H0.0). Consequently, π prevails over F_r at low salt concentrations ([KCNS] < 0.30 mol dm^{-3}), whereas at concentrations higher than 0.30 mol dm^{-3} the repulsive forces between solvated nearest-neighbor SPE units become important and C_p tends to a constant value. If values of C_p at a given salt concentration (i.e., [KCNS] = 1.0 mol dm^{-3}) are represented as a function of F_1 (including also data for S0.0/H1.0 and S1.0/H0.0) in order to compare the quantitative behavior associated with the different copolymeric hydrogels studied here, Figure 7 is obtained. It is apparent from this plot that C_p is maximum at $0.45 < F_1 < 0.75$. It should be recalled that in this same region of copolymer composition, the concentration of HEMA–SPE diads is maximum,[9,13] which indicates that the nearest-neighbor interactions are also of great relevance on considering salt uptake (the same profile was obtained for the water uptake behavior at 293 K for these copolymers[9]).

Network Parameters. The variation of Young's moduli E of homopolymeric hydrogels prepared from HEMA and SPE with the degree of swelling in aqueous KCNS solutions was discussed in a previous paper.[8] It was noted that poly(SPE) hydrogels exhibited values of E that were independent of the overall degree of swelling W. In contrast, E decreased exponentially with W for poly(HEMA) hydrogels. Changes of Young's moduli of HEMA–SPE-based hydrogels swollen in pure water with the copolymer composition have also been discussed elsewhere.[9] This study disclosed the loss of mechanical properties as the copolymer became richer in SPE as a consequence of poorer cross-linking dictated by kinetic factors of the polymerization process in which the xerogels were made. Consequently, the mechanical properties of the copolymeric hydrogels must be expected to change with copolymer composition and concentration of KCNS in the swelling medium. In the present work, the mechanical properties of the hydrogels will be discussed as a function of KCNS concentration in order to facilitate the understanding of the changes observed. The variation of Young's moduli E with the concentration of KCNS is given in Figure 8 for the five hydrogels. These plots reveal that, at low salt concentrations ([KCNS] < 0.45 mol dm^{-3} and [KCNS] < 0.30 mol dm^{-3} for S0.6/H0.4 and S0.75/H0.25, respectively), E is sensibly constant. At [KCNS] > 0.45 mol dm^{-3} ([KCNS] > 0.30 mol dm^{-3} for S0.6/H0.4 and S0.75/H0.25), E undergoes a sharp decrease which is more apparent at low copolymer compositions ($F_1 = 0.15$ and 0.30). The explanation of these results must be related to the swelling behavior of these gels, since variations of E can only be due to a plasticizing or reinforcing effect brought about by the solvents (water and salt). Figure 3 is especially interesting in this context to correlate mechanical and swelling properties. As can be observed from this figure, at [KCNS] < 0.45 mol dm^{-3} N_1 and N_3 show increasing trends, whereas, at higher concentrations, only N_3 increases, N_1 being sensibly constant. Consequently, it would appear as if the water molecules counteract the plasticizing effect of KCNS in the low concentration region. As the number of water molecules per reduced monomeric unit does not increase in the same proportion as N_3 at higher salt concentrations, the so-called plasticizing effect becomes apparent and E decreases.

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 mentioned above, can be obtained experimentally via[14]

$$\phi_2^2(\chi_T - 0.5) + V[\nu_e\phi_2^{1/3} - (\nu_e/2)\phi_2] = 0 \qquad (15)$$

In eq 15, ϕ_2 is the volume fraction of polymer in the hydrogel, V is the molar volume of solvent (aqueous KCNS), which is calculated from the composition of the aqueous salt in conjunction with the molar volume of water (18×10^{-3} dm^3 mol^{-1}) and the molar volume of KCNS (51.54×10^{-3} dm^3 mol^{-1}), and ν_e is the effective cross-linking density (moles of cross-links per unit volume of xerogel). It should be pointed out that the application of

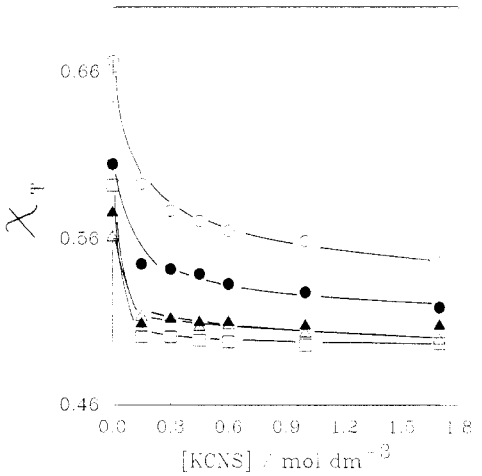

Figure 9. Overall interaction parameter χ_T as a function of the molar concentration of KCNS for (○) S0.15/H0.85, (●) S0.3/H0.7, (△) S0.45/H0.55, (▲) S0.6/H0.4, and (□) S0.75/H0.25.

eq 15 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 entropy derived from specific interactions between neighboring components are neglected. Compression stress–strain moduli G in conjunction with the values of ϕ_2 for copolymers swollen in water can yield the effective cross-linking densities ν_e directly when copolymerization is conducted in bulk.[9-11] However, for the present systems water was included within the reaction medium to an extent dependent on the feed composition (see the Experimental Section) and hence a correction is required[15-17] to calculate ν_e from G. For this purpose the total volume of the reaction medium at formation, i.e., copolymer + water, was employed for the volume of the strain-free reference state.[17] The resultant corrected values of $\nu_e/10^{-3}$ mol dm^{-3} were 82.4, 52.6, 35.3, 23.1, and 29.4 for S0.15/H0.85, S0.3/H0.7, S0.45/H0.55, S0.6/H0.4, and S0.75/H0.25, respectively. Except for the first of these, the effective cross-linking densities are smaller than the value of 56×10^{-3} mol dm^{-3} calculated purely on the basis of the initial concentration of EDMA. The corrected values of ν_e were used to calculate the values of χ_T from eq 15.

Figure 9 shows the dependence of the overall interaction parameter χ_T on the salt concentration. It is noteworthy from this figure that χ_T undergoes the greatest decrease at low salt concentrations ([KCNS] < 0.30 mol dm^{-3}). At higher concentrations χ_T is constant and independent of the salt concentration for all copolymeric gels except S0.15/H0.85. In the case of S0.15/H0.85, χ_T decreases gradually with the KCNS concentration similarly to S0.0/H1.0; values of χ_T at high salt concentrations (i.e., [KCNS] = 1 mol dm^{-3}) for the different copolymeric hydrogels are 0.559, 0.528, 0.504, 0.509, and 0.496 for S0.15/H0.85, S0.3/H0.7, S0.45/H0.55, S0.6/H0.4, and S0.75/H0.25, respectively. These values of χ_T indicate an increasing hydrophilicity of the gels with increasing F_1 as expected from the results obtained for the homopolymeric hydrogels;[8] viz., χ_T for S1.0/H0.0 decreases sharply from 0.673 at [KCNS] = 0 mol dm^{-3} to a constant value of 0.49 independent of salt concentration, and χ_T for S0.0/H1.0 decreases gradually from 0.88 in pure water to 0.62 at [KCNS] = 1.7 mol dm^{-3}. From the results given above it is apparent that χ_T in KCNS solutions is not influenced by the nature of the nearest neighbor, since no maximum or minimum of this quantity can be observed as a function of F_1. It should be recalled that this effect was of great importance in the case of the swelling behavior in water[9] and the partition coefficient in KCNS solutions (see above).

Application of the Donnan-type equilibrium theory in conjunction with the equilibrium thermodynamics of ternary systems[14] allows one to separate χ_T into some of its contributions. Full derivation has been given in our previous paper,[8] and it suffices here to present only the final expression whereby the salt/water (χ_{31}) and the salt/polymer (χ_{32}) interaction parameters can be obtained, viz.

$$\begin{vmatrix} A & B \\ D & E \end{vmatrix} \cdot \begin{vmatrix} \chi_{31} \\ \chi_{32} \end{vmatrix} = \begin{vmatrix} C \\ F \end{vmatrix} \tag{16}$$

where

$$A = (\phi_3/2.86)(\phi_2 + \phi_3) \tag{17}$$

$$B = -\phi_2\phi_3/2.86 \tag{18}$$

$$C = \ln X_1^*\gamma_1^* - \{\ln \phi_1 + (1 - \phi_1) - (\phi_3/2.86) + \chi_{12}\phi_2(\phi_2 + \phi_3)\} - V_1\nu_e(\phi_2^{1/3} - (\phi_2/2)) \tag{19}$$

$$D = \phi_1(\phi_1 + \phi_2) \tag{20}$$

$$E = \phi_2(\phi_1 + \phi_2) \tag{21}$$

$$F = \ln X_3^*\gamma_3^* - \{\ln \phi_3 + (1 - \phi_3) - 2.86\phi_3 - 2.86\chi_{12}\phi_1\phi_2\} - V_3\nu_e(\phi_2^{1/3} - (\phi_2/2)) \tag{22}$$

In eqs 17–22, ϕ_1, ϕ_2, and ϕ_3 are the volume fractions of water, polymer, and KCNS, respectively, in the hydrogel at swelling equilibrium; χ_{12} is the water/polymer interaction parameter; X_1^* and X_3^* are the mole fractions of water and KCNS, respectively, in the external swelling medium at equilibrium; γ_1^* and γ_3^* are the activity coefficients of water and KCNS, respectively, in the external swelling medium at equilibrium; V_1 and V_3 are the molar volumes of water and KCNS, respectively, and the factor 2.86 appears as the ratio of V_3 to V_1.

Literature data[18] on aqueous KCNS solutions provide values of γ_3^* as a function of X_3^*. Analysis of them gives the following: Within the range $0.965 < X_1^* < 1$, $\ln \gamma_3^* = -0.107 \ln X_3^* - 0.939$, and for $0.89 < X_1^* < 0.965$, $\ln \gamma_3^* = -0.0686 \ln X_3^* - 0.821$. By means of the Gibbs–Duhem equation, as described previously,[8] values of γ_1^* can then be derived as a function of X_1^*; viz., within the range $0.965 < X_1^* < 1$, $\ln \gamma_1^* = -0.107 \ln X_1^*$, and for $0.89 < X_1^* < 0.965$, $\ln \gamma_3^* = -0.0686 \ln X_1^*$. χ_{31} and χ_{32} can be obtained by simply solving a system of two equations and two unknowns (eq 16).

Because of overcrowding of data points when represented graphically, the values of χ_{32} and χ_{31} are listed in Table I. With regard to the salt/polymer interaction parameter, the following features emerge: (i) at [KCNS] = 0.15 mol dm^{-3}, all copolymeric hydrogels show the same trend; viz., χ_{32} is approximately zero. This behavior contrasts with the values obtained for S0.0/H1.0 and S1.0/H0.0 for which high positive values are obtained; (ii) at [KCNS] ≥ 0.30 mol dm^{-3}, χ_{32} exhibits a minimum at values −3 and −5 according to the copolymer, the corresponding copolymer compositions F_1 at the minima lying between 0.45 and 0.6. It should be noted that these negative values of χ_{32} and those reported before[8] for [KCNS] = 0.15 mol dm^{-3} indicate spontaneous interactions between polymer and salt for all copolymeric hydrogels studied here. With regard to the variation of χ_{31} with F_1, it is apparent from Table I that this thermodynamic parameter has a constant value of ca. 0.3–0.4 for the copolymeric compositions S0.45/H0.55, S0.6/H0.4, and S0.75/H0.25 (which coincides with the behavior found for homopolymeric gel S1.0/H0.0), whereas small variations of χ_{31} between −0.5 and 0.3 and

Table I. Interaction Parameters χ_{31} and χ_{32} for Hydrogels of Different Compositions in Various Concentrations of KCNS

copolymer composition F_1	[KCNS]/(mol dm^{-3}) 0.15		0.30		0.45		0.60		1.0		1.7	
	χ_{31}	χ_{32}	χ_{31}	χ_{32}	χ_{31}	χ_{32}	χ_{31}	χ_{32}	χ_{31}	χ_{32}	χ_{31}	χ_{32}
0.0	−13	26.3	−6.2	7.1	−4.2	5.4	−3.0	4.4	−1.5	2.8	−0.5	0.7
0.15	−0.5	0.4	0.2	−0.4	0.1	−0.3	0.1	−0.3	0.3	−1.3	0.3	−2.0
0.30	0.1	0.3	0.2	−0.6	0.3	−1.1	0.3	−2.5	0.3	−2.3	0.3	−3.0
0.45	0.4	−0.1	0.3	−3.0	0.4	−3.0	0.4	−3.0	0.4	−4.0	0.3	−4.5
0.60	0.4	0.0	0.4	−3.4	0.4	−3.4	0.4	−3.6	0.4	−4.5	0.3	−4.7
0.75	0.4	−0.4	0.4	−2.6	0.4	−2.6	0.4	−3.6	0.4	−4.3	0.3	−4.4
1.0	−0.2	13.0	0.3	3.3	0.3	0.9	0.3	0.7	0.3	−1.2	0.1	−1.7

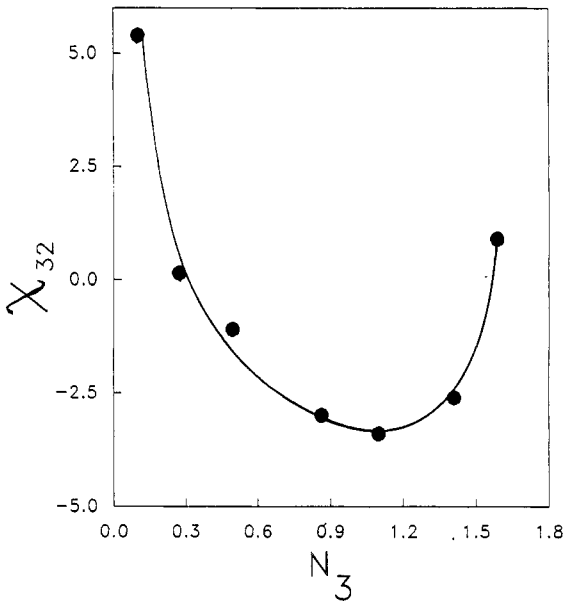

Figure 10. Variation of the salt/polymer (χ_{32}) interaction parameter with the number of salt molecules per monomeric unit N_3 for [KCNS] = 0.45 mol dm^{-3}.

between 0.1 and 0.3 have been obtained for the copolymeric hydrogels S0.15/H0.85 and S0.3/H0.7, respectively. This behavior is qualitatively similar to that found for the homopolymeric gel S0.0/H1.0 for which very different values of χ_{31} where obtained for each salt concentration (see $F_1 = 0$ in Table I and ref 8 for a detailed explanation).

The results obtained for the parameter χ_{32} represent quantitative evidence of the importance of the interactions between nearest neighbors in the sulfobetainic hydrogel poly(SPE) (S1.0/H0.0). In a preceding paper,[8] the values of χ_{32} as a function of the concentration of KCNS were discussed in terms of N_3, i.e., the number of salt molecules per monomeric unit. It appeared from that discussion that the salt/polymer interaction is only a thermodynamically favorable process when each sulfobetaine group is surrounded by approximately three or more KCNS molecules. That is, the disrupture of the association between neighboring sulfobetaine groups requires at least three KCNS molecules. From the present work on the properties of copolymeric gels prepared from the monomers HEMA and SPE, it is apparent that, for these hydrogels, spontaneous interaction between salt and polymer does not require high values of N_3 as can be deduced from Figure 3a. Thus, if some values of χ_{32} (Table I) are compared with corresponding values of N_3 for a given concentration of KCNS, for example, 0.45 mol dm^{-3}, it can be observed that higher values of N_3 are not necessarily related to lower values of χ_{32} and accordingly to a more spontaneous interaction between salt and polymer. A plot of χ_{32} as a function of N_3 relating to [KCNS] = 0.45 mol dm^{-3} is given in Figure 10. However, in this connection it should be recalled that the values of N_3 have been calculated by assuming a monomer unit comprised of both monomers in a proportion given by the copolymer composition F_1. The values of N_3 were obtained from eq 23 in which g_2 and g_3 are the masses of copolymer and salt within the copolymeric hydrogel, respectively, 97 g mol^{-1} is the molar mass of the salt, and M_2 is the reduced molar mass of a monomer unit in a copolymer, defined in eq 9.

$$N_3 = \frac{(g_3/97)}{(g_2/M_2)} \tag{23}$$

Accordingly, the values of N_3 given in Figure 10 could be underestimated with respect to the role of the SPE monomer units. If we assume that the salt molecules which ingress into the hydrogel interact primarily with the latter units (which could be a very reasonable approach), then a more appropriate quantity than N_3' to quantify the binding of salt to a monomer unit would be N_3 defined in eq 24 where W_{SPE} is the weight fraction of SPE in the dry copolymer and M_S has already been defined in eq 9.

$$N_3' = \frac{(g_3/97)}{(g_2 W_{SPE}/M_S)} \tag{24}$$

Values of N_3' evaluated for each copolymeric hydrogel are all of similar magnitude, viz., 1.8, 1.7, 1.9, 1.8, and 1.9 for S0.15/H0.85, S0.3/H0.7, S0.45/H0.55, S0.6/H0.4, and S0.75/H0.25, respectively. These results indicate that the thermodynamic behavior of SPE/HEMA hydrogels with regard to the parameter χ_{32} cannot be explained by simply considering a higher concentration of salt molecules within the gel and emphasizes the importance of the nearest-neighbor interaction within sulfobetaine-based hydrogels. It is noteworthy that the minimum in χ_{32} coincides with the maximum in SPE-HEMA diads[9,13] and that increasing the content of SPE–SPE diads (S0.75/H0.25) is associated with a less negative χ_{32} and accordingly a less spontaneous salt/polymer interaction.

Finally, it is interesting to note that, despite the negative values of χ_{32} and moderately positive values of χ_{31} obtained for these gels, none of the values of χ_T is lower than 0.5. Consequently, the overall interactions within these systems are not thermodynamically favored. This fact can be explained by using a simple additive law for χ_T:

$$\chi_T = a\chi_{12} + b\chi_{32} + c\chi_{31} \tag{25}$$

where a, b, and c are dimensionless coefficients which are related to the fractional contributions of water/polymer (χ_{12}), salt/polymer (χ_{32}), and salt/water (χ_{31}) interactions within the gels. Recalling that the values of χ_{12} for these copolymeric gels are 0.67, 0.61, 0.56, 0.58, and 0.59 for S0.15/H0.85, S0.3/H0.7, S0.45/H0.55, S0.6/H0.4, and S0.75/H0.25, respectively, it can be concluded that the values of χ_T are governed primarily by these parameters; that is, the fractional contribution of water/polymer interactions is much higher than those of the salt/polymer and salt/water interactions.

Acknowledgment. J.M.R. thanks the Ministerio de Educación y Ciencia of the Spanish Government for the provision of a maintenance grant.

References and Notes

(1) Schulz, D. N.; Peiffer, D. G.; Agarwal, P. K.; Larabee, J.; Kaladas, J. J.; Soni, L.; Handwerker, B.; Garner, R. T. *Polymer* **1986**, *27*, 1734.
(2) Breitenbach, J. W.; Karlinger, H. *Monatsh. Chem.* **1949**, *80*, 312.
(3) Katchalsky, A.; Lifson, S.; Eisenberg, H. *J. Polym. Sci.* **1951**, *7*, 571; **1952**, *8*, 476.
(4) Salamone, J. C.; Volksen, W.; Olson, A. P.; Israel, S. C. *Polymer* **1978**, *19*, 1157.
(5) Monroy Soto, V. M.; Galin, J. C. *Polymer* **1984**, *25*, 254.
(6) Salamone, J. C.; Volksen, W.; Israel, S. C.; Raia, D. C. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1974**, *15* (2), 291.
(7) Salamone, J. C.; Volksen, W.; Israel, S. C.; Olson, A. P.; Raia, D. C. *Polymer* **1977**, *18*, 1058.
(8) Huglin, M. B.; Rego, J. M. *Macromolecules* **1991**, *24*, 2556.
(9) Rego, J. M.; Huglin, M. B. *Polym. J. (Jpn.)* **1991**, *23*, 1426.
(10) Huglin, M. B.; Rehab, M. M. A.-M.; Zakaria, M. B. *Macromolecules* **1986**, *19*, 2986.
(11) Davis, T. P.; Huglin, M. B.; Yip, D. C. F. *Polymer* **1988**, *29*, 701.
(12) Dušek, K.; Bohdanecký, M.; Vošický, V. *Collect. Czech. Chem. Commun.* **1977**, *42*, 1599.
(13) Huglin, M. B.; Rego, J. M. *Colloid Polym. Sci.* **1992**, *270*, 234.
(14) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; Chapter XIII.
(15) Tanaka, T. *Phys. Rev. Lett.* **1978**, *40*, 820.
(16) Flory, P. J. *Proc. R. Soc. London, Ser. A* **1976**, *351*, 351.
(17) Fasina, A. B.; Stepto, R. F. T. *Makromol. Chem.* **1981**, *182*, 2479.
(18) Hatsopoulos, N. G.; Keenan, J. H. *Principles of General Thermodynamics*; John Wiley: New York, 1965; p 489.