

# Influence of temperature on swelling and mechanical properties of a sulphobetaine hydrogel

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The swelling and mechanical properties of a hydrogel based on the zwitterionic monomer *N,N*-dimethyl-*N*-methacryloyloxyethyl-*N*-(3-sulphopropyl)ammonium betaine crosslinked with ethylene glycol dimethacrylate have been determined as a function of temperature. The volumetric swelling has been found to decrease slightly with temperature. On the other hand, the Young's modulus as well as the experimental crosslink density increase with temperature. The results obtained have been explained by examining the changes with temperature of the partial molar Gibbs free energy of dilution in conjunction with the variation of its enthalpic and entropic contributions.

(Keywords: hydrogel; zwitterion; degree of swelling; Young's modulus; interaction parameter; free energy of dilution)

## INTRODUCTION

The general name 'sulphobetaine-based polymers' refers to a type of macromolecule in which a zwitterion or 'inner salt' has been incorporated in the side chain. The solution behaviour of some poly(zwitterions)<sup>1-3</sup> discloses the following general features for these materials in aqueous systems: (i) they are mostly insoluble in water<sup>4</sup> or display an unusual phase behaviour as a function of concentration<sup>5</sup>; (ii) the presence of salts enhances chain expansion (anti-polyelectrolyte effect), although it still remains low; and (iii) the behaviour of poly(sulphobetaines) in aqueous salt solutions does not deviate significantly from that of random coils of moderate flexibility in a thermodynamically poor solvent.

The possible application of sulphobetaine-based polymers as hydrogels was suggested by Salamone *et al.*<sup>4,5</sup>. As expected, these authors found that the hydration level for this type of material is low, viz. the gravimetric water content *W* (= weight per cent of water in swollen gel) varies from 35 to 46% depending on the nature of the monomer to which the zwitterionic group is attached. However, their studies did not involve quantitative work and only provided very scant data on degree of swelling and influence of presence of a salt on the gravimetric swelling behaviour. Thus, studies involving mechanical properties as well as equilibrium thermodynamics properties of swollen networks as a function of temperature and salt concentration are worthy of attention in order to rationalize the current obscure facts concerning swelling behaviour of poly(zwitterions).

In this paper, it is our intention to examine the swelling and (compression) stress-strain behaviour of hydrogels based on the zwitterionic monomer *N,N*-dimethyl-*N*-methacryloyloxyethyl-*N*-(3-sulphopropyl)ammonium betaine (SPE) (Figure 1) crosslinked with ethylene glycol

dimethacrylate (EDMA) as a function of temperature. In a parallel paper, the influence of the 'salting in' salt KSCN on the mechanical and swelling properties of hydrogels based on SPE is to be reported.

## EXPERIMENTAL

### Materials

SPE (Rasching Co.) and EDMA (Aldrich Chem. Co.) were used as received. Doubly distilled deionized water was used for polymerization, swelling and stress-strain experiments.

### Polymerization

An aqueous solution of SPE (50 g dl<sup>-1</sup>) and EDMA (0.5 wt%) was prepared gravimetrically, outgassed with gaseous nitrogen and irradiated with  $\gamma$  irradiation from a 9000 Ci <sup>60</sup>Co source. The  $\gamma$  irradiation dose was 1 Mrad, the dose rate being 0.01 Mrad h<sup>-1</sup> 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

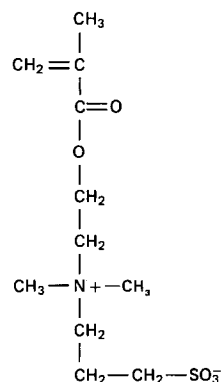


Figure 1 Molecular structure for the monomer SPE

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after the polymerization was complete and clear flexible rods of hydrogel were finally obtained. The resultant hydrogel rods were swollen to equilibrium in water for 2 months. During this time the unreacted monomer was removed by changing the swelling medium once a day. Parallel to this swelling to equilibrium of the SPE hydrogels, pre-weighed dry fragments of them were Soxhlet extracted for 24 h in hot water. A sol fraction of 10 wt% was obtained, which indicates that 90 wt% conversion was attained.

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 discs (diameter  $\sim 11$  mm and thickness  $\sim 2$  mm) for measurement of swelling and cylindrical pellets (diameter  $\sim 11$  mm and thickness  $\sim 11$  mm) for measurements of compression modulus.

#### Equilibrium water content of hydrogels

The equilibrium water content of the hydrogels  $W$  (wt%) was determined gravimetrically. Dry weighed xerogel discs were equilibrated in deionized water at 293 K for 2 weeks. Since the xerogel discs used here were previously subjected to the procedure described before to remove unreacted monomer, the  $W$  values given here are equilibrium ones. The reproducibility was tested by measuring  $W$  for six different discs. The standard deviation found for  $W$  was  $\pm 0.01$ .

#### Volumetric swelling at different temperatures

The volume fraction of polymer within a hydrogel  $\phi_2$  is given, at a particular temperature, by:

$$\phi_2 = (D_0/D)^3 \quad (1)$$

where  $D_0$  and  $D$  are the diameters of dry and swollen discs, respectively.  $D_0$  was measured at 293 K with a micrometer. Values of  $D$  were obtained at eight temperatures within the range 278–343 K. 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<sup>6</sup>.

#### Compression measurements

Elastic moduli of the hydrogels were determined by (compression) stress-strain experiments. Full experimental details of the assembly used are given elsewhere<sup>7</sup>.

## RESULTS AND DISCUSSION

#### Swelling properties

The gravimetric water content  $W$  found for this type of hydrogel was 62.3%. This value is much higher than those observed for hydrogels based on vinylimidazolium sulphobetaines<sup>4</sup>, which show  $W$  values ranging from 35 to 46%. This difference can be reasonably attributed to the higher hydrophobicity associated with the aromatic groups present in vinylimidazolium sulphobetaine type hydrogels. Comparison of  $W$  for PSPE with  $W$  for poly(2-hydroxyethyl methylacrylate) (PHEMA) is also useful in order to understand the relevance of the presence of the zwitterionic group in the swelling properties of PSPE, since both polymers, PSPE and PHEMA, are methacrylates. The latter shows a  $W$  value in the interval 35–41%<sup>8–10</sup>. It is apparent, therefore, that the sulpho-

betainic character of SPE does enhance the water uptake capability of the hydrophobic methacrylic chain. The increase, however, is not especially pronounced owing to the incorporation of methylene groups alongside the sulphonate and ammonium moieties.

With regard to the influence of temperature on  $\phi_2$ , the latter decreases with the former in the temperature range 278–303 K, changing from 0.412 at 278 K to 0.338 at 303 K. In the temperature interval 303–343 K,  $\phi_2$  shows a constant value of 0.338. Furthermore, the discs change from opaque (278–293 K) to transparent (293–343 K). Detailed discussion of the dependence of  $\phi_2$  on temperature is made later in this paper.

#### Network parameters

Young's moduli  $E$  were obtained as the initial slopes of plots of stress ( $\tau$ ) vs. strain ( $\lambda - 1$ ). Here  $\tau$  is the applied force per unit area of hydrogel and  $\lambda$  is the ratio of deformed length to undeformed length of hydrogel. Over the range of strain covered, 0 to  $-0.07$ , the plots were linear.

The theoretical crosslink density  $\nu_t$  has been calculated from:

$$\nu_t = Cf/2 \quad (2)$$

where  $C$  ( $\text{mol dm}^{-3}$ ) is the concentration of crosslinking agent of functionality  $f$ . For EDMA,  $f = 4$ . The value of  $C$  was found from the weight concentration of EDMA and by taking the density  $\rho$  of the xerogel as  $1.10 \text{ kg dm}^{-3}$ . The latter was determined by direct weighing and micrometrically measured dimensions of the dried discs and pellets used. The effective crosslink density was calculated from the compression-strain<sup>11</sup> results via equations (3) and (4) in which  $R$  is the gas constant,  $T$  (K) is the temperature and  $\nu_e$  is the effective crosslink density:

$$\tau = G(\lambda - \lambda^{-2}) \quad (3)$$

$$G = RT\nu_e\phi_2^{-1/3} \quad (4)$$

At low strains, i.e. 0 to about  $-0.07$ , plots of  $\tau$  vs.  $(\lambda - \lambda^{-2})$  according to equation (3) were linear, thereby yielding the compression moduli  $G$  as the slopes, from which values of  $\nu_e$  were isolated via equation (4). Values of the polymer-water interaction parameter  $\chi$  were calculated from the following expression valid at swelling equilibrium<sup>12</sup>:

$$\ln(1 - \phi_2) + \phi_2 + \chi\phi_2^2 + \nu_e V_1 (\phi_2^{1/3} - 2\phi_2 f^{-1}) = 0 \quad (5)$$

In equation (5), values of the molar volume of water  $V_1$  ( $\text{dm}^3 \text{ mol}^{-1}$ ) at different temperatures were obtained from:

$$V_1 = 10^{-3} [18.05 + 3.6 \times 10^{-3} (T - 298)] \quad (6)$$

Figure 2a shows the variation of the Young's modulus  $E$  as a function of temperature. Surprisingly enough, for this hydrogel increasing temperature is associated with increasing modulus, the latter varying between  $0.037 \text{ MN m}^{-2}$  at 278 K and  $0.044 \text{ MN m}^{-2}$  at 343 K. As mentioned before, this change in modulus with temperature is associated with a decrease of  $\phi_2$ , which indicates that water is not plasticizing the gel but, on the contrary, improves its mechanical properties. These low values found for the moduli are similar to those reported for poly(*N*-vinyl-2-pyrrolidone) (PVP)<sup>7</sup> for the same crosslinker and the same crosslinker concentration. In

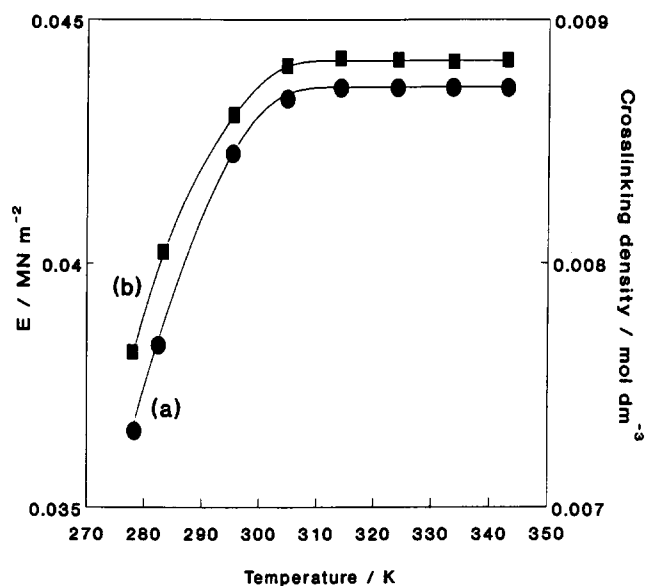


Figure 2 Variation of (a) Young's modulus and (b) experimental crosslink density  $v_e$  with temperature (K)

the case of PVP hydrogels, low moduli were justified as a consequence of their high water content, i.e. 95 wt%. The water content for PSPE hydrogels is 34 wt% lower than  $W$  for PVP hydrogels, and therefore the low moduli found for the former cannot be attributed to a high degree of swelling. The high content of methylene groups in PSPE appears to be a more likely explanation.

With regard to  $v_i$  and  $v_e$ , the former was found to be  $56 \times 10^{-3} \text{ mol dm}^{-3}$ . On the other hand,  $v_e$  displayed values dependent on temperature according to the modulus variation aforementioned. Thus,  $v_e$  changed from  $7.6 \times 10^{-3} \text{ mol dm}^{-3}$  at 278 K to  $8.8 \times 10^{-3} \text{ mol dm}^{-3}$  at 343 K. These  $v_e$  values suggest that: (i) the crosslinking is inefficient ( $v_e$  is about  $v_i/6$ ) and (ii) water enhances  $v_e$ . This latter observation could be due to the formation of hydrogen bonds between sulphate groups in neighbouring monomeric units and water<sup>3</sup>.

The crosslinking inefficiency is also reflected by the sol fraction obtained (10 wt%). The experimental evidence (the low  $v_e$  values and the existence of a sol fraction) indicates the high degree of inhomogeneity of these networks. In a previous paper<sup>7</sup>, this inefficiency of crosslinking was explained by considering the preparation of the xerogel as a copolymerization of crosslinker and functional monomer conducted to high conversion. Although the reactivity ratios for this pair of monomers are not known, they can be estimated approximately using the  $Q, e$  scheme. The  $Q, e$  values for EDMA<sup>13</sup> are 0.88 and 0.24, respectively, and 1.59 and 1.74 for SPE<sup>14</sup>. These  $Q, e$  values yield calculated reactivity ratios of  $r_1 = 0.79$  and  $r_2 = 0.13$ . The mole fraction  $f_1$  of EDMA in the feed was calculated to be 0.007. The variation of fractional conversion  $\theta$  with the instantaneous feed composition  $f_1$  has been calculated as described elsewhere<sup>7</sup>. Furthermore, the dependence of conversion on the mean copolymer cumulative mole fraction  $\langle C_c \rangle$  for EDMA has been evaluated by means of a Monte Carlo simulation of radical copolymerization, the basis of which has been explained in ref. 15. The total number of molecules in the feed used was 65 000 and the rest of the required input data has already been defined previously (reactivity ratios, feed composition and conversion).

Figure 3a shows the compositional drift associated with the polymerization conditions used here. According to this figure, 89% of the total amount of initial crosslinker concentration has reacted at a fractional conversion  $\theta$  of 0.3 and all of it is reacted at  $\theta = 0.6$ . It is understood that this kinetic study only considers one of the two vinyl groups of EDMA. Accordingly, crosslinking via the second group can take place at  $\theta > 0.6$ . This would explain why only 10 wt% of sol fraction (unreacted monomer, oligomers and homopolymer) has been extracted. These observations are confirmed by Figure 3b in which  $\theta$  has been represented as a function of  $\langle C_c \rangle$ . At very low values of conversion,  $\langle C_c \rangle$  is 0.027, which is much higher than the mole fraction of EDMA in the feed. This indicates, as pointed out earlier, that the crosslinker is reacting mainly in the very early stages of the polymerization, which gives rise to a wide mesh size distribution. Naturally, in the course of the reaction towards high  $\theta$ ,  $\langle C_c \rangle$  tends to the initial monomer feed composition.

The influence of temperature on the dimensions of hydrogels has been categorized into three types<sup>6</sup>: (a) the swelling increases with temperature—this behaviour is typified by poly(dihydroxypropyl methacrylate)<sup>16</sup>; (b) the swelling decreases with  $T$ , as found for poly(hydroxypropyl acrylate)<sup>17–19</sup>, poly(hydroxypropyl methacrylamide)<sup>20</sup>, poly(vinyl acetate)<sup>21,22</sup> and VP/butyl acrylate copolymeric hydrogels<sup>6</sup>; (c) there is a combined effect of swelling decreasing with  $T$  down to a minimum value and thereafter increasing at higher  $T$ . This has been observed for PHEMA hydrogels<sup>18,19</sup> and a copolymer of VP/hydroxypropyl methacrylate<sup>23</sup>. PSPE hydrogels fall into category (a).

Figure 4a shows the dependence of  $\chi$  on  $T$ . The decrease of  $\chi$  with increasing  $T$  (K) was fitted to a polynomial of the second degree:

$$\chi = 2.679 - 1.23 \times 10^{-2}T + 1.86 \times 10^{-5}T^2 \quad (7)$$

$\chi$  varies from 0.70 at 278 K to 0.65 at 343 K. These high values of  $\chi$  ( $>0.5$ ) corroborate the findings given in the introduction on the solution behaviour of poly(zwitterions), viz. their insolubility in water.

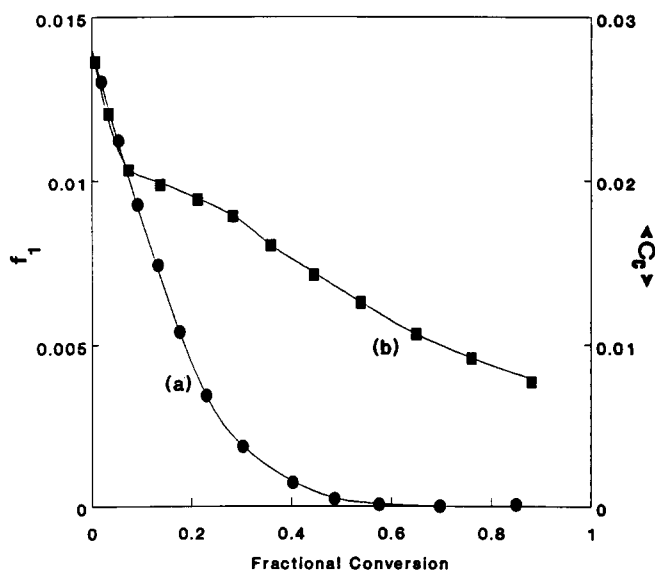


Figure 3 Change of (a) EDMA instantaneous feed composition  $f_1$  and (b) copolymer cumulative composition in EDMA with fractional conversion  $\theta$

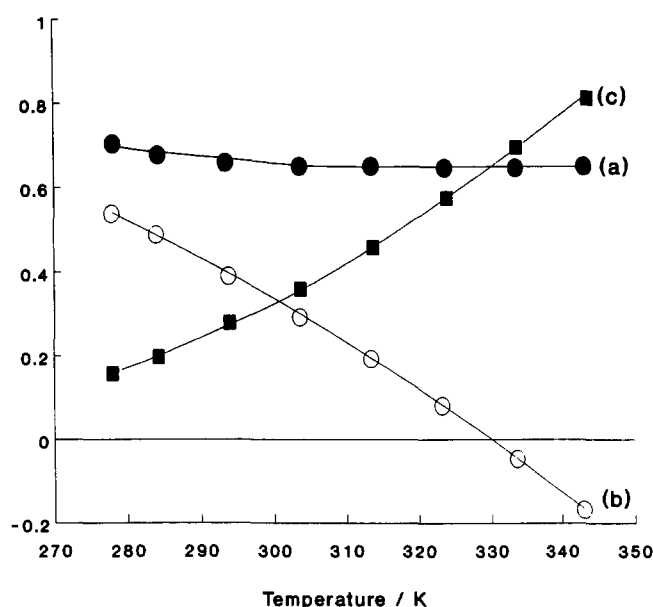


Figure 4 Variation with temperature (K) of the interaction parameter  $\chi$  (a) and its enthalpic  $\chi_H$  (b) and entropic  $\chi_S$  (c) components for PSPE hydrogels

Further analysis of the polymer–solvent interaction was made by separating  $\chi$  into its enthalpic ( $\chi_H$ ) and entropic ( $\chi_S$ ) components:

$$\chi = \chi_H + \chi_S \quad (8)$$

$$\chi_H = -T(d\chi/dT) \quad (9)$$

$$\chi_S = \chi + T(d\chi/dT) \quad (10)$$

The use of this simple subdivision is forced by the impossibility of isolating all the contributions unambiguously and quantitatively from more complex modifications of the original  $\chi$  parameter, which afford general forms of the dependence of  $\chi$  on  $T$ <sup>24–28</sup>.

The dependences of  $\chi_H$  and  $\chi_S$  on  $T$  are given in Figures 4b and 4c respectively. The behaviour associated with  $\chi_H$  is of particular interest, since negative values of this magnitude have been the dominant feature for several previous hydrogels studied by us<sup>6,7,29</sup>. For PSPE hydrogels,  $\chi_H$  is positive in the temperature range 278–330 K and negative at higher  $T$ . Discussion of this point is clearer if the partial molar enthalpy of dilution  $\overline{\Delta H}_1$  ( $\text{J mol}^{-1}$ ) and the partial molar entropy of dilution  $\overline{\Delta S}_1$  ( $\text{J mol}^{-1} \text{K}^{-1}$ ) are calculated according to the following equations<sup>30</sup>:

$$\overline{\Delta H}_1 = RT\phi_2^2\chi_H \quad (11)$$

$$\overline{\Delta S}_1 = R\phi_2^2(0.5 - \chi_S) \quad (12)$$

The partial molar free energy of mixing  $\overline{\Delta G}_1$  ( $\text{J mol}^{-1}$ ) is readily calculated from equations (11) and (12) as:

$$\overline{\Delta G}_1 = RT\phi_2^2(\chi - 0.5) \quad (13)$$

The change of the thermodynamic magnitudes defined above with  $T$  is represented in Figures 5a ( $\overline{\Delta H}_1$ ), 5b ( $T\overline{\Delta S}_1$ ) and 5c ( $\overline{\Delta G}_1$ ). The following main features arise from these figures: (i)  $\overline{\Delta H}_1$  has positive values in the temperature range 278–327 K and negative ones at higher  $T$ ; (ii)  $T\overline{\Delta S}_1$  is greater than zero for  $T$  in the range 278–315 K and negative at higher  $T$ ; and (iii)  $\overline{\Delta G}_1$  is greater than zero in the entire temperature range and shows the highest values at the lowest  $T$ , viz. 278–303 K.

Positive values of  $\overline{\Delta G}_1$  indicate that the swelling of PSPE hydrogels is an unfavourable thermodynamic process. However, points (i) and (ii) show that the reason for this overall trend differs according to the temperature regime. Thus, in the temperature range 278–323 K, the positive enthalpic contribution produces  $\overline{\Delta G}_1$  values bigger than zero, whereas from 323 K onwards, although the process is enthalpically favoured, the overall swelling process remains unfavourable owing to the negative entropy of dilution.

The thermodynamic features of swelling of PSPE hydrogels described before allow one to propose a swelling model for PSPE hydrogels. Between 278 and 323 K ( $\overline{\Delta H}_1 > 0$  and  $\overline{\Delta S}_1 > 0$ ), the like–like interactions are dominant since the groups amenable to interact with water (sulphonate and ammonium) undergo primarily intra- or interchain association. The increase in entropy (of the solvent inside the gel relative to the pure solvent) can be ascribed to the presence of water in the vicinity of the ionic atmosphere of the charged groups, which prevents formation of aqueous aggregates (hydrophobic interaction). It must be borne in mind that these contributions to  $\overline{\Delta G}_1$  are very small (at 278 K,  $\overline{\Delta H}_1$  is  $212.3 \text{ J mol}^{-1}$  and  $\overline{\Delta S}_1$  in  $0.48 \text{ J mol}^{-1} \text{K}^{-1}$ ). At temperatures higher than 323 K, the enthalpy of dilution becomes negative. This indicates that, at these temperatures, water molecules are undergoing spontaneous interactions with sulphonate and ammonium groups in the PSPE. In principle, these should produce a favoured swelling process. However, the negative entropic contribution also observed at these temperatures counteracts the enthalpic contribution. This negative  $\overline{\Delta S}_1$  can only be attributed to the structuring of water owing to the effective interaction between water molecules and the immobile charges in PSPE. The structuring of water yields a more ordered system and, accordingly, a smaller entropy than the one expected for the pure solvent. In this connection, it should be noted that the ammonium group is a strong water structure maker<sup>31</sup>. The results obtained indicate that the structuring of water

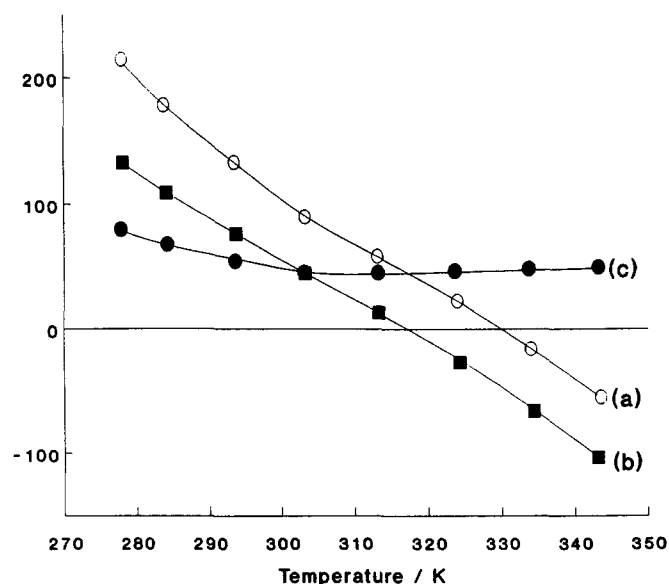


Figure 5 Variation with temperature (K) of (a) the enthalpy of dilution  $\overline{\Delta H}_1$  ( $\text{J mol}^{-1}$ ), (b) the entropy of dilution  $T\overline{\Delta S}_1$  ( $\text{J mol}^{-1}$ ) and (c) the Gibbs free energy of dilution  $\overline{\Delta G}_1$  ( $\text{J mol}^{-1}$ ) for PSPE hydrogels

prevails over the exothermic polymer–water interaction and  $\Delta G_1$  remains positive at high temperatures. Moreover, the increase of Young's modulus and crosslink density discussed previously in this paper is consistent with the increasing structuring of water molecules with increasing temperature.

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