Properties of poly(*N*-vinyl-2-pyrrolidone) hydrogels crosslinked with ethyleneglycol dimethacrylate

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N-Vinyl-2-pyrrolidone (VP) in the presence of ethyleneglycol dimethacrylate (EDMA) has been polymerized to high conversion by γ-irradiation. Poly(*N*-vinyl-2-pyrrolidone) (PVP) hydrogels were obtained by swelling the resultant solid xerogels to equilibrium in water. The hydrogels were characterized by differential scanning calorimetry, compression–strain measurements and determinations of sol fraction, water content and dimensions. For EDMA contents within the range 0.5–5.0 wt%, Young's moduli and the polymer–water interaction parameter χ lay within the intervals 0.019–0.504 MN m^{-2} and 0.491–0.572, respectively, at 294 K. At a fixed EDMA concentration, an increase from 275 to 342 K resulted in a small increase and a small decrease in χ and in water content, respectively, but Young's modulus and the effective crosslinking density (ν_e) remained practically independent of temperature. Inefficient crosslinking and inhomogeneity of the products are indicated by (i) the presence of large sol fractions and (ii) small values of ν_e relative to the theoretical crosslinking densities. The findings are supported by calculation of the compositional drift of unreacted monomer at all stages of the copolymerization (crosslinking) reaction. The water contents of the hydrogels were very high ($\sim$95 wt%) and were reduced significantly only at a high content of EDMA. The ratio of the contents of non-freezing water to total water within the hydrogels increased with increasing extent of crosslinking.

(Keywords: poly(*N*-vinyl-2-pyrrolidone); ethyleneglycol dimethacrylate; hydrogel; crosslinking density; γ irradiation; Young's modulus)

INTRODUCTION

N-Vinyl-2-pyrrolidone (VP) is readily polymerized by several means to produce a polymer, poly(*N*-vinyl-2-pyrrolidone) (PVP), which is soluble in water and also in a small number of organic solvents. Because of its hydrophilicity, VP is frequently copolymerized with hydrophobic monomers in the presence of a crosslinking agent to produce xerogels, which afford a wide variety of useful hydrogels when swollen in water. Linear PVP has several applications, especially pharmaceutical ones[1,2]. However, although the crosslinked form of PVP has a very high water absorbency, it is rarely used as a hydrogel because of its fragility. Consequently, these hydrogels have been subjected to relatively few studies with regard to their mechanical properties.

The objects of the present work are primarily (a) to investigate the mechanical properties of PVP hydrogels via uniaxial compression measurements, (b) to assess the influence of crosslinking agent on the equilibrium water content of the gels and to examine the structure of the imbibed water, and (c) to compare the properties of PVP hydrogels with those already established[3–6] for certain VP-containing copolymers.

In addition to those already quoted, the following abbreviations are adopted either alone or prefixed by P to denote the polymeric form where appropriate: BA, n-butyl acrylate; EDMA, ethyleneglycol dimethacrylate; HEMA, 2-hydroxyethyl methacrylate; HPM, hydroxypropyl methacrylate; MMA, methyl methacrylate; TFE, tetrafluoroethylene; TPT, 1,1,1-trimethylolpropane trimethacrylate; VNO, 2-vinyl-pyridine-*N*-oxide.

EXPERIMENTAL

Materials

VP (Aldrich Chem. Co.) was purified as before[4–6] (b.p. 341 K at 2 mmHg pressure). EDMA (Ancomer, type ATM 3) was purified by column chromatography using silica gel as absorbent and n-hexane/ethyl acetate (7/3 vol/vol) as eluant. Doubly distilled water was used for swelling and for d.s.c. measurements on water.

Polymerization

Mixtures of VP with EDMA were made up gravimetrically, outgassed, irradiated in sealed ampoules and post-cured as described in detail elsewhere[3–6]. In all cases the γ-irradiation dose was 1 Mrad obtained from the 9000 Ci ^{60}Co source at Salford University, the dose rate being 0.01 Mrad h^{-1} as determined by Fricke dosimetry. The resultant solid rods of xerogel were lathe cut[3] to produce thin discs (diameter $\sim$8–10 mm; thickness $\sim$2 mm) for measurements of swelling[5,6] and cylindrical pellets (diameter $\sim$8–10 mm; thickness $\sim$8–10 mm) for measurements of compression modulus[6].

Equilibrium water content of hydrogels

Dimensions of the dry discs and pellets were measured with a micrometer and the weighed samples were equilibrated in deionized water at 294 K, the times to attain equilibrium swelling being 2–4 weeks and 10–12

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weeks for the discs and pellets, respectively. These times allowed not only for swelling by water but also for removal of water-soluble material from the samples. During the swelling period the water was changed at frequent intervals. The equilibrium water content, i.e. the percentage by weight of water within the swollen hydrogel, based on the original dry weight of xerogel is thus only an apparent value, which is smaller than the true value. The latter, denoted by W, was calculated after the loss in weight due to extraction had been determined.

Volumetric swelling at different temperatures

At a particular temperature T, the volume fraction ϕ_2 of polymer within a hydrogel is given by

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

in which D_0 and D are the diameters of dry and swollen discs, respectively. Values of D were obtained at 10 temperatures within the range 275–342 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[6].

Compression measurements

Elastic moduli of the hydrogels were determined by stress (compression)–strain measurements. The compression rig, in which the main chamber containing water was of stainless steel, was used for our previous experiments on BA/VP copolymeric hydrogels[6]. The apparatus used in the present work was basically similar except for the replacement of stainless steel by Perspex (clear PMMA). Because details were omitted in the earlier report, they are provided here.

The assembly (*Figure 1*) consists of a micrometer dial gauge (A) (with its internal spring removed) capable of measuring displacement accurately to 0.02 mm. A brass pan (B) was affixed via a small screw to the upper section of shaft (C) and a spring (D) was positioned between the gauge and the brass pan. A cylindrical block of PTFE (E) was fastened to the lower end of the shaft (F). The gauge was mounted on a heavy metal retort stand (G) by means of a movable clamp (H) so that the height could be adjusted to accommodate hydrogel samples of different thicknesses. The hydrogel pellet (I) was placed centrally on a PTFE stand (J) which was placed centrally inside a double-walled water bath (K) made of Perspex. Note that the upper portion of J had small holes (e.g. L) close to its periphery to ensure homogeneity of the water and its temperature within the whole of the bath. One of these holes served also as a thermometer pocket. No barrelling effects were noted during compression. Sufficient water was placed in the bath K to cover the sample. Temperature was controlled by circulating water from an external thermostat through the double walls of bath K.

The spring (D) was calibrated in the absence of any hydrogel sample and thus the modulus of the spring could be subtracted from subsequent measurements made with the hydrogel. Standard weights were placed on B in increasing amounts and the subsequent deformation of D was recorded on A. The stress–strain characteristics of D were linear. This mode of calibration also corrected for any small effects of buoyancy and friction in the system.

Actual measurements on the hydrogel were made by carefully lowering A via the clamp H so as to bring the block E into contact with the upper surface of the sample. The gauge A was zeroed by means of its adjustment screw. Weights were placed on B and the deformation was registered on A. After each reading the weight was removed and the sample was allowed to recover to its initial height. The friction inherent in the assembly could be readily and reproducibly overcome by lightly tapping the base of the apparatus. Measurements were made on equilibrated samples at 294 K. On changing to a different temperature a further period of 4 h equilibration at this new temperature prior to measurements was found to be adequate.

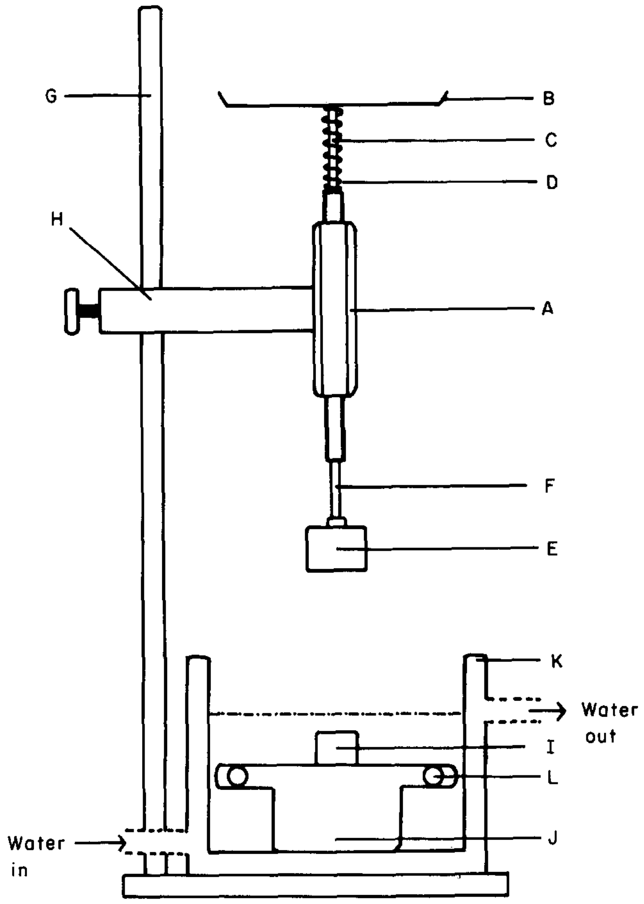

Figure 1 Uniaxial compression apparatus for measuring stress–strain data on hydrogels. For meaning of letters, see text

Differential scanning calorimetry

The d.s.c. attachment to the Mettler thermal analyser (model TA 3000) was employed. Surface-dried hydrogel (~4–20 mg) was placed in a d.s.c. pan, which was sealed. The temperature was reduced to 213 K and then raised to 298 K at a heating rate of 5°C min^{-1}. A peak corresponding to the melting endotherm of water occurred between 263 and 283 K, the peak maximum being located usually at 272–274 K. The breadth of the peak depended on the content of normal freezing water present in the sample. The mass of freezing water was obtained by integration of the peak area, using facilities attached to the instrument, in conjunction with the enthalpy of fusion of pure water, ΔH_f. Using pure water alone a value of $\Delta H_f = 329.2$ J g^{-1} was obtained as the average of 12 determinations each involving a different mass of water in the pan. This value is about 1% smaller than the literature value[7] of 333.6 J g^{-1}. The mass of non-freezing water in a hydrogel was obtained as the difference between that known from the total equilibrium water content and the mass of freezing water. Expressed as percentages by weight of the total weight of hydrogel, the contents of total, freezing and non-freezing water are denoted by W, W_f and W_{nf} respectively.

In some instances the d.s.c. pan was pierced and heated to 473 K after a satisfactory endotherm had been recorded. This high temperature was maintained for 10 min or until constant weight was reached. In this way the total mass of water in the hydrogel could be confirmed as the loss in weight. The result always agreed to within 1% with the value obtained from the equilibrium water content using the normal method of surface drying and weighing.

RESULTS

Swelling properties

Table 1 summarizes the swelling properties of PVP hydrogels prepared in the presence of five different concentrations of EDMA within the range 0.50–5.0 wt%. The high sol fraction present is only reduced by about a half if 2 wt% EDMA is incorporated, but even at relatively high concentrations of crosslinker the sol fraction remains significant. The equilibrium water content W is very high ($\sim$95 wt%) and an appreciable reduction in W is obtained only at a very high content of 5 wt% EDMA. Although the densities of polymer and water are dissimilar, the values of W and of the volume fraction of water in the gel ($=1-\phi_2$) are practically the same. This is merely a consequence of the very low content of polymer in the hydrogel and the small influence of the density of the polymer.

The effect of temperature on dimensions was studied for only one particular hydrogel, viz. that prepared in the presence of 1 wt% of EDMA. A small, but measurable, decrease of 8.5% in D was noted over the increase of (342–275) = 67 K in temperature. This corresponds to an increase in ϕ_2 of $\sim$0.45% per Kelvin.

Network parameters

Young's moduli E were obtained as the slopes in plots of stress (τ) vs. strain ($\lambda-1$). Here τ is the applied force per unit area of hydrogel and λ 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 crosslinking density ν_t is given as follows in terms of the concentration C (mol dm^{-3}) of crosslinking agent of functionality f:

$$\nu_t = Cf/2 \tag{2}$$

Table 1 Swelling properties at 294 K of PVP hydrogels prepared in the presence of different concentrations of EDMA

Concentration of EDMA (wt%)	Sol fraction (wt%)	W (wt%)	ϕ_2
0.50	26.2	95.7	0.039
0.75	25.2	95.6	0.041
1.00	22.5	95.0	0.050
2.00	13.5	94.2	0.058
5.00	12.5	77.4	0.227

Table 2 Network parameters at 294 K of PVP hydrogels prepared in the presence of different concentrations of EDMA

Concentration of EDMA (wt%)	$\nu_t \times 10^3$ (mol dm^{-3})	$\nu_e \times 10^3$ (mol dm^{-3})	E (MN m^{-2})	M_c (kg mol^{-1})	χ
0.50	62	5.7	0.019	216	0.491
0.75	93	6.5	0.020	189	0.492
1.00	124	10.6	0.038	116	0.492
2.00	248	10.7	0.039	115	0.500
5.00	616	114	0.504	10.7	0.572

Because $f=4$ for EDMA, equation (2) reduces to

$$\nu_t = 2C$$

The values of C were calculated from the weight concentration of EDMA by using 198.2 g mol^{-1} as the molar mass of EDMA and by taking the density of xerogel ρ as 1.230 kg dm^{-3}. This latter value is the average of densities obtained from direct weighings and micrometrically measured dimensions of all the dried discs and pellets used (the value of ρ was virtually independent of the concentration of EDMA over range of EDMA concentrations used here). The effective crosslinking density ν_e, in contrast, is a purely experimental quantity and was obtained from compression–strain results via[8]:

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

$$G = RT\nu_e\phi_2^{-1/3} \tag{4}$$

At low strains, i.e. 0 to about -0.07, plots of τ vs. $(\lambda-\lambda^{-2})$ according to (3) were linear, thereby yielding the compression moduli G as the slopes from which values of ν_e were isolated via (4). In (4), RT has its normal meaning and τ is the force per unit area of xerogel. Values of the polymer–water interaction parameter χ were calculated from the following expression valid at swelling equilibrium[9]:

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

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

$$V_1 = 10^{-3}[18.05 + 3.6\times10^{-3}(T-298)]$$

From the values of ν_e the molar mass per crosslink (M_c) was calculated via:

$$M_c = \rho/\nu_e \tag{6}$$

Results from compression measurements refer to 294 K for samples of different EDMA content. The values of ν_t, ν_e, E, M_c and χ at 294 K are given in *Table 2*. Similar measurements relating solely to a sample containing 1 wt% EDMA were made at 10 temperatures within the range 283–323 K. The moduli were practically independent of temperature. This finding, in conjunction

Table 3 Total, freezing and non-freezing water contents of PVP hydrogels prepared in the presence of different concentrations of EDMA

Concentration of EDMA (wt%)	W (wt%)	W_f (wt%)	W_{nf} (wt%)	W_{nf}/W
0.50	95.7	85.7	10.0	0.104
0.75	95.6	84.6	11.0	0.115
1.00	95.0	81.8	13.2	0.139
5.00	77.4	66.5	10.9	0.141

with the observed small increase of ϕ_2 with T, resulted in the values of ν_e being almost constant over the temperature range. The increase of χ with increasing T (K) was fitted to a polynomial of the second degree:

$$\chi = 0.416 + 2.71 \times 10^{-4} T - 4.90 \times 10^{-8} T^2 \qquad (7)$$

Freezing water content

D.s.c. analysis was conducted on four samples of PVP hydrogel containing 0.5, 0.75, 1.0 and 5.0 wt% EDMA. The values of W, W_f and W_{nf} are listed in *Table 3*. For EDMA contents up to 1 wt%, W decreases by a very small amount, but the fall in W_f from 85.7 to 81.8% on increasing the concentration of EDMA is rather more significant. A large fall in both W and W_f is observed only at 5 wt% EDMA. The ratio of the non-freezing water content relative to the total water content increases smoothly with the concentration of hydrophobic crosslinking agent.

DISCUSSION

The effective and theoretical crosslinking densities of hydrogels are rarely equal to each other, the dependence of the former on the latter usually being of the following form:

$$\nu_e = \alpha + \beta \nu_t \qquad (8)$$

in which β is a measure of crosslinking efficiency and α results from a form of crosslinking induced even in the absence of any added crosslinking agent. For example, $\beta = 0.52$ for PHEMA hydrogels crosslinked with EDMA in the presence of solvent[10], and $\beta = 0.82$ for PHEMA hydrogels crosslinked with EDMA in bulk and polymerized via γ-irradiation[11]. For BA/VP copolymeric hydrogels crosslinked by TPT and polymerized via γ-irradiation the value of β decreased with increasing content of VP in the copolymer[12]. In all these systems the swelling medium, water, is a non-solvent for the linear polymer and hence a contribution to ν_e is made by unbroken, hydrophobic, intermolecular bonding.

For the present hydrogels the variation of ν_e with ν_t is curvilinear and (8) does not hold. Consequently it is not possible to isolate a value of β. With regard to α, a small finite value might be anticipated because of the simultaneous formation and crosslinking of PVP during its preparation via irradiation. In this connection it is relevant to note that a radiation G (crosslink) value of $\sim 0.13\ \text{heV}^{-1}$ has been reported[13] for irradiated PVP. As already indicated, it is not possible to extrapolate the present data to yield a value of α. However, at the lowest EDMA concentration used, $\nu_e = 5.7 \times 10^{-3}\ \text{mol dm}^{-3}$ and hence the value of α (corresponding to zero concentration of EDMA) is predicted to be slightly smaller. This is consistent with the value of $5.0 \times 10^{-3}\ \text{mol dm}^{-3}$ derived from an analysis of BA/VP/TPT hydrogels extrapolated to zero contents of BA and TPT[12].

Although a precise value cannot be assigned to β, the values of ν_e are uniformly less than $\nu_t/10$, which is indicative of inefficient crosslinking. The high sol fractions of 20–26 wt% for gels prepared in the presence of 0.5–1.0 wt% EDMA reflect the inefficiency of crosslinking and thus an inhomogeneous network.

Further investigation of crosslinking was made by considering the preparation of the xerogel as an EDMA(1)/VP(2) copolymerization conducted to high conversion. The relevant monomer reactivity ratios are not known, but the Q and e values from the literature[14] are 0.88 and 0.24, respectively, for EDMA, and 0.14 and -1.14, respectively, for VP. These yield calculated reactivity ratios of $r_1 = 4.51$ and $r_2 = 0.03$. The Skeist procedure[15] in the convenient integrated form due to Meyer and Lowry[16] allows one to calculate the instantaneous compositions of monomer mixture and of copolymer at all stages of fractional conversion θ thus:

$$\theta = 1 - (f_{1j}/f_{1i})^a[(1-f_{1j})/(1-f_{1i})]^b[(f_{1i}-d)/(f_{1j}-d)]^c \qquad (9)$$

where $a = r_2/(1-r_2)$, $b = r_1/(1-r_1)$, $c = (1-r_1r_2)/(1-r_1)(1-r_2)]$ and $d = (1-r_2)/(2-r_1-r_2)$. In (9), f_{1i} is the mole fraction of EDMA in the monomer mixture at a stage i and f_{1j} is the corresponding value at a later stage j of the copolymerization. By incorporating the copolymer composition equation for small finite i–j stages one can thereby calculate also the instantaneous mole fraction F_1 of EDMA in the copolymer. The computations were written in FORTRAN 77 for use on the Prime 750. A Calcomp 105 plotter was used to produce the diagrams of f_1 at different conversions (*Figure 2*) and F_1 at different conversions (*Figure 3*) for the five different EDMA/VP compositions. At $\theta = 0$, stage i represents the initial conditions prior to reaction and the EDMA wt% concentrations of 0.5–5.0 correspond to initial values of f_1 within the range 0.0025–0.0287. The curves of *Figure 3* show the existence of broad compositional heterogeneity of copolymer and indicate that at low–moderate conversion the copolymer is exceedingly rich in VP; hence the high sol fraction.

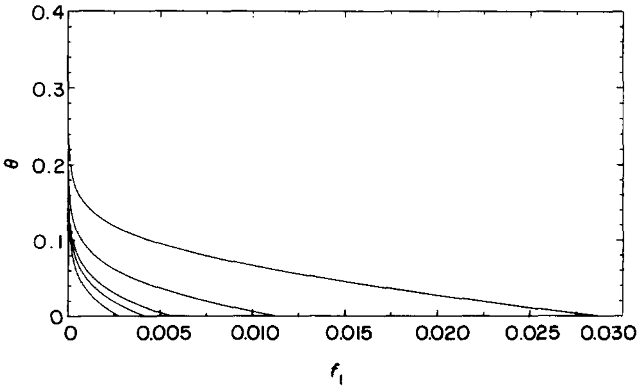

Figure 2 Instantaneous mole fraction f_1 of EDMA in EDMA/VP at different stages of fractional conversion θ. Values of f_1 in initial feed mixture are 0.0028, 0.0042, 0.0056, 0.0113 and 0.0287 in the sequence lowest→highest curves

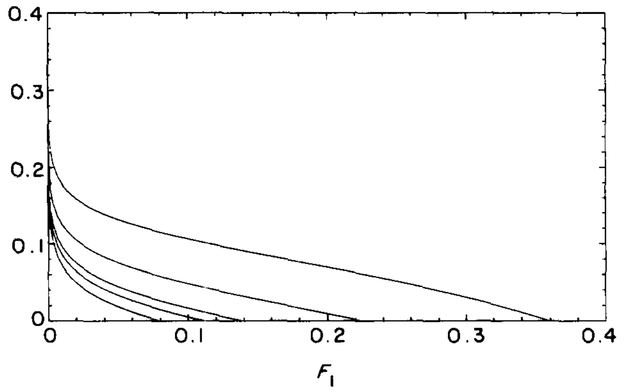

Figure 3 Instantaneous mole fraction F_1 of EDMA in EDMA/VP copolymer at different stages of fractional conversion θ. In the sequence lowest→highest curves the compositions of initial feed mixture are as indicated in *Figure 2*

Similarly in *Figure 2* the monomer composition is seen to approach nearly pure VP at low conversions. The smaller the initial value of f_1 the lower is the conversion at which the content of EDMA in the monomer mixture tends to zero. Thereon, i.e. at higher conversion, the product consists of practically pure PVP (as seen in *Figure 3* also). The sol fractions are high and the crosslinking (i.e. copolymerization) efficiency is low. The sol fractions may well have been even higher but for the slight crosslinking due solely to γ-irradiation. The absence of direct proportionality between ν_e and ν_t is a reflection of this inhomogeneous crosslinking.

The very high value of ν_e ($=0.114\,\mathrm{mol\,dm^{-3}}$) for the PVP prepared in the presence of 5 wt% EDMA is partly associated with the significant content of the hydrophobic moiety, EDMA, incorporated in the polymer, which in itself imparts some mechanical strength and reduction in swelling regardless of any crosslinking effects. A reduction in crosslinking efficiency of EDMA with increasing VP content in HEMA/VP hydrogels has been observed[17], but in general the influence of EDMA is difficult to predict and depends on the nature of comonomer or comonomers.

Reported data on the mechanical moduli of PVP hydrogels are sparse owing to the inherent difficulty of making measurements on these fragile, highly swollen materials. Conventional extensiometers are unsuitable because of the practical difficulty of clamping the gels firmly. The apparatus described here is well suited to cater for such materials. A tensile strength of $0.176\,\mathrm{MN\,m^{-2}}$ has been reported[18] for a PVP hydrogel ($W=86$ wt%) crosslinked with 0.5 mol% 2,2′-(p-phenylenedioxy)-diethyl dimethacrylate.

Good and Cantow[19] have obtained values of χ ranging from 0.495 to 0.565 for PVP hydrogels crosslinked with a difunctional allylic monomer. The increase in χ with increasing crosslinker concentration was explained by the hydrophobicity of the crosslinker. A similar trend is exhibited here (see *Table 2*) and the same explanation would appear to be tenable.

The influence of temperature on swelling may be compared with that reported elsewhere for hydrogels of PVP and VP-containing copolymers. A fall in W from 94.5 to 91.7 wt% at three temperatures over the increasing range 293–343 K has been observed by Breitenbach[20] for PVP crosslinked with diallylic compounds. This is comparable with the fall of W from 94.1 to 92.3 wt% found here for several temperatures within the interval 275–342 K. Exothermic swelling has been reported also for copolymeric hydrogels of VP with VNO[21], MMA[22] and BA[6]. The decrease in W with increasing T followed by an increase in W at still higher temperatures, which is known for PHEMA[23], is also manifested by copolymeric hydrogels of VP with HPM[24].

Temperature effects were studied here only for the sample containing 1 wt% EDMA. Neither the deswelling nor the increase in χ with T (*Figure 4*) is particularly pronounced. Thus the lowest and highest values of χ were 0.487 and 0.503 at 275 and 342 K, respectively. The parameter χ itself is composed of enthalpic (χ_H) and entropic (χ_S) contributions, both of which are obtainable from a combination of χ and its temperature dependence:

$$\chi_H = -T(\mathrm{d}\chi/\mathrm{d}T) \tag{10}$$

$$\chi_S = \chi + T(\mathrm{d}\chi/\mathrm{d}T) \tag{11}$$

Values of χ_H and χ_S at several temperatures were calculated via equations (7), (10) and (11) and are plotted *versus* temperature in *Figure 4*. The large positive values of χ_S predominate over the small negative values of χ_H in determining the overall value of χ. The partial molar enthalpies ($\Delta\bar{H}_1$) and entropies ($\Delta\bar{S}_1$) of dilution are obtained from χ_H and χ_S respectively, viz:

$$\Delta\bar{H}_1 = RT\phi_2^2\chi_H$$

$$\Delta\bar{S}_1 = R\phi_2(0.50-\chi_S)$$

Over the temperature range covered, both $\Delta\bar{H}_1$ and $\Delta\bar{S}_1$ are negative, the largest numerical values obtaining at the highest temperature, 342 K. These values are $\Delta\bar{H}_1 = -0.92\,\mathrm{J\,mol^{-1}}$ and $\Delta\bar{S}_1 = -0.044\,\mathrm{J\,K^{-1}\,mol^{-1}}$. The magnitudes of these are extremely small (cf. also the low percentage change in W and D over a wide range of T) and indicate an almost athermal swelling process. In contrast, for a BA/VP copolymeric hydrogel containing 70 wt% VP, the values of $\Delta\bar{H}_1$ and $\Delta\bar{S}_1$ at 342 K are about $-1.6\,\mathrm{kJ\,mol^{-1}}$ and $-9.3\,\mathrm{J\,K^{-1}\,mol^{-1}}$, respectively[6].

In their studies on PHEMA hydrogels Jhon *et al.*[25,26] proposed the existence of three distinct forms of water within the gels, namely bulk, interfacial and bound water. Here the d.s.c. technique allows one to legitimately assign two forms, i.e. freezing and non-freezing water. In

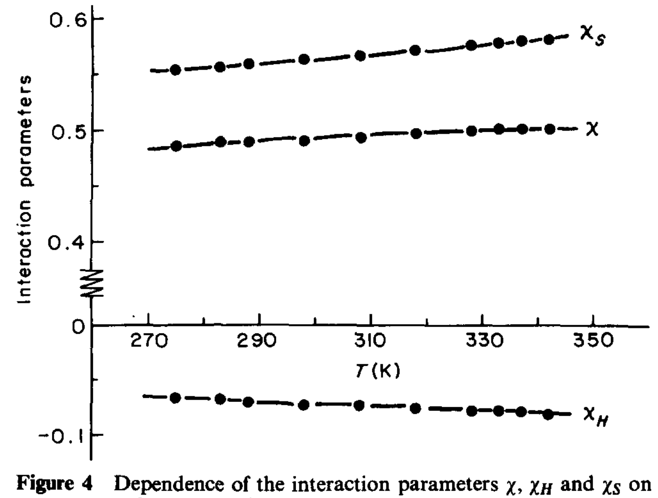

Figure 4 Dependence of the interaction parameters χ, χ_H and χ_S on temperature for PVP hydrogels crosslinked with 1 wt% EDMA

poly(vinyl alcohol-*co*-itaconic acid) membranes, Higuchi and Lijima[27] found that the ratio of non-freezing water to total water (W_{nf}/W) increased with decreasing content of total water, which is qualitatively similar to the trend observed here for PVP. However in the present gels the increase in W_{nf}/W within the EDMA contents 0.5–1.0 wt% is quite small (0.104 to 0.139). These gels are of course very similar with respect to their ν_e values and total water contents. At a high EDMA content of 5 wt% the ratio W_{nf}/W is increased only slightly to 0.141 despite a large fall in the total value content. The main observed change was a fall of ~20 wt% in the value of W_f and hence it is inferred that only bulk (freezing) water is lost on incorporating a large quantity of EDMA in the network.

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