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The swelling and collapse of hydrogen bonded polymer gels

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Abstract

The volume phase transitions in hydrogen bonded polymer gels are investigated. The elastic contribution is obtained by a modification of the Flory–Rehner approach proposed previously, where the affine deformation assumption is abandoned and instead the assumptions of the c* model of de Gennes are adopted. The mixing term is modified to account for hydrogen bonding. The calculations (both binary and ternary) clearly indicate the possibility of abrupt volume phase transition. Also the existence of LCST and UCST within an accessible temperature range is predicted for gels in mixed solvent systems involving hydrogen bonding.

Keywords: Volume phase transition; c* Theorem; Association model

1. Introduction

Gel phase transitions have been widely studied since the first observation of gel collapse by Tanaka [1]. It has been well demonstrated that small changes in the external conditions can bring about drastic changes in the state of the gel. For example gels of some polymers undergo a discontinuous volume change upon changes in temperature [1,2], solvent composition [3,4], ionic composition [5] or in some cases the application of a small electric field [6]. However the presence of ionizable groups or sufficient polymer chain stiffness has been found to be essential for such abrupt phase transitions to occur [3,7]. Also, most of the phase transitions studied experimentally are in aqueous systems [10]. Recently it has been proposed such discontinuous volume changes are possible in gels where hydrogen bonding is involved [8]. Attempts have been made to develop theoretical frameworks to describe the phase transitions in both ionizable and hydrogen bonded gels [3,7,9,11]. In this communication we explore in detail the role of hydrogen bonding in the swelling and collapse of polymeric networks swollen in organic solvents where hydrogen bonding is involved.

Recent work by the Painter and Coleman [12] has focused on the effect of strong specific interactions on the miscibility of polymer blends. A lattice model has been developed that apparently provides a good description of the phase behavior of such blends [13]. Also we have proposed a simple model to describe the swelling of polymeric networks [14]. Thus an extension of our work to study the swelling and collapse of polymer networks where hydrogen bonding is involved can be done in a straightforward manner. We follow the general approach used in many studies of polymer gels and assume the separability of the elastic and mixing components of the free energy. Accordingly, using the lattice model developed by Painter et al. [13], the Flory–Huggins can be easily modified to account for hydrogen bonding interactions. The elastic energy term has been described using the classical Flory–Rehner theory [15].

Various studies over the last few years have clearly demonstrated that there are major problems with this approach [16–20]. The separability of the elastic and mixing free energies has been questioned [21,22]. However the most significant deficiency of the Flory–Rehner approach involves the assumption that the deformation of the elementary chains is in some way affine with the macroscopic deformation (swelling in our case) of the sample. Further using neutron scattering, Bastide et al. [18] have demonstrated that the dimensions of the elementary chains of the network are approximately equal to the dimensions of the equivalent non-crosslinked chains in solutions of the same concentrations. This is much less than would be expected on the basis of an affine deformation model.

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These results are in good agreement with the c* theorem of de Gennes [23] who proposed that in a good solvent the swollen coils of the network largely exclude one another from a volume that is more or less defined by the radius of gyration. Since the chains are forced into contact at their cross-link points, the gel is analogous to the situation at the overlap threshold in a semi-dilute solution. Accordingly, Bastide et al. [17] proposed that the swelling of a gel proceeds by a process of topological rearrangements or disinterspersion of the cross-link points and demonstrated that an analysis based on the scaling approach proposed by de Gennes for semi-dilute solutions is in good agreement with the experimental observations. We have previously proposed [14] a simple modification to the Flory–Rehner approach that abandons the affine assumption and instead uses the assumptions of the c* model of de Gennes in order to obtain a relationship between the chain expansion and the degree of swelling. The model appears to provide a good description of the swelling and deswelling behavior of model polymer networks and provides an explanation for the anomalous results. Here we will extend and combine this model with the treatment of hydrogen bonding interactions in order to describe the swelling and collapse of polymer networks.

2. Theory

The free energy for the equilibrium swelling of a perfect network was obtained by making three basic and familiar assumptions.

1. The free energy of the gel can be written as a sum of two separate components describing the elastic free energy and mixing free energy respectively.
2. These components of the free energy can be expressed in terms of the classical elastic free energy and the Flory–Huggins theory, modified to account for hydrogen bonding.
3. Following de Gennes, we assume that at equilibrium in a good solvent the chains expand to an extent that they would in a dilute solution of the same solvent at the same concentration. The cross-link points rearrange or disintersperse to the extent that the gel can be considered to be a collection of spheres or ‘blobs’ of individual network chains that as far as possible exclude segments of other chains from their volume, but are forced into contact at their cross-link points.

Using the first two assumptions the free energy for the equilibrium swelling of perfect network of functionality ‘*f*’ of very long chains each made up of N statistical units or segments can be written down immediately while the final assumption provides the connection between the volume fraction of the polymer segments ϕ_B (or the degree of swelling $Q = 1/\phi_B$) and the chain expansion factor [14] ‘α’. The free energy is given by

$$\frac{\Delta G}{kT} = \nu\left[\frac{3}{2}(\alpha^2 - 1) - \ln\alpha^3\right] - \xi\ln\phi_B + n_A\ln(1-\phi_B) + n_A\phi_B\chi + \frac{\Delta G_H}{RT} \tag{1}$$

where n_A is the number of solvent molecules (A), ϕ_A, ϕ_B are the volume fractions of the solvent and polymer respectively, ξ is the cycle rank of the network, ν is the number of chains and α is the chain expansion factor. The mixing part of the free energy is simply given by the Flory–Huggins theory where χ is the Flory–Huggins interaction parameter. Also ΔG_H is the free energy contribution from hydrogen bonding. Note that the mixing term is not simply an empirical modification of the Flory–Huggins equations. The same result can be obtained by using a lattice model to describe the distribution of hydrogen bonded species [13] details of which are given in a previous publication.

A number of points concerning Eq. (1) are important. First, apart from the ΔG_H term, this equation is simply the Flory–Rehner results. However differences arise when we consider the relationship between ϕ_B ($= 1/Q$), the chain expansion factor ‘α’. Also the inclusion of the logarithmic term $\xi\ln\phi_B$ is justified [14,24] because it accounts for the entropy of disinterspersion of the cross-link junctions over the volume of the networks. The presence of the dangling ends or pendant chains and physical entanglements are neglected. In the c* model the pendant chains will still swell and exclude other chains from their sphere of influence and so the effect of a small number of pendant chains should be small as the experimental results of Bastide et al. [17] indicate. The role of physical entanglements is more complex and determines the extent of folding/unfolding of the junction points.

The equations for the chemical potential is obtained in the usual manner by differentiating Eq (1) with respect to n_A, the number of solvent molecules, to obtain:

$$\frac{\Delta\mu_A}{kT} = -\left[3\nu\left(\alpha\frac{1}{\alpha}\right)\frac{\phi_B^2}{N\nu}\right]\frac{\partial\alpha}{\partial\phi_B} + \frac{\xi\phi_B}{N\nu} + \ln(1-\phi_B) + \phi_B + \phi_B^2\chi + \frac{\Delta\mu_H}{RT} \tag{2}$$

3. Packing conditions

In models that assume an affine deformation, an expression for $\partial\alpha/\partial\phi_B$ is obtained from the condition $\phi_B = 1/\alpha^3$. In the c* model, the chains act as swollen coils effectively excluding neighbors from their volume. Thus a relationship between α and ϕ_B can be obtained using packing conditions. However, it would be necessary to use two concentration terms ϕ_B and ϕ_g depending on whether the ‘void volume’ (remember that the gel is considered to be a collection of spheres) is included in the calculation of the total volume. The first of these, ϕ_B reflects the overall or average concentration of the polymer segments within the spheres occupied by each of the swollen coils and is given by

$$\phi_B = \frac{(\pi/6)Nl^3}{(\pi/6)(\alpha)N^{1/2}l)^3} = \frac{1}{\alpha^3 N^{1/2}} \tag{3}$$

Here the end-to-end distance is used as a measure of the coil diameter. The chains are assumed to consist of spherical beads of diameter 'l'. The second concentration variable ϕ_g, reflects the average concentration of the segments in the gel as a whole. This will depend on how the swollen coils pack. Thus the packing conditions and consequently the relationship between ϕ_B and ϕ_g would be affected significantly by entanglements, presence of pendant chains and other network imperfections. In general we can write

$$\phi_g = P\,\phi_B \tag{4}$$

where P is a geometric or packing factor which depends on the functionality 'f' and the amount of network imperfections, but should be largely independent of α. As a first approximation, the volume fraction of polymer segments in the gel can be obtained from a simple calculation of the number of segments in a sphere of radius $\alpha N^{0.5} l$ surrounding a given cross-link point or junction. Thus the packing factor can be written as

$$P = f/8 \tag{5}$$

This would be true for tetrafunctional networks but is only a crude approximation for other functionalities and would fail for high values of 'f'.

The use of two concentration variables will not in any way change the free energy expression except for the logarithmic term describing the entropy of disinterspersion of the junction points. This will depend on the volume of the gel and would therefore be written as $\xi \ln \phi_g$ However the chemical potential will not be affected in any way as,

$$\frac{\partial \phi_g}{\partial \phi_B} = P \tag{6}$$

The chemical potential of the solvent in the gel can be obtained using

$$\frac{\partial \alpha}{\partial \phi_B} = -\frac{\alpha^4 N^{1/2}}{3} = -\frac{\alpha}{3\phi_B} \tag{7}$$

and is given by

$$\frac{\Delta\mu_A}{kT} = (\alpha^2 - 1)\frac{\phi_B}{N} + \frac{\xi}{\nu}\frac{\phi_B}{N} + \ln(1-\phi_B) + \phi_B + \phi_B^2\chi + \frac{\Delta\mu_H}{RT} \tag{8}$$

This is very similar in form to the Flory–Rehner results except for the expression for the chain expansion factor α. For simplicity, we assume that $P \approx 1$.

4. The hydrogen bonding term:

The association model used previously to obtain the phase behavior of polymer blends [12] can be also used for polymer solutions and gels. The model essentially starts with the randomly mixed components as a reference state. The free energy changes corresponding to the formation of specific interactions are then accounted for as an excess free energy term by determining the probability that the mixture would spontaneously occur in a configuration equivalent to that of a hydrogen bonded mixture. The associated species are allowed random contacts with one another so that a final equation of the form

$$\frac{\Delta G_M}{RT} = \frac{\Delta G_{FH}}{RT} + \frac{\Delta G_H}{RT} \tag{9}$$

is obtained. Here ΔG_{FH} is the Flory–Huggins free energy and ΔG_H is the hydrogen bonding contribution. Accordingly, the phase behavior is a balance between favorable (to mixing) hydrogen bonding interactions and an unfavorable χ term which is assumed to represent the dispersive (physical) forces. All the parameters to calculate the hydrogen bonding contribution can be determined from spectroscopic measurements and we assume that χ can be determined from the solubility parameters and is thus independent of composition. The composition dependence of the interactions comes from the hydrogen bonding part ΔG_H. In polymer solutions and gels, equation of state effects also play an important role in determining the phase behavior. The association model can be readily extended [25] to include the equation of state effects but it makes the calculations complex. For simplicity we have used the traditional method to account for size differences by adding the fudge factor (0.34) to the value determined from solubility parameters [26]

$$\chi = (\delta_A - \delta_B)^2 \frac{V_{ref}}{RT} + 0.34 \tag{10}$$

where δ_A and δ_B are the solubility parameters of components A and B respectively and V_{ref} is the reference volume.

Recent experimental results on polymer blends have suggested the effects of chain connectivity on the polymer phase behavior [27]. A simple model to account for these connectivity effects has been formulated [28] but this does not lend itself to simple calculations. Fortunately a semi-empirical correction term compensates for this effect and has allowed us to successfully calculate the phase behavior of a wide range of polymer blends [12]. Also it was found that the equilibrium constants describing the polymer/solvent interactions are within error nearly the same as those for the equivalent low molecular weight model compounds [27]. Thus the equilibrium constants obtained from model compounds can be directly applied to polymer solutions and gels within the error of determining these quantities. This implies that the correlation effects are not as significant in polymer solutions (as opposed to polymer

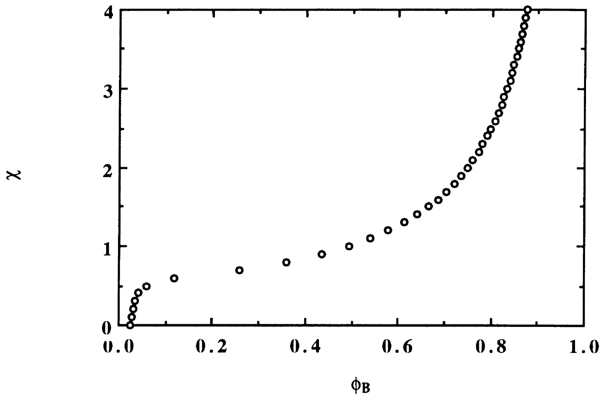


Fig. 1. Phase behavior of a gel, where no hydrogen bonding is involved as a function of χ.

blends) and we can simply apply the association model in its uncorrected and rigorous form. Note that the hydrogen bonding interactions of various functional groups (OH, COOH, CONH) in the pure state are described in different ways and hence ΔG_H has different forms [12].

5. Calculations

Instead of calculating the equilibrium curves (chemical potential of solvent in the gel $= 0$) to describe the swelling of the polymer networks, we shall concentrate on calculating the spinodals. The position and magnitude of the phase transitions would vary slightly from that obtained from equilibrium calculations, but at present we are only interested in the trends. The equation for the spinodal can be written as [12]

$$\frac{\partial^2(\Delta G/kT)}{\partial\phi_B^2} = 0 \tag{11}$$

where ΔG is the free energy per mole of lattice sites. The equations are given in Appendix A and have been described in detail in previous publications [12]. Note that for purpose of calculations we arbitrarily describe a chemical repeat of the polymer as the average unit containing one functional group capable of hydrogen bonding interaction (e.g. OH, COOH, CONH etc.). This definition merely serves to define a molar volume that is used to scale the free energy contribution to a common reference volume (see Ref. [12] for a complete discussion of this point).

While calculating the elastic energy contribution the value of 'α' the chain expansion factor, will vary with solvent quality (χ value) according to Eqs. (3) and (8). At high temperature, where the solvent can be considered 'good' the relationship obtained between 'α' ϕ_B and N from packing considerations holds (Eq. 3). However, when the solvent becomes poor ($\chi > 0.5$), we assume that the individual chains attain their unperturbed dimensions ($\alpha = 1$). Indeed Beltzung et al. [29], for example, found that $\alpha = 1$ for poly(dimethyl siloxane) (PDMS) networks swollen in toluene ($\chi > 0.5$ over most of the composition range). Accordingly, for a network in poor solvent conditions, the elastic contribution to the free energy comes solely from the Flory logarithmic term describing the disinterspersion of the cross-link points over the volume of the gel relative to the dry network.

The situation that is not well described is the cross-over from good to poor solvent conditions, where there is no simple way to obtain a relationship between α and ϕ_B. In order to model the phase behavior over the entire range of temperature, we will make a crude assumption; that the network behaves as a collection of excluded volume spheres with

$$\phi_B = \frac{1}{\alpha^3 N^{1/2}} \tag{12}$$

and that this relationship holds up to the concentration corresponding to $\phi_B = N^{-0.5}$ (i.e. $\alpha = 1$). At higher concentrations it is assumed that α is always equal to 1 and therefore there is no contribution to the free energy from the elastic deformation of the chains. Clearly, calculations of this region of the phase diagrams would be improved by using some sort of blob model to account for the chain overlap, as in the treatment of the osmotic deswelling, but at this point we wish to maintain maximum simplicity, so for now we will use this assumption and proceed to examine calculated chemical potentials and phase behaviors.

Before proceeding to examine the hydrogen bonded polymer gel systems, we first present the hypothetical phase behavior (calculated using Eqs. (8) and (11) but without the hydrogen bonding term) in Fig. 1 of a perfect Polystyrene (PS) network ($f = 3$ $N = 25$) swollen in a hypothetical solvent as a function of χ, the Flory interaction parameter. It displays a gradual deswelling of the network with increasing values of χ (or decreasing temperature corresponding to an UCST). Erman and Flory [11] noted that this type of gradual change, as opposed to an abrupt transition is to be expected for a gel where the composition dependence of χ is below a certain threshold level. The occurrence of a sharp transition and corresponding tri-phasic equilibria has most often been observed where there are ionic forces or a strong dependence of χ on composition. We can now turn our attention to the effects of specific interactions as these interactions are strongly composition and temperature dependent and give rise to both the upper solution and lower solution critical temperature (UCST and LCST) in both polymer solutions and blends.

We confine our attention to a rather simple example of a series of hydrogen bonded polymer gels, consisting of networks of styrene–vinyl phenol copolymers [STVPh(x)l where x is the mole percent of vinyl phenol in the copolymer. The OH groups of the vinyl phenol segments self-associate or hydrogen bond to one another in the pure state, such that the stoichiometry of hydrogen bonding is more accurately described by using an equilibrium constant for the formation of dimers, K_2, that is different from the

Table 1
Parameters used to calculate phase transition in STVPh(x)/n-MMK

Solvent or group	Solubility parameter (cal. cm^{-3})$^{0.5}$	Molar volume (cm^3 mole^{-1})		
Methyl methyl ketone	9.4	74.3		
Methylene	8.0	16.5		
Styrene–vinyl phenol copolymers—STVPh(x) x = mol% of VPh				
Parameter	$x = 100$	$x = 25$	$x = 10$	$x = 5$
δ(cal. cm^{-3})$^{0.5}$	10.6	9.8	9.6	9.55
K_B	66.8	17.5	7.1	3.6
K_2	21.0	5.5	2.2	1.1
K_A (with MEK)	100.0	26.2	10.6	5.3
h_B (kcal)	5.2	5.2	5.2	5.2
h_2 (kcal)	5.6	5.6	5.6	5.6
h_A (with MEK) (kcal)	3.75	3.75	3.75	3.75

formation of the subsequent h-mers, K_B. Also the extent of the self-association varies with the styrene content which merely acts as a diluent. In copolymers with low vinyl phenol content, the concentration of the OH groups per unit volume is less (than in pure Poly(vinyl phenol) [PVPh]), so there are fewer polymer/polymer (OH–OH) and polymer/solvent hydrogen bonds. Such copolymers have been extensively studied and the equilibrium constants that accurately describe the experimentally observed distribution of hydrogen bonds have been previously obtained [12]. The equations used to calculate the chemical potential of these networks are presented in Appendix A (Eq. (8) and Eq. (A-3) to Eq. (A-6)). Table 1 lists all the parameters, together with the equilibrium constants determining the self-association and inter-association used for the calculations.

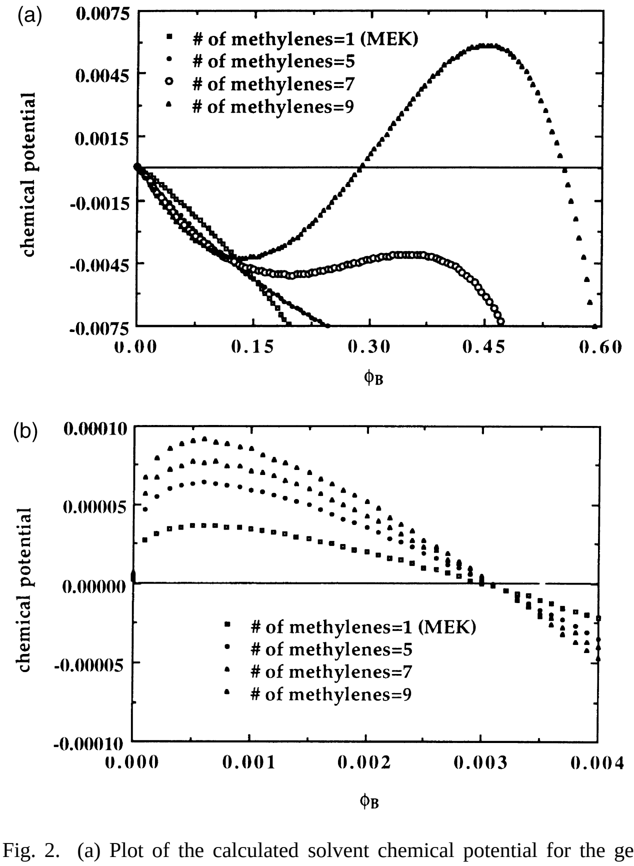
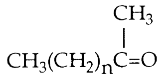


Fig. 2. (a) Plot of the calculated solvent chemical potential for the gel systems STVPh(5)/n-MMK for different values of n. (b) An expanded version of plot (a).

Fig. 2(a and b) show the calculated values of the chemical potential for the swelling of STVPh(5) networks in solvents of the general type



$$CH_3(CH_2)_n\overset{\overset{\displaystyle CH_3}{|}}{C}{=}O$$

where n is allowed to vary. This does two things;

1. It reduces the number of polymer/solvent hydrogen bonds by reducing the number of C=O groups per unit volume.
2. It also lowers the solubility parameter of the solvent thereby reducing the value of χ.

Note that $n = 1$ corresponds to the swelling of STVPh(5) networks in methyl ethyl ketone (MEK). As seen from Fig. 2(b), the model predicts that the degree of equilibrium swelling ($Q = 1/\phi_B$, ϕ_B corresponds to the polymer fraction, where the solvent chemical potential = 0) of STVPh(5) in MEK would be high. In initial work in this laboratory, we have synthesized STVPh(5) and STVPh(10) networks and both these networks were indeed highly swollen in MEK. Also as the number of methylenes (n) in the solvent increases, the miscibility tends to decrease. Eventually for a certain threshold ‘n’, we predict tri-phasic equilibrium.

Fig. 3(a and b) illustrate the effect of the mole percent of vinyl phenol on the swelling of STVPh(x) networks in n-methyl methyl ketone (n-MMK) for $n = 8$. There are four curves corresponding to the values of $x = 100$, 25, 10 and 5 and each is plotted as a function of the polymer volume fraction ϕ_B. Notice the disappearance of the tri-phasic

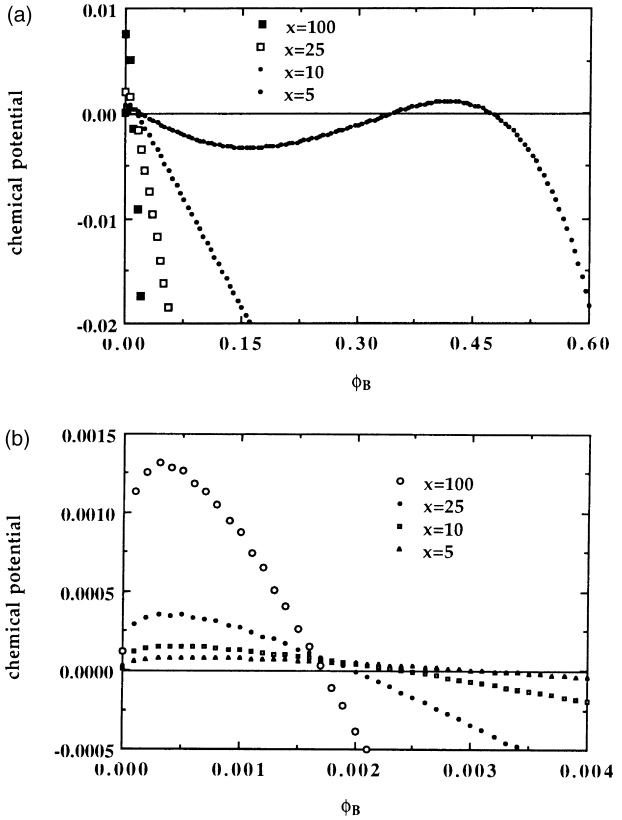


Fig. 3. (a) The calculated solvent chemical potential of 8-MMK swollen STVPh(*x*) networks for varying vinyl phenol mole%. The plot (b) is simply an expanded version of (a).

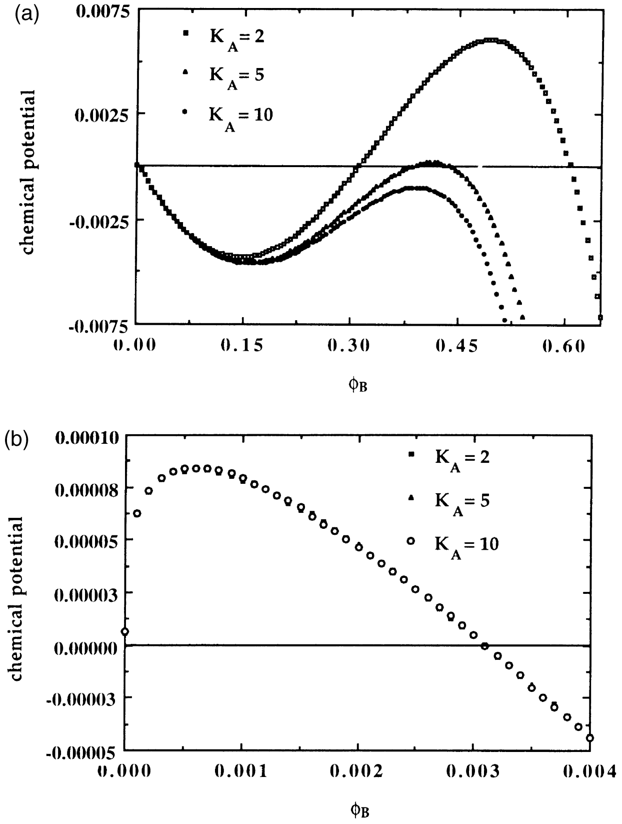


Fig. 4. Plots of the effect of varying the inter-association equilibrium constant $K_{A'}$ on the calculated chemical potential in the gel system STVPh(5)/8-MMK.

equilibrium (volume phase transition) as the system tends to become miscible for increasing values of *x*. Thus, volume phase transitions can be observed for STV-Ph(*x*) networks swollen in *n*-MMK, as the value of *x* decreases and that of *n* increases. Before proceeding to calculate the spinodals, a few points regarding the effects of the different parameters on the degree of swelling (*Q*) need to be mentioned.

By equating the Eq. (8) for the chemical potential of the solvent to zero, the degree of swelling ($Q = 1/\phi_B$) for a network can be calculated. The factor ξ/ν in Eq. (8) is related to the functionality ‘f’ by

$$\frac{\xi}{\nu} = 1 - \frac{2}{f} \qquad (13)$$

In all our calculations we have assumed that $f = 3$. The self-association equilibrium constants K_2 and K_B are those determined from previous spectroscopic measurements of STVPh(*x*) copolymers while the interassociation equilibrium constant K_A, has been assumed. However, as seen from Fig. 4(a and b), the effect of the variation of K_A on the degree of swelling ($Q = 1/\phi_B$) of STVPh(5) networks in a hypothetical solvent *n*-MMK for $n = 8$ is small (Fig. 4(b)). This might at first sight seem surprising but the free energy of hydrogen bond formation is related to ln K_A. Hence for small ϕ_B, large variations in K_A produce relatively small variations in the calculated values of the free energy and chemical potential. However at large ϕ_B, the magnitude of the phase transitions decreases (Fig. 4(a)) as K_A increases (miscibility increases).

As might be expected, the calculations are more sensitive to the mole percent of vinyl phenol groups in the copolymer as illustrated in Fig. 3(b). The degree of swelling (*Q*) increases, as the vinyl phenol content increases. We have calculated the value of χ from the solubility parameters (Eq. 10), which are determined by the group contribution method. Obviously, there are errors in determining the solubility parameters. Fig. 5(b) shows the effect of the variation of the solubility parameter of the solvent (and the consequent variation of χ) on the degree of swelling. The calculations predict a smaller degree of swelling as the solvent quality decreases (χ increases). Fig. 5(a) shows the calculated values of the chemical potential for the swelling of STVPh(5) in *n*-MMK for $n = 8$. The chemical potentials are plotted for three different values of *N* (number of statistical segments per chain). It can be seen that as the value of *N* decreases (i.e. degree of cross-linking increases), the calculated degrees of swelling ($Q = 1/\phi_B$) increases substantially. However, it must be recognised that we have defined a polymer chemical repeat as an average unit which contains one vinyl phenol group. The implicit

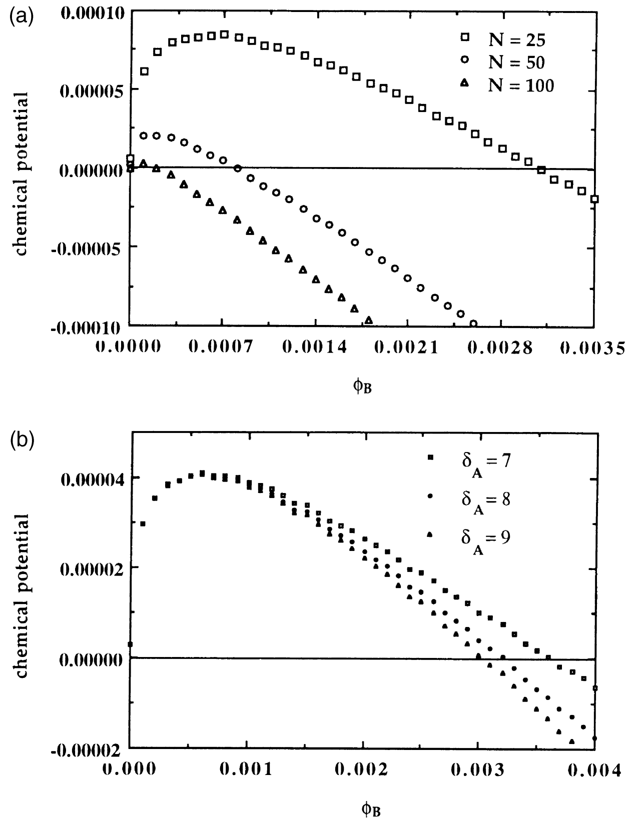


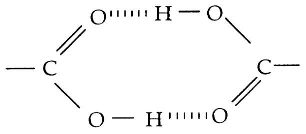
Fig. 5. Plots of the effect of varying (a) the number of statistical segments between cross points N and (b) the solubility parameter of the solvent (δ_A) on the calculated chemical potential of the solvent in STVPh(5) gels.

assumption that is important is that the vinyl phenol groups are randomly distributed through the sample. Hence as the mole percent of the vinyl phenol groups decreases, the average size of the chemical repeat unit increases as reflected by an increase in the molar volume. Subsequently copolymers with lower vinyl phenol contents but equal N will have a higher number of repeat units between cross-link points.

6. Calculation of phase behavior

We now proceed to calculate the spinodal curves of polymer gels where hydrogen bonding is involved. It is assumed that $N = 25$ and $f = 3$ for all the subsequent calculations. Fig. 5(a) shows the phase behavior of STVPh(5) networks swollen in n-MMK for two different values of n. The volume phase transition corresponding to the spinodal curves plotted in Fig. 6(a) are shown in Fig. 6(b) to get a better understanding of how the volume phase transitions are related to the spinodal curves. It clearly illustrates the presence of an abrupt transition as the temperature increases. Also the size of the transition increases noticeably as the number of methylenes in the solvent increases. This is obviously because of the decreasing quality of the solvent as indicated by the spinodal curves. A comparison of Figs 6 and 1 illustrates the effect of hydrogen bonding. The phase transition in Fig. 1 is continuous resulting in a gradual deswelling in contrast to the discontinuous transition in STVPh(5) networks swollen in n-MMK for $n > 6$. The presence of the phase at low polymer concentration in the spinodal corresponds to the swelling of the network in the solvent due to the presence of chemical cross-links. At higher concentrations, the spinodal suggests the presence of an LCST in the phase behavior of the corresponding uncross-linked polymer solutions.

Recently Tanaka et al. [8,30,31] observed gel transitions in aqueous poly(acrylic acid) gels with a decrease in temperature. This is not surprising in light of the behavior of the acid blends [12], which suggest that acid systems are more likely to display UCST rather than an LCST behavior. This is presumably related to the strong hydrogen bonded dimer pairs formed. In comparison to the self-association of the OH groups in STVPh(x) copolymers, the carboxylic acid groups form strongly hydrogen bonded cyclic dimers as shown below



The self-association equilibrium constant is also described by K_B although only dimers are formed. Consequently, the equations for acid systems have a different form, details of which are given in Ref. [12]. The final equations are presented in Appendix A (Eq. (A-8) to Eq. (A-10)).

The phase behavior of poly(methacrylic acid) networks swollen in n-MMK for $n = 5$ is plotted in Fig. 7(a). All the parameters used in these calculations are listed in Table 2. As seen from the plot, such acid systems have a UCST and is in agreement with the experimental results of Tanaka et al. [30,31] (we are only interested in the trends). A point of interest is the possible bimodal phase behavior as seen from Fig. 7(a). It is clearly demonstrated in Fig. 7(b), where we have the assumed $\delta = 7(\mathrm{cal.\,cm}^{-3})^{0.5}$ and $r = 1$. All the other parameters are assumed to be the same as before (Table 2). Such a bimodal behavior of the phase diagram would require the presence of three local minima in the free energy curves. Tanaka et al. [30,31] have observed the presence of four phases in pure aqueous poly(acrylic acid) gels and up to seven phases were obtained by changing the pH of the gels with the addition of HCl or NaOH in styrene–acrylic acid copolymer gels. The number of phases and transition thresholds depend on the ratio of the cationic and anionic monomers in the polymer network. Our calculation results are preliminary and more simulations and experimental results are needed to verify the bimodal behavior of poly(acid) solutions and gels. A more detailed account of the acid systems will be the subject of a future paper.

So far we have restricted ourselves to the calculation of

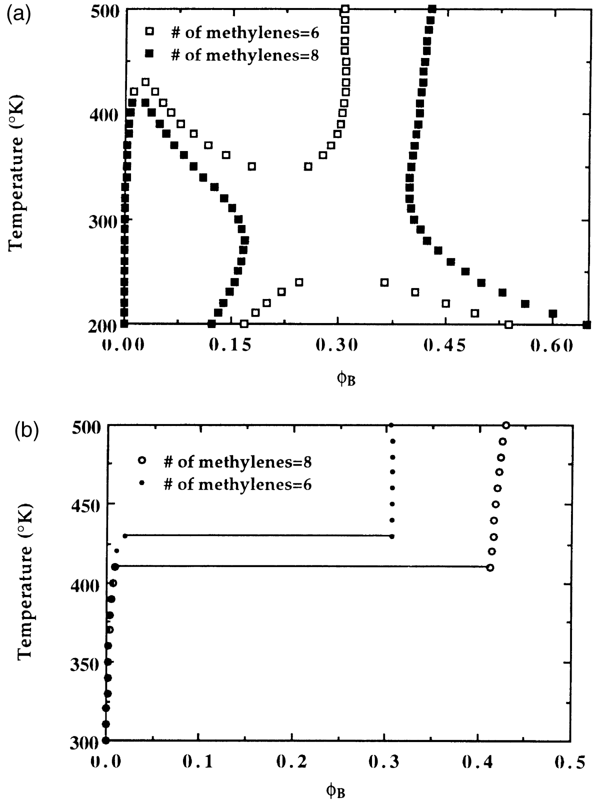


Fig. 6. (a) The calculated spinodal curves for the gel system STVPh(5)/*n*-MMK ($n = 6,8$) and (b) the corresponding volume phase transition for the gel system.

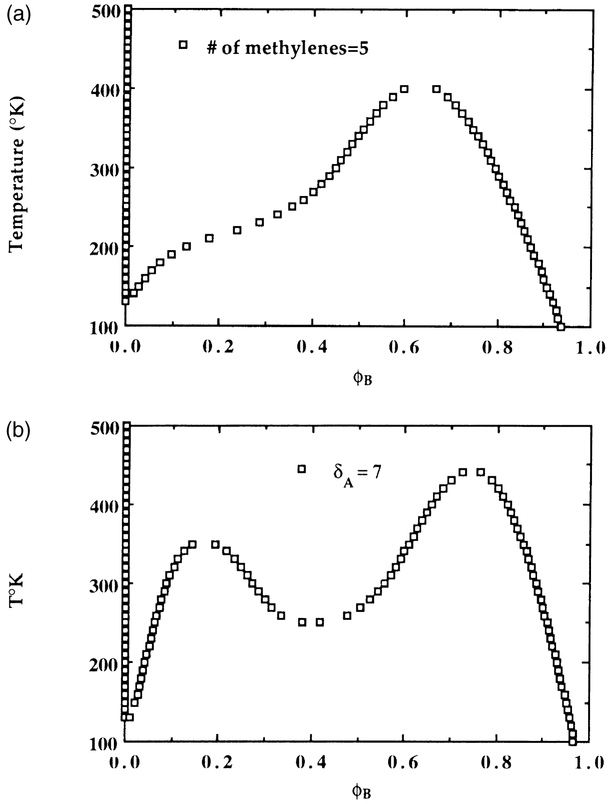


Fig. 7. Plots of the calculated spinodal curves for PMAA gels swollen in (a) 5-MMK and (b) a hypothetical solvent ($\delta_A = 7$).

phase behavior of binary systems. However, it has demonstrated that some networks (for example poly(acrylamide) networks$_2$) undergo a sharp transition or collapse in mixed solvent systems, by changing the concentration of the third solvent or by changing the temperature. Again the presence of ionizable groups or sufficient chain stiffness is vital for the occurrence of such abrupt volume transitions. Such transitions should, in principle, also occur in networks where hydrogen bonding interactions are involved.

Rather than reducing these systems to binary Flory–Huggins systems by applying the single-liquid approximation [32], we shall calculate the spinodals by using the ternary model successfully used by Tompa [33], Patterson [34] and others [35]. Recently Zhang [36] has presented a simple but comprehensive review on the effect of hydrogen bonding interactions on the phase behavior in ternary polymer blends. This can be easily extended to polymer solutions and gels. We present one example to complete our discussion on the swelling and collapse of gels where hydrogen bonding is involved. Obviously it can be extended to other systems. We shall concentrate our calculations on the ternary system STVPh(5)/MEK/Cyclohexane. The calculations shown in Fig. 3(b) have demonstrated that STVPh(5) networks are highly swollen in MEK. For the ternary system, we simplify our calculations by assuming that the ratio of the MEK/Cyclohexane (or in other cases solvent/nonsolvent) (n_s) to remain constant. The calculations are performed in two different ways: one at constant temperature, the ratio n_s is varied in order to obtain a phase map (n_s versus ϕ_B) and the other by keeping the ratio n_s constant and calculating the spinodal. The equations used for the calculations of the ternary phase behavior are given in Appendix A (Eq. (A-11) to Eq. (A-16)) and the parameters are listed in Table 3.

Table 2
Parameters used to calculate the phase behavior of PMAA

Parameters	Poly(methacrylic acid)	Solvent
Molar volume (Vcc/mol)	81.5	156.8
δ (cal. cm^{-3})$^{0.5}$	13.0	8.7
$K_B \times 10^{-4}$ at 25°C	17.3	–
K_A	–	10000
h_B (kcal)	14.4	–
h_A (kcal)	–	5.0

The effect of changing n_s at $T = 25$°C for the ternary gel system STVPh(5)/MEK/Cyclohexane is plotted in Fig. 8(a). As n_s decreases, the amount of solvent decreases and hence the solvent quality (towards the polymer segments) decreases. We should observe a sharp phase transition for $n_s \approx 6$ or 7. This is equivalent to our calculations for the binary system STVPh(5)/*n*-MMK. More interesting is the temperature dependence of the phase behavior for

Table 3
Parameters of the gel system STVPh(5)/MEK/Cyclohexane

Parameters	STVPh(5)	MEK	Cyclohexane
Molar volume (cc/mol)	1884.1	90.8	99.0
δ (cal. cm^{-3})$^{0.5}$	9.55	9.1	8.0
K_B	3.6	–	–
K_2	1.1	–	–
K_A	–	5.3	–
K_C	–	–	0
h_B (kcal)	5.2	–	–
h_2 (kcal)	5.6	–	–
h_A (kcal)	–	3.75	–
h_C (kcal)	–	–	3.75

STVPh(5)/MEK/Cyclohexane. Fig. 8(b) shows this dependence for two different values of n_s. As seen from the figure, for a range of n_s, the LCST and UCST would be close to another thus raising the possibility of a phase transition on either increasing or decreasing the temperature (the gel is assumed to be at room temperature to begin with). Thus, for STVPh(5) networks swollen in a mixed solvent, MEK/Cyclohexane, for a certain ratio of MEK/Cyclohexane, an increase or decrease in temperature by approximately 50–60°C will bring about sharp transitions. The usual phase transitions observed in gels have been due to the presence of an LCST or UCST or even immiscibility loops as in the case of certain ionic gels. This may be the first case in gels, where the LCST and UCST are within an accessible temperature range thus raising the possibility of interesting applications.

To complete our discussion on ternary polymer gels, the effect of a third equilibrium constant K_C (inter-association between the third solvent and the polymer segments) is shown in Fig. 8(a). In this case as the value of K_C increases, the ternary gel becomes miscible and thus no abrupt phase transitions are observed. However following the discussion of Zhang [36] many more cases can be considered, giving a variety of possible phase transitions depending on a delicate balance between $\Delta\chi$ and ΔK.

7. Conclusion

We have examined the volume phase transition of polymer gels where hydrogen bonding is involved. Based on a previously proposed model, the swelling is assumed to proceed by a process of chain disinterspersion. The c* theorem of de Gennes is used to obtain a relationship between chain expansion and the degree of swelling (Q). The hydrogen bonding interactions are described by an association model developed by Painter et al. to calculate the phase behavior of polymer mixtures.

Calculations show that for STVPh(x) networks with low vinyl phenol content, volume phase transitions may be observed with an increase in temperature indicating the presence of an LCST. The situation is reversed for poly(methacrylic acid) gels where volume phase transition is predicted with a decrease in temperature, as observed experimentally by Tanaka et al. Also, the possibility of bimodal phase behavior is raised, which may explain the experimental observation of multiple phases in poly(acrylic acid) gels by Tanaka et al. For swollen networks in a mixed solvent, calculations reveal the presence of an LCST and a UCST within an accessible temperature range for certain conditions (solvent/nonsolvent ratios).

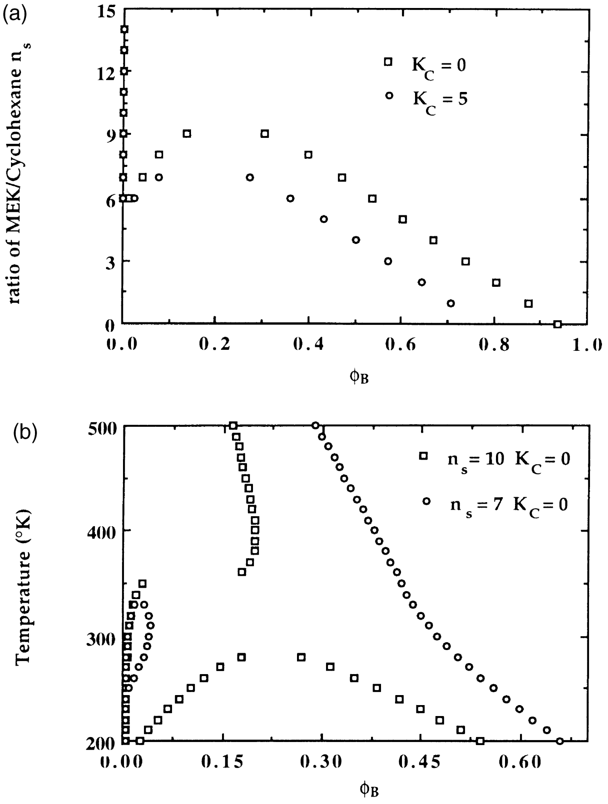


Fig. 8. (a) Calculated phase map of STVPh(5) networks swollen in different ratios of the mixed solvent MEK/Cyclohexane at constant temperature. (b) Calculated phase behavior (spinodal) of STVPh(5) networks swollen in the mixed solvent MEK/Cyclohexane for two different ratios of MEK/Cyclohexane.

Another intriguing effect of hydrogen bonding is the large changes in chain dimension upon swelling that is implied by Fig. 3(b), where it can be seen that the calculated degree of swelling of the networks increase with increasing vinyl phenol content (some caution is in order here, because this may be an artifact of assuming a random distribution of segments in the swollen spheres).

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Appendix A

The stoichiometry of hydrogen bonding depends on the association of the self-associating species in the pure state. For example the OH groups in STVPh(***x***) copolymers self-associate such that the dimer formation is described by a different equilibrium constant, in comparison to the equilibrium constant describing subsequent ***h***-mer (***h*** > 2) formation. In the case of acids the COOH functional groups self-associate in the form of cyclic dimers. Thus $\boldsymbol{\Delta G}_\mathrm{H}$ and $\boldsymbol{\Delta\mu}_\mathrm{H}$ will have different forms. Here we only present the equations for the two cases.

A.1. STVPh(*x*) copolymer gels

The hydrogen bonding free energy per mole of lattice sites is given by:

$$\frac{\Delta G_\mathrm{H}}{RT} = \phi_\mathrm{B} \ln\left(\frac{\phi_{\mathrm{b}_1}}{\phi^0_{\mathrm{B}_1}}\right) + \frac{\phi_\mathrm{A}}{r} \ln \phi_{\mathrm{A}_1} + \phi_\mathrm{B}\left[\left(\frac{\Gamma^0_1}{\Gamma^0_2}\right) - \left(\frac{\Gamma_1}{\Gamma_2}\right)\right] + \phi_\mathrm{B}\left(\frac{\Gamma_1}{\Gamma_2}\right)\left(\frac{x}{1+x}\right) - \left[\frac{\phi_\mathrm{B}}{h^0} \ln \phi_\mathrm{B} + \frac{\phi_\mathrm{A}}{r} \ln \phi_\mathrm{A}\right] \tag{A-1}$$

where

$$\chi = \frac{K_\mathrm{A}\phi_{\mathrm{A}_1}}{r} \tag{A-2}$$

Also,

$$\overline{h^0} = \frac{\Gamma^0_2}{\Gamma^0_1} \tag{A-3}$$

is the number average degree of association in pure B. The contribution to the partial molar free energy of A is then:

$$\frac{\Delta\mu_{\mathrm{A_H}}}{RT} = \ln\left(\frac{\phi_{\mathrm{A}_1}}{\phi_\mathrm{A}}\right) - r\phi_{\mathrm{B}_1}\Gamma_1 + \phi_\mathrm{B}\frac{r}{\overline{h^0}} \tag{A-4}$$

The stoichiometric relationships are simply obtained from material balance considerations;

$$\phi_\mathrm{B} = \phi_{\mathrm{B}_1}\Gamma_2\left(1 + \frac{K_\mathrm{A}\phi_{\mathrm{A}_1}}{r}\right) \text{ and } \phi_\mathrm{A} = \phi_{\mathrm{A}_1}(1 + K_\mathrm{A}\phi_{\mathrm{B}_1}\Gamma_1) \tag{A-5}$$

where,

$$\Gamma_1 = \left(1 - \frac{K_2}{K_\mathrm{B}}\right) + \frac{K_2}{K_\mathrm{B}}\frac{1}{\left(1 - K_\mathrm{B}\phi_{\mathrm{B}_1}\right)} \text{ and } \Gamma_2 = \left(1 - \frac{K_2}{K_\mathrm{B}}\right) + \frac{K_2}{K_\mathrm{B}}\frac{1}{\left(1 - K_\mathrm{B}\phi_{\mathrm{B}_1}\right)^2} \tag{A-6}$$

K_2, K_B are the self-association equilibrium constants for dimer formation and *h*-mer ($h > 2$) formation respectively, K_A is the inter-association equilibrium constant and ϕ_{A_1}, ϕ_{B_1} are the volume fractions of the solvent and polymer segments that are not hydrogen bonded, $\phi^0_{\mathrm{B}_1}$ is the volume fraction of the polymer segments in pure B that are not hydrogen bonded and *r* is the ratio of the molar volumes $V_\mathrm{A}/V_\mathrm{B}$.

A.2. Poly(methacrylic acid) gels

The hydrogen bonding free energy contribution per mole of lattice sites is given by

$$\frac{\Delta G_\mathrm{H}}{RT} = \phi_\mathrm{B} \ln\left(\frac{\phi_{\mathrm{B}_1}}{\phi^0_{\mathrm{B}_1}}\right) + \frac{\phi_\mathrm{A}}{r} \ln \phi_{\mathrm{A}_1} + \phi_\mathrm{B}\left[\phi^0_{\mathrm{B}_1}\left(1 + K_\mathrm{B}\phi^0_{\mathrm{B}_1}\right)\right] - \phi_{\mathrm{B}_1}(1 + K_\mathrm{B}\phi_{\mathrm{B}_1}) - \left[\frac{\phi_\mathrm{B}}{\overline{h^0}} \ln \phi_\mathrm{B} + \frac{\phi_\mathrm{A}}{r} \ln \phi_\mathrm{A}\right] \tag{A-7}$$

where,

$$\overline{h^0} = \frac{1 + 2K_\mathrm{B}\phi^0_{\mathrm{B}_1}}{1 + K_\mathrm{B}\phi^0_{\mathrm{B}_1}} \tag{A-8}$$

while the contribution to the chemical potential of the solvent is

$$\frac{\Delta\mu_{\mathrm{A_H}}}{RT} = \ln\left(\frac{\phi_{\mathrm{A}_1}}{\phi_\mathrm{A}}\right) - r\phi_{\mathrm{B}_1}(1 + K_\mathrm{B}\phi_{\mathrm{B}_1}) + \phi_\mathrm{B}\frac{r}{\overline{h^0}} \tag{A-9}$$

Also, we have the following stoichiometric relationships:

$$\phi_\mathrm{B} = \phi_{\mathrm{B}_1}\left[1 + \frac{K_\mathrm{A}\phi_{\mathrm{A}_1}}{r}\right] + 2K_\mathrm{B}(\phi_{\mathrm{B}_1})^2 \text{ and } \phi_\mathrm{A} = \phi_{\mathrm{A}_1}(1 + K_\mathrm{A}\phi_{\mathrm{B}_1}) \tag{A-10}$$

where K_B and K_A are the equilibrium constant describing the self-association and inter-association respectively, and ϕ_{A_1}, ϕ_{B_1} and $\phi^0_{\mathrm{B}_1}$ are as defined above.

A.3. Ternary solution theory

The free energy of a ternary gel where hydrogen bonding is involved is given by

$$\frac{\Delta G}{kT} = \nu\left[\frac{3}{2}(\alpha^2 - 1) - \ln\alpha^3\right] - \xi\ln\phi_B + n_A\ln\phi_A + n_C\ln\phi_C + n_A\phi_B\chi_{AB} + n_A\phi_C\chi_{AC} + n_C\phi_B\chi_{CB} + \frac{\Delta G_H}{RT} \quad \text{(A-11)}$$

where ϕ_B,ϕ_A and ϕ_C are the volume fractions of the polymer segments and the solvents A and C respectively, and χ_{ij} is the Flory–Huggins binary interaction parameter between component i and j, respectively, given by

$$\chi_{ij} = (\delta_i - \delta_j)^2\frac{V_{\mathrm{ref}}}{RT} + 0.34 \quad \text{(A-12)}$$

Note that while calculating the interaction parameter between A and C (solvents), the addition of the fudge factor (0.34) is not necessary. ΔG_H is the hydrogen bonding contribution to the free energy and is given by:

$$\frac{\Delta G_H}{RT} = n_B\ln\left(\frac{\phi_{B_1}}{\phi_{B_1}}\right) + n_A\ln\phi_{A_1} + n_C\ln\phi_{C_1} - n_B\left[\frac{\phi_{B_1}\Gamma_1}{\phi_B} - \phi^0_{B_1}\Gamma^0_1\right] - \left[\frac{n_B}{h^0}\ln\phi_B + n_A\ln\phi_A + n_C\ln\phi_C\right] \quad \text{(A-13)}$$

where K_C is the equilibrium constant between the polymer segments and the third solvent and ϕ_{C_1} is the volume fraction of C that is not hydrogen bonded. For a inert solvent, $K_C = 0$ and $\phi_{C_1} = \phi_C$. As for binary systems, the stoichiometric equations are obtained from material balance considerations;

$$\phi_B = \phi_{B_1}\Gamma_2\left(1 + \frac{K_A\phi_{A_1}}{r_A} + \frac{K_C\phi_{C_1}}{r_C}\right) \quad \text{(A-14)}$$

Following Tompa, the spinodal phase behavior can be calculated using

$$\frac{\partial^2\Delta G}{\partial\phi_B^2}\frac{\partial^2\Delta G}{\partial\phi_A^2} - \left(\frac{\partial^2\Delta G}{\partial\phi_B\partial\phi_A}\right) = 0 \quad \text{(A-16)}$$

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