Thermodynamics of Aqueous Systems Containing Hydrophilic Polymers or Gels

A quasichemical partition function is applied to represent the thermodynamic properties of aqueous solutions of nonelectrolytes, including linear polymers and crosslinked polymers (gels). The partition function extends conventional lattice theory; to take into account strong specific interactions (hydrogen bonds) as encountered in aqueous solutions, each molecule (polymer segment) may possess three energetically different types of contact sites. We distinguish between sites that interact through dispersion forces and sites that can participate in a hydrogen bond; hydrogen-bonding sites are divided into electron-pair donating sites and electron-pair accepting sites. The Helmholtz energy of the mixture is obtained using an oriented quasichemical approximation. The final equation contains three independent adjustable binary parameters; these are the exchange energies for different types of contact pairs. To represent quantitatively upper or lower critical solution phenomena, we include the semitheoretical fluctuation correction recently proposed by de Pablo. Comparison with experimental data indicates that the proposed molecular-thermodynamic model may be useful for representing phase equilibria for a variety of aqueous systems including swelling equilibria for hydrophilic gels.

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Introduction

Water-soluble polymers are specialty chemicals used in a variety of consumer-oriented materials such as cosmetics, food additives, pharmaceuticals and personal-care products. Little is known about the thermodynamic properties of aqueous polymer solutions. This work reports some initial studies toward increasing our understanding of aqueous polymer phase behavior, and toward improving our ability to correlate that phase behavior.

Several molecular-thermodynamic models have been used to describe binary vapor-liquid equilibria and semidilute ternary liquid-liquid equilibria in aqueous polymer solutions (e.g., Edmond and Ogsten, 1968; King et al., 1988; Kang and Sandler, 1989). However, presently available models are not applicable to liquid-liquid equilibria for concentrated aqueous polymer solutions, especially for those solutions that exhibit a lower consolute temperature. We present here an oriented quasichemical model which is promising for describing such systems. We also apply this model to phase equilibria in aqueous mixtures containing hydrophilic gels. Gels are useful for drug delivery devices (e.g., Hoffman, 1987; Siegel et al., 1988), for separation operations in biotechnology (Freitas and Cussler, 1987), and for processing of agricultural products (Trank et al., 1988).

The thermodynamic properties of aqueous polymer solutions cannot be correlated by simple lattice models such as Flory-Huggins theory. Phase equilibria in these systems are influenced by strong, orientation-dependent interaction forces, such as hydrogen bonds. Conventional polymer-solution models (e.g., Patterson, 1969; Flory, 1970) do not take into account deviations from random mixing caused by these orientation-dependent interactions.

In recent years, several authors have proposed for polymer solutions molecular-thermodynamic models that attempt to account for nonrandom mixing. These models are based often on the local-composition concept where expressions for local composition are obtained either from essentially empirical relations (e.g., Brandani, 1979; Rubio and Renuncio, 1980; Canovas et al., 1982; Kang and Sandler, 1988) or else are derived from Guggenheim's traditional quasichemical approximation (e.g.,

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Panayiotou and Vera, 1980; Panayiotou, 1984; Kumar et al., 1987). However, these models are not suitable for describing aqueous polymer systems; in particular, they are unable to account for observed order-disorder transitions leading to lower critical solution temperatures.

To account for orientational effects, Kehiaian et al. (1978), Abusleme and Vera (1985a, b), and Smirnova and Victorov (1987) have proposed group-solution models. These models consider the different groups to be independent of the molecule to which the groups belong and are, therefore, not suitable for describing order-disorder transitions in aqueous polymer solutions.

While an upper critical solution temperature (UCST) is readily understood in terms of intermolecular forces, interpretation of a lower critical solution temperature (LCST) is more difficult (Rowlinson and Swinton, 1982). Generally, an LCST is observed when either of the following conditions prevails:

1. *Large differences in thermal expansion of solvent and solute.* This situation is often encountered in polymer/volatile-solvent systems [e.g., poly(styrene)/acetone (Siow et al., 1972; Zeman and Patterson, 1972)] when the system temperature approaches the critical temperature of the solvent. As temperature rises, the solvent expands more rapidly than the solute; solubility decreases until two separate phases are formed. This behavior is well described by free-volume theories [e.g., Flory, 1970; Patterson, 1969; Lacombe and Sanchez, 1976; Sanchez and Lacombe, 1978)].

2. *Order-disorder transitions, as encountered in systems of molecules capable of forming hydrogen bonds, e.g., water/nicotine (Campbell et al., 1958) and water/poly(ethyleneglycol) (Malcolm and Rowlinson, 1957).* More than 50 years ago, Hirschfelder et al. (1937) suggested a qualitative physical picture to explain the occurrence of LCST's in hydrogen-bonding systems: mutual solubility at temperatures below the LCST is attributed to highly orientation-dependent interactions (hydrogen bonds) between unlike species. As the temperature rises, molecular rotation increases, causing hydrogen bonds to break. If dispersion-force interactions between unlike species are weaker than those between like species, the system splits into two phases.

In this paper we are concerned with aqueous solutions at ordinary temperatures; therefore, the free-volume theories are not useful here.

Models that attempt to incorporate order-disorder transitions were proposed in the early 1950s by Barker (1952), Barker and Fock (1953), and Tompa (1953). Barker and Fock considered a lattice with coordination number z where each site is occupied by one molecule of either species 1 or 2. One or more of the z contact points of each molecule was taken to be energetically different from the others. Barker and Fock developed this model with the quasichemical approximation and were able to show that, in principle, this model was capable of predicting LCST's and UCST's for suitable choices of interaction parameters. However, Barker and Fock were not able to reproduce liquid-liquid equilibria quantitatively. Further, their model is restricted to solutions of equal-sized molecules and, therefore, it is not directly applicable to aqueous polymer solutions.

Sjoeberg and Karlstroem (1989) have presented a model for ternary aqueous systems. The authors assume that, as temperature rises, polymer conformation changes from a hydrophilic to a hydrophobic state.

To describe binary systems of nearly equal-sized molecules with oriented interactions, decorated lattice models have been proposed that are "exactly soluble" in the sense that they can be mapped onto a three-dimensional Ising model for which known solutions exist (e.g., Wheeler, 1975; Andersen and Wheeler, 1978). The mathematical complexity of these models makes extension to polymer solutions and multicomponent systems difficult.

We describe here a theory which, in spirit, is similar to that of Barker and Fock; our goal is to interpret and quantitatively correlate phase equilibria in aqueous polymer solutions. Our partition function is formally similar to that of Abusleme and Vera (1985b), as discussed near the end of the next section.

Lattice Theory for a Mixture of Hydrogen-Bonding Liquids

Figure 1 shows a two-dimensional representation of our lattice model. The coordination number of the lattice is z (usually taken to be 10). Each molecule possesses zq contact sites through which it can interact with nearest neighbors. For linear or branched-chain molecules, zq is related to r, the number of segments per molecule, by

$$zq = r(z - 2) + 2 \tag{1}$$

To account for hydrogen bonding, we stipulate that the contact sites (or surface regions) of a molecule (polymer segment) can exhibit different potential energies. Each molecule (segment) of species i can possess three types of contact sites: hydrogen-bond donating sites, hydrogen-bond accepting sites, and sites which interact through dispersion forces. (Here we define electron-pair acceptors as hydrogen-bond donating sites and electron-pair donors as hydrogen-bond accepting sites.) We use z_i^α and z_i^β, respectively, to denote the number of hydrogen-bond donating and hydrogen-bond accepting sites per segment of mol-

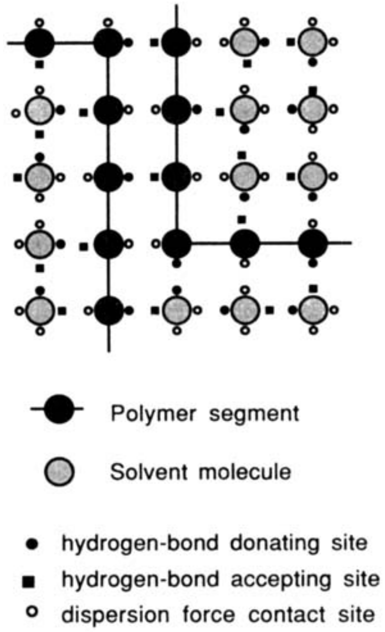

Figure 1. Two-dimensional representation of the oriented lattice model.

ecule i. The remaining contacts, z_i^D $(= z - z_i^\alpha - z_i^\beta)$, interact through dispersion forces.

For a given molecule, z_i^α and z_i^β are determined from molecular structure. Water, for example, can participate in two hydrogen bonds as a donor $(z_i^\alpha = 2)$ and in two hydrogen bonds as an acceptor $(z_i^\beta = 2)$. Some organic compounds can participate in hydrogen bonds only as donors $(z_i^\beta = 0)$ or only as acceptors $(z_i^\alpha = 0)$; examples include chloroform and (neglecting end groups) polyethylene glycol.

For a binary system in which each component contains α, β, and D sites, there are 21 different types of contact pairs, N_{kl}. Here, k and l are contact-site indices, with a different index for α, β, and D sites on each molecule i. In the simplest case, where the interaction energies u_{kl} between all contact pairs are identical, all molecules (resp. contact sites) are randomly distributed over the lattice. The numbers of different kl pairs are then given by the overall probability that two contact sites of a given type are nearest neighbors. These numbers are readily calculated from the overall composition and the number of different contact sites per molecule (segment). Guggenheim (1952) calls this simple case the zeroth approximation.

For those cases where molecules have homogeneous surface potentials (i.e., we do not distinguish between different types of contacts) but where $u_{ij} \neq u_{ii} \neq u_{jj}$, we can also calculate the number of ij contact pairs using Guggenheim's traditional quasichemical approximation. We then obtain modest deviations from random mixing. Guggenheim calls this case the first approximation.

However, for systems in which strong specific interactions are significantly different from weak interactions, we expect large deviations from random mixing. To take these large deviations into account, we write the partition function Q for a hydrogen-bonding fluid in the form

$$Q = Q_{\text{comb,random}}\, Q_{\text{comb,nonrandom}}\, Q_E\, Q_{\text{vib,rot}} \tag{2}$$

where

$Q_{\text{comb,random}}$ = random contribution to combinatorial factor depending only on number of molecules and molecular size

$Q_{\text{comb,nonrandom}}$ = nonrandom contribution to combinatorial factor depending primarily on the interaction energies between different types of pairs relative to thermal energy kT, where k is Boltzmann's constant

Q_E = energetic contribution to the partition function

$Q_{\text{vib,rot}}$ = contributions to the partition function from molecular vibrations and rotations

To obtain an expression for the Gibbs energy of mixing from the partition function, we assume that, at the pressures and temperatures of interest here, the change in molar volume upon mixing is negligible:

$$[\Delta G_{\text{mixing}}]_{T,P} \approx [\Delta A_{\text{mixing}}]_{T,V} = -kT \ln Q_{\text{mixing}} \tag{3}$$

where A is the Helmholtz energy.
The chemical potential per molecule of component i is calculated from the partition function according to

$$\Delta\mu_i = \mu_i - \mu_i^o = \frac{\partial(G_{\text{mixture}} - G_i^o)}{\partial N_i} \approx -kT\frac{\partial \ln Q_{\text{mixing}}}{\partial N_i} \tag{4}$$

where N_i is the number of molecules of species i. The differentiation in Eq. 4 is at constant temperature, constant pressure, and constant N_j.

Superscript ^{o} refers to the standard state, which is chosen to be that of the pure component at system temperature and pressure. Q_{mixing} is given by

$$Q_{\text{mixing}} = Q_{\text{mixture}} / \prod_i Q_{\text{pure}\,i} \tag{5}$$

Following Guggenheim (1952), we assume that the vibrational and rotational contributions to the partition function do not change significantly upon mixing; therefore, the $Q_{\text{vib,rot}}$ terms cancel out in Eq. 5.

For the random contribution to the combinatorial factor, we use an expression given by Guggenheim (1944a). In the derivation of this combinatorial factor, the relation between r and q is given by Eq. 1 which holds only for linear or branched-chain molecules. As discussed later, to calculate swelling equilibria in systems containing crosslinked polymers, we use for Q_{random} the Flory-Huggins combinatorial term. Both random combinatorial terms are functions of only the numbers and sizes of the molecules in the mixture.

To obtain an expression for the nonrandom combinatorial term, we use an oriented quasichemical approximation that is an extension of the quasichemical approximation suggested by Guggenheim (1944b). This extension follows from distinguishing between sites denoted by α, β, and D as outlined below.

The energy contribution to the partition function is given by

$$Q_E = \exp - (E_{\text{latt}}/kT) \tag{6}$$

For the lattice energy E_{latt}, we assume pairwise additivity of interaction energies.

To calculate $Q_{\text{nonrandom}}$ and Q_E, it is necessary to evaluate the numbers of different contact pairs as a function of composition, temperature, and the interaction energies between contacts. As suggested by Panayiotou and Vera (1980), we express the numbers of nonrandom contact pairs in terms of nonrandom factors Γ so that in a system containing m components, for a given pair

$$N_{ij}^{\alpha\beta} = (N_{ij}^{\alpha\beta})_r \Gamma_{ij}^{\alpha\beta} \quad (i = 1, m; j = 1, m) \tag{7a}$$

$$N_{ij}^{\alpha D} = (N_{ij}^{\alpha D})_r \Gamma_{ij}^{\alpha D} \quad (i = 1, m; j = 1, m) \tag{7b}$$

$$N_{ij}^{\beta D} = (N_{ij}^{\beta D})_r \Gamma_{ij}^{\beta D} \quad (i = 1, m; j = 1, m) \tag{7c}$$

$$N_{ij}^{\alpha\alpha} = (N_{ij}^{\alpha\alpha})_r \Gamma_{ij}^{\alpha\alpha} \quad (i = 1, m; j = 1, m) \tag{7d}$$

$$N_{ij}^{\beta\beta} = (N_{ij}^{\beta\beta})_r \Gamma_{ij}^{\beta\beta} \quad (i = 1, m; j = 1, m) \tag{7e}$$

$$N_{ij}^{DD} = (N_{ij}^{DD})_r \Gamma_{ij}^{DD} \quad (i = 1, m; j = 1, m) \tag{7f}$$

where subscript r denotes random mixing. The nonrandom factors Γ are evaluated from minimization of the Helmholtz energy, with constraints from contact-site balances. We then obtain quasichemical equations of the form

$$\frac{[\Gamma_{ij}^{\alpha\beta}]^2}{[\Gamma_{ii}^{\alpha\alpha}][\Gamma_{jj}^{\beta\beta}]} = \exp - [2\omega_{ij}^{\alpha\beta}/kT] \quad (i = 1, m; j = 1, m) \tag{8a}$$

$$\frac{[\Gamma_{ij}^{\alpha D}]^2}{[\Gamma_{ii}^{\alpha\alpha}][\Gamma_{jj}^{DD}]} = \exp - [2\omega_{ij}^{\alpha D}/kT] \quad (i = 1, m; j = 1, m) \tag{8b}$$

$$\frac{[\Gamma_{ij}^{\beta D}]^2}{[\Gamma_{ii}^{\beta\beta}][\Gamma_{jj}^{DD}]} = \exp - [2\omega_{ij}^{\beta D}/kT] \quad (i = 1, m; j = 1, m) \tag{8c}$$

$$\frac{[\Gamma_{ij}^{\alpha\alpha}]^2}{[\Gamma_{ii}^{\alpha\alpha}][\Gamma_{jj}^{\alpha\alpha}]} = \exp - [2\omega_{ij}^{\alpha\alpha}/kT] \quad (i = 1, m; j = 1, m; i \neq j) \tag{8d}$$

$$\frac{[\Gamma_{ij}^{\beta\beta}]^2}{[\Gamma_{ii}^{\beta\beta}][\Gamma_{jj}^{\beta\beta}]} = \exp - [2\omega_{ij}^{\beta\beta}/kT] \quad (i = 1, m; j = 1, m; i \neq j) \tag{8e}$$

$$\frac{[\Gamma_{ij}^{DD}]^2}{[\Gamma_{ii}^{DD}][\Gamma_{jj}^{DD}]} = \exp - [2\omega_{ij}^{DD}/kT] \quad (i = 1, m; j = 1, m; i \neq j) \tag{8f}$$

where the exchange energies ω are given by

$$\omega_{ij}^{\alpha\beta} = u_{ij}^{\alpha\beta} - \tfrac{1}{2}u_{ii}^{\alpha\alpha} - \tfrac{1}{2}u_{jj}^{\beta\beta} \quad (i = 1, m; j = 1, m) \tag{9a}$$

$$\omega_{ij}^{\alpha D} = u_{ij}^{\alpha D} - \tfrac{1}{2}u_{ii}^{\alpha\alpha} - \tfrac{1}{2}u_{jj}^{DD} \quad (i = 1, m; j = 1, m) \tag{9b}$$

$$\omega_{ij}^{\beta D} = u_{ij}^{\beta D} - \tfrac{1}{2}u_{ii}^{\beta\beta} - \tfrac{1}{2}u_{jj}^{DD} \quad (i = 1, m; j = 1, m) \tag{9c}$$

$$\omega_{ij}^{\alpha\alpha} = u_{ij}^{\alpha\alpha} - \tfrac{1}{2}u_{ii}^{\alpha\alpha} - \tfrac{1}{2}u_{jj}^{\alpha\alpha} \quad (i = 1, m; j = 1, m; i \neq j) \tag{9d}$$

$$\omega_{ij}^{\beta\beta} = u_{ij}^{\beta\beta} - \tfrac{1}{2}u_{ii}^{\beta\beta} - \tfrac{1}{2}u_{jj}^{\beta\beta} \quad (i = 1, m; j = 1, m; i \neq j) \tag{9e}$$

$$\omega_{ij}^{DD} = u_{ij}^{DD} - \tfrac{1}{2}u_{ii}^{DD} - \tfrac{1}{2}u_{ii}^{DD} \quad (i = 1, m; j = 1, m; i \neq j) \tag{9f}$$

The contact-site balance equations in a system of m components can be written as

$$\Gamma_{ii}^{\alpha\alpha} = \frac{1 - \left[\sum_j \theta_j^{\alpha}\Gamma_{ij}^{\alpha\alpha} + \sum_j \theta_j^{\beta}\Gamma_{ij}^{\alpha\beta} + \sum_j \theta_j^{D}\Gamma_{ij}^{\alpha D} + \theta_i^{\beta}\Gamma_{ii}^{\alpha\beta} + \theta_i^{D}\Gamma_{ii}^{\alpha D}\right]}{\theta_i^{\alpha}} \tag{10a}$$

$$\Gamma_{ii}^{\beta\beta} = \frac{1 - \left[\sum_j \theta_j^{\alpha}\Gamma_{ij}^{\beta\alpha} + \sum_j \theta_j^{\beta}\Gamma_{ij}^{\beta\beta} + \sum_j \theta_j^{D}\Gamma_{ij}^{\beta D} + \theta_i^{\alpha}\Gamma_{ii}^{\beta\alpha} + \theta_i^{D}\Gamma_{ii}^{\beta D}\right]}{\theta_i^{\beta}} \tag{10b}$$

$$\Gamma_{ii}^{DD} = \frac{1 - \left[\sum_j \theta_j^{\alpha}\Gamma_{ij}^{D\alpha} + \sum_j \theta_j^{\beta}\Gamma_{ij}^{D\beta} + \sum_j \theta_j^{D}\Gamma_{ij}^{DD} + \theta_i^{\alpha}\Gamma_{ii}^{D\alpha} + \theta_i^{\beta}\Gamma_{ii}^{D\beta}\right]}{\theta_i^{D}} \tag{10c}$$

where

$$i = 1, m; j = 1, m; j \neq i$$

Here θ_i^{α}, θ_i^{β}, and θ_i^{D} are contact-site fractions, defined by

$$\theta_i^{\alpha} \equiv \frac{z_i^{\alpha} q_i N_i}{Nzq}; \quad \theta_i^{\beta} \equiv \frac{z_i^{\beta} q_i N_i}{Nzq}; \quad \theta_i^{D} \equiv \frac{z_i^{D} q_i N_i}{Nzq} \tag{11}$$

with $Nzq = z\,\Sigma_i\, q_i N_i$

Details leading to Eqs. 8 and 10 are given as supplementary material.

To describe a binary system, we require 21 nonrandom factors Γ. To obtain them, we have 15 quasichemical equations (four equations each of types 8a, 8b, and 8c, and one equation each of types 8d, 8e, and 8f) in addition to six contact-site balance equations (two equations each of types 10a, 10b, and 10c).

For solutions of linear or branched polymers, we obtain for the chemical potential per mole of component i

$$\Delta\mu_i = -RT\left[r_i\left(\frac{1}{2}z - 1\right)\ln\phi_i - \frac{1}{2}zq_i\ln\theta_i - 1 + \frac{\phi_i}{x_i} + \frac{1}{2}zq_i\left(1 - \frac{\phi_i}{\theta_i}\right) + \frac{1}{2}z_i^{\alpha}q_i\ln\frac{[\Gamma_{ii}^{\alpha\alpha}]_{\text{pure}}}{[\Gamma_{ii}^{\alpha\alpha}]_{\text{mix}}} + \frac{1}{2}z_i^{\beta}q_i\ln\frac{[\Gamma_{ii}^{\beta\beta}]_{\text{pure}}}{[\Gamma_{ii}^{\beta\beta}]_{\text{mix}}} + \frac{1}{2}z_i^{D}q_i\ln\frac{[\Gamma_{ii}^{DD}]_{\text{pure}}}{[\Gamma_{ii}^{DD}]_{\text{mix}}}\right] \tag{12}$$

where ϕ is the volume fraction:

$$\phi_i = \frac{N_i r_i}{\sum_j N_j r_j}$$

and θ is the surface fraction:

$$\theta_i = \frac{N_i q_i}{\sum_j N_j q_j}$$

The first five terms of the righthand side of Eq. 12 give contributions from random mixing; the last three terms give the nonrandomness contribution and the energetic contribution.

If we do not allow for hydrogen-bonding contacts, then z_i^α and z_i^β become equal to zero and the nonrandom factors for the pure components Γ_{ii} are equal to unity. In that event, our model reduces to the first approximation suggested by Guggenheim (1952). If we equate interaction energies between all contact pairs (i.e., if we set all exchange energies to zero), then the nonrandom factors are unity for the pure components and for the mixture, and the last three terms of Eq. 12 are equal to zero. In that case, our model reduces to Guggenheim's zeroth approximation (Guggenheim, 1952).

The similarity of our partition function to that of Abusleme and Vera (1985b) becomes apparent if we regard our model as a group-contribution model that contains three groups (α, β, and D). However, unlike Abusleme and Vera, we assume different interaction potentials for the same group, depending on whether it belongs to molecule A or molecule B. Thus, while our final equations are similar to those of Abusleme and Vera, our physical picture leading to these equations is significantly different.

Details of the derivation of the partition function and the expression for the chemical potential are available as supplementary material.

Comparison with Experimental Data

To calculate phase equilibria, the chemical potential of every component in the mixture must be evaluated as a function of temperature, composition and interaction energies. Structural parameters r_i, q_i, z_i^α, and z_i^β are obtained from molecular size (number of structural units per molecule) and from molecular structure (e.g., number of possible hydrogen bonds per structural unit). For water, we use $r = 1$, $q = 1$, $z^\alpha = 2$, and $z^\beta = 2$.

The exchange energies are adjustable binary parameters. For a binary system in which both components contain α, β and D contact sites, there are 15 different exchange energies. To make tractable the number of adjustable parameters, we group exchange energies into four categories and make a reasonable simplifying assumption for each of the first three. The four groups (and the simplifying assumptions) are as follows:

1) Energies of hydrogen bonding between like molecules: $\omega_{11}^{\alpha\beta} = \omega_{22}^{\alpha\beta}$

2) Energies of hydrogen bonding between unlike molecules: $\omega_{12}^{\alpha\beta} = \omega_{21}^{\alpha\beta}$

3) Weak attractions between hydrogen bonding and nonhydrogen bonding contacts:

$$\omega_{11}^{\alpha D} = \omega_{11}^{\beta D} = \omega_{22}^{\alpha D} = \omega_{22}^{\beta D} = \omega_{12}^{\alpha D} = \omega_{12}^{\beta D} = \omega_{21}^{\alpha D} = \omega_{21}^{\beta D}$$

4) Weak attractions between unlike molecules: ω_{12}^{DD}

Exchange energies of types 1 and 2 are always negative, reflecting the favorable energetics of hydrogen-bond formation. Exchange energies of type 4 are typically positive, indicating that van der Waals interactions between unlike molecules are less than the arithmetic mean of interactions between like molecules. Finally, exchange energies of type 3 are negative due to the unfavorable energetics of α-α and β-β contacts, relative to α-D and β-D contacts.

Two exchange energies have been omitted from the above discussion: $\omega_{12}^{\alpha\alpha}$ and $\omega_{12}^{\beta\beta}$. Interaction potentials for α-α and β-β contacts between unlike molecules are not likely to be significantly different from those between like molecules. Thus, $\omega_{12}^{\alpha\alpha}$ and $\omega_{12}^{\beta\beta}$ are set to zero in all cases.

A final simplification is to fix the value of the pure-component hydrogen-bonding exchange energies ($\omega_{11}^{\alpha\beta}$ and $\omega_{22}^{\alpha\beta}$) at a constant (negative) value for all systems. From experience with data reduction, we find that good quantitative representation of experimental data is obtained when

$$\omega_{11}^{\alpha\beta}/k = \omega_{22}^{\alpha\beta}/k = -200.0\ K$$

and when the remaining parameters are adjusted. Thus, in a binary system, we have three adjustable exchange-energy parameters: $\omega_{12}^{\alpha\beta}$ ($=\omega_{21}^{\alpha\beta}$), ω_{12}^{DD}, and ω^{D*}. The parameter ω^{D*} refers to exchange energies of type 3, where $* = \alpha$ or β, and the exchange energy is identical for 1-1, 2-2, 1-2, and 2-1 contacts.

The simplifications made here reduce to three the number of adjustable parameters in the model without sacrificing the physical picture used in deriving the partition function. While these simplifications may appear extreme, it is important to remember that energy parameters used to correlate experimental data are relative—not absolute representations of underlying molecular interactions. (See recent computer simulation studies of Madden et al., 1989.) Thus, while we have fixed the values of $\omega_{11}^{\alpha\beta}$ and $\omega_{22}^{\alpha\beta}$, the remaining parameters indicate the relative magnitudes (and signs) of other interactions with respect to these fixed values.

When compared to computer calculations, Madden found that Guggenheim's quasichemical theory agrees fairly well with simulation over a wide concentration range; the other lattice models Madden considered agreed less favorably with simulation. Madden's work thus lends support to our choice of quasichemical theory as a framework for developing an oriented lattice model.

In the following sections, we apply the oriented quasichemical model to vapor-liquid equilibria (VLE) and liquid-liquid equilibria (LLE) for several aqueous solutions containing molecules of different sizes.

Vapor-Liquid Equilibria

Figure 2 shows vapor-liquid equilibria for aqueous solutions of poly(ethyleneglycol) (PEG) and poly(propyleneglycol) (PPG) (Malcolm and Rowlinson, 1957). The activity of the solvent is plotted as a function of volume fraction of the polymer for

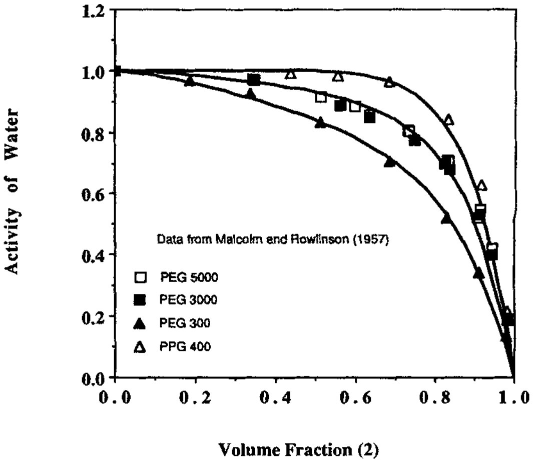

Figure 2. VLE for the system water(1)/PEG(2) at 338 K and the system water(1)/PPG(2) at 323 K.

Table 1. Parameters for VLE Calculations in Aqueous Systems

Solute (2)	r_2	q_2	z_2^α	z_2^β	$\omega_{12}^{\alpha\beta}/k$ K	ω_{12}^{DD}/k K	ω^{D*}/k K
PEG 5000	150.0	120.2	0	1.9	−473.3	120.0	−200.0
PEG 3000	90.0	72.2	0	1.9	−473.3	120.0	−200.0
PEG 300	9.0	7.4	0	1.9	−617.6	120.0	−200.0
PPG 400	12.0	9.8	0	1.4	−306.0	110.3	−75.0

k = Boltzmann constant
* = α or β

PEG solutions of different molecular weights. The solvent-activity data for the low molecular-weight (300) PEG differ appreciably from those for the higher molecular-weight fractions. This difference is probably due to the terminal −OH groups which have considerable influence on the behavior of the low molecular-weight fractions. Because we neglected end groups in determining z_2^α and z_2^β for PEG, it was necessary to allow one binary parameter, $\omega_{12}^{\alpha\beta}$, to differ for the low and high molecular-weight fractions. Table 1 gives parameters used to fit VLE data.

Figure 2 shows that the model can represent the data within experimental error. However, such fitting is not remarkable. Other, simply Gibbs-energy models also fit these VLE data. It is much more difficult to fit binary liquid-liquid equilibrium data.

Liquid-Liquid Equilibria

Figures 3 and 4 show experimental and calculated LLE for aqueous systems containing molecules ranging in molecular weight between 56 (propenal) and 290,000 poly(N-isopropylacrylamide). Table 2 gives parameters used to correlate LLE.

The systems phenol/water and propenal/water exhibit upper critical solution temperatures. However, PEG/water, PPG/water and poly(N-isopropylacrylamide)/water exhibit lower critical solution temperatures. These LCST's are caused by order-disorder transitions due to the breakage of hydrogen bonds with increasing temperature. While conventional polymer-solution models can predict the existence of UCST's, they cannot predict the existence of LCST's that are caused by order-disorder transitions, unless we assign unreasonable temperature dependences to the energy parameters. The broken lines in Figures 3 and 4 show coexistence curves calculated from our model. Without modification, the oriented quasichemical model is able to reproduce qualitatively upper as well as lower critical solution temperatures with temperature-independent parameters. In all systems, we observe that, remote from the critical point, agreement between experimental and calculated results is good; however, as the critical point is approached, deviations become unacceptably large.

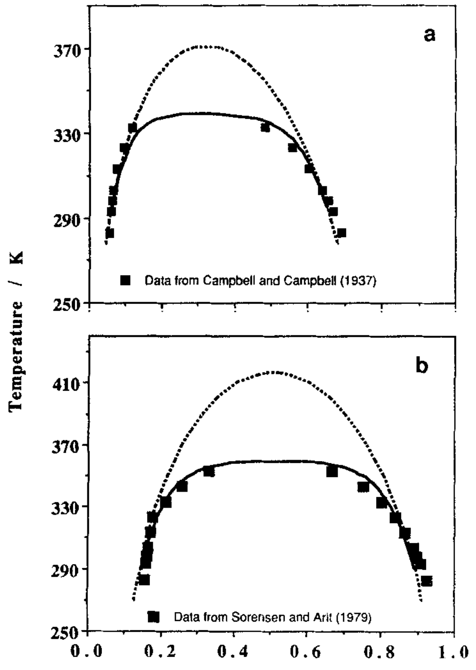

Figure 3. LLE for the systems: a) water(1)/phenol(2), b) water(1)/propenal(2).

Solid lines are calculated from the corrected model; broken lines are calculated from the uncorrected model.

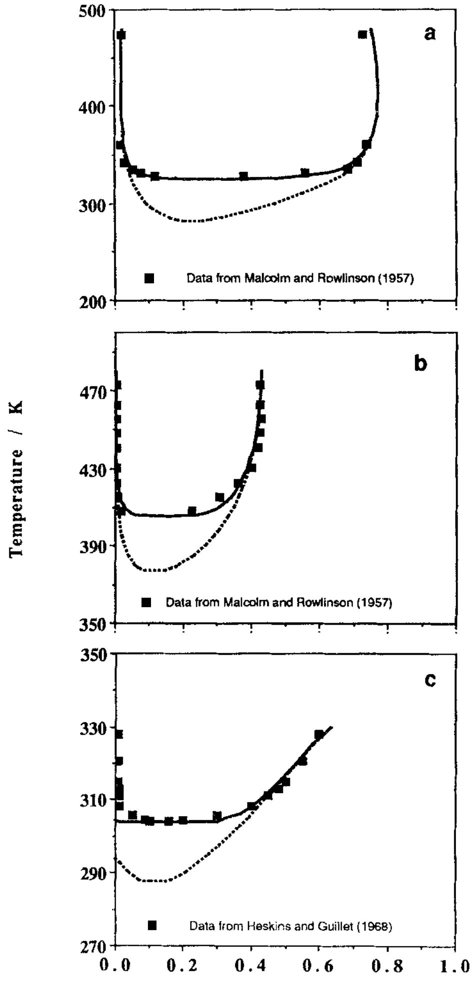

Figure 4. LLE for the systems: a) water(1)/PPG 400(2); b) water(1)/PEG 5000(2); and c) water(1)/PIPAA 290000(2).

Solid lines are calculated from the corrected model; broken lines are calculated from the uncorrected model.

Table 2. Parameters for LLE Calculations in Aqueous Systems

Solute (2)	r_2	q_2	z_2^α	z_2^β	$\omega_{12}^{\alpha\beta}/k$ K	ω_{12}^{DD}/k K	ω^{D*}/k K	K	a	b
Propenal	2.25	2.0	0	1.0	−756.4	197.5	−145.0	0.100	−10.0	0.36
Phenol	4.0	3.4	0.3	0.6	−661.0	115.0	−10.0	0.092	−15.0	0.36
PPG 400	12.0	9.8	0	1.4	−103.3	260.1	−120.0	0.264	−20.0	0.36
PEG 5000	150.0	120.2	0	1.9	−884.5	220.3	−103.0	0.430	−15.0	0.36
PIPAA 290000	300.0	2,400	1.1	1.1	−1,354.	700.0	−137.2	1.00	−10.0	0.36

Parameters $\omega_{12}^{\alpha\beta}$, ω_{12}^{DD}, and ω^{D*} are adjustable binary parameters. Parameters r_2, q_2, z_2^α, and z_2^β are determined from the molecular structure of the solute. Parameters K, a, and b are determined from theoretical criteria (stability criteria and scaling-law exponents) and from the coordinates of the critical point.

k = Boltzmann constant

$*$ = α or β

These deviations are caused by two effects:

a) For simplicity, we have here assumed that the exchange energies are temperature-independent. This assumption neglects the effect of lattice expansion and, more important, it neglects changes in rotational and vibrational partition functions due to mixing.

b) The oriented quasichemical model is classical in the sense that it does not take into account fluctuations of compositions around mean equilibrium values. Near the critical point of a system, these fluctuations become important and, very close to the critical point, they determine the properties of the system (Sengers and Levelt Sengers, 1978).

De Pablo and Prausnitz (1988) have developed a semitheoretical correction to take these fluctuations into account. Along the coexistence curve, the excess Gibbs energy can be expressed as

$$G^E = G^E_{\text{conv}}F \tag{13}$$

where G^E_{conv} is the excess Gibbs energy calculated from a "conventional" model (such as ours) and F is a decay function that describes the effect of fluctuations as a function of distance from the critical point. For a binary system, along the coexistence curve, F is only a function of temperature. As suggested by de Pablo, F is given by

$$F = 1 - K\exp a\left[\left(\frac{T_c - T}{T_c}\right)^2\right]^b \tag{14}$$

where T_c is the critical temperature of the system. At the critical point, $F = 1 - K$ and therefore K can be calculated from stability criteria. Constants a and b are not adjustable parameters; they are determined from known exponents in scaling laws, as discussed by de Pablo and Prausnitz (1988). Constant a is always negative and constant b is always positive.

The solid lines in Figures 3 and 4 show that, by introducing de Pablo's correction into our model, a much better representation of the data can be achieved. It is important to note that parameters K, a and b are *not* adjustable binary parameters. They are determined only from theoretical criteria and from the experimental coordinates of the critical point.

Swelling Equilibria for Hydrophilic Gels

Gels are crosslinked-polymer networks that can absorb solvent but are insoluble in the solvent. The equilibrium solvent content of the gel depends upon temperature, polymer-solvent interaction and the elastic forces in the network that counteract swelling. It has been observed that, with changing temperature, some gels can undergo phase transitions from a highly swollen (high solvent content) state to a collapsed (low solvent content) state (Tanaka, 1978; Hirokawa and Tanaka, 1984; Hoffman, 1987; Freitas and Cussler, 1987). Gels of polymers that exhibit an UCST are collapsed at low temperatures and swell as the temperature rises. Gels of polymers that exhibit a LCST show the inverted behavior; they are swollen at low temperatures and collapse as the temperature rises. We have applied the oriented quasichemical theory to describe swelling equilibria in the system water/poly(N-isopropylacrylamide).

Since the chemical potential given by Eq. 12 is valid only for mixtures of linear or branched molecules, we must use another expression for the random contribution to the combinatorial factor. Further, in a crosslinked polymer, elastic forces in the polymer network counteract swelling; these forces contribute to the Gibbs energy. According to Flory (1953), the chemical potential of a solvent in a gel phase coexisting with pure solvent is given by

$$\mu_1 - \mu_1^o = \Delta\mu_1 = \Delta\mu_{1,\text{mixing}} + \Delta\mu_{1,\text{elastic}} \tag{15}$$

We use the Flory-Huggins combinatorial term for the random contribution to $\Delta\mu_{1,\text{mixing}}$. The nonrandom and energetic contributions to the partition function are the same as those described above for systems containing noncrosslinked polymers. In a system containing a crosslinked-polymer network, the number of polymer molecules (not the number of segments) approaches zero (Flory, 1953). In this limit we obtain

$$\Delta\mu_{1,\text{mixing}} = RT\left[\ln\phi_1 + \phi_2 - \frac{1}{2}z_1^\alpha q_1 \ln\frac{[\Gamma_{11}^{\alpha\alpha}]_{\text{pure}}}{[\Gamma_{11}^{\alpha\alpha}]_{\text{mix}}} - \frac{1}{2}z_1^\beta q_1 \ln\frac{[\Gamma_{11}^{\beta\beta}]_{\text{pure}}}{[\Gamma_{11}^{\beta\beta}]_{\text{mix}}} - \frac{1}{2}z_1^D \ln\frac{[\Gamma_{11}^{DD}]_{\text{pure}}}{[\Gamma_{11}^{DD}]_{\text{mix}}}\right] \tag{16}$$

where ϕ_1 is the volume fraction of the solvent and ϕ_2 is the volume fraction of the gel in the gel phase. An expression for the contribution of elastic forces to the chemical potential can be obtained from the theory of rubber elasticity. We use an expression given by Flory (1953)

$$\Delta\mu_{1,\text{elastic}} = RT\left[\frac{v_1}{v_u}\phi_2^o(\rho - \rho_t)\left[\left(\frac{\phi_2}{\phi_2^o}\right)^{1/3} - \frac{\phi_2}{2\phi_2^o}\right]\right] \tag{17}$$

where

v_1 = molar volume of solvent

v_u = molar volume of monomer unit
ϕ_2^o = volume fraction of the gel in the standard state (i.e., the volume fraction of the gel in the state at which it is prepared)
ρ = fraction of monomer units that are connected via crosslinks
ρ_t = fraction of chains in the network terminated by a crosslink only on one end, which do not contribute to elasticity

Appendix I gives details concerning calculation of swelling equilibria.

Figure 5 shows experimental and calculated swelling equilibria for the system water/poly(*N*-isopropylacrylamide) gel (Freitas, 1987) which shows an inverted phase transition; the ratio of volume of gel in equilibrium with water (V) to that of dry gel (V_o) is plotted against temperature. The calculated curve is obtained using Eqs. 15–17 and using the procedure outlined in Appendix I. The gel composition parameters required in Eq. 17 are obtained from conditions under which the gel is prepared ($\rho = 0.018$, $\phi_2^o = 0.07$); the value of ρ_t is estimated to be 0.0001. For the exchange energies, we use the parameters obtained from correlating LLE for the uncrosslinked poly(*N*-isopropylacrylamide)/water system (Table 2). Thus, the calculated curve shown in Figure 5 has *not* been fit to the experimental swelling data; this curve is a prediction based on the known gel composition at preparation, and on independently-obtained exchange-energy parameters.

The semiquantitative agreement of the predicted swelling equilibria with experiment is encouraging. The predicted gel-collapse temperature is approximately three degrees lower than the observed collapse temperature. This is not surprising, however, considering that the calculated critical temperature for the uncrosslinked system is also too low when using the uncorrected version of our model. If the exchange energies were correlated to the experimental swelling data, the collapse temperature would be reproduced more accurately.

The calculations predict higher degrees of swelling at low temperatures than those observed experimentally. This disagreement is probably due to the expression we have used to describe the elastic effects on swelling. Equation 17 assumes that the chains in the gel network are distributed in a Gaussian manner about their average chain lengths. While this assumption is reasonable for short chain extensions, it introduces significant errors at high degrees of swelling. A large body of information exists on rubber elasticity (Mark and Erman, 1988; Erman and Flory, 1986; Treloar, 1958), and more accurate expressions for the elastic contribution to the Gibbs energy of swelling are available. We used Eq. 17 because its simplicity was consistent with our goal to demonstrate the applicability of the oriented quasichemical model for describing gel swelling equilibria.

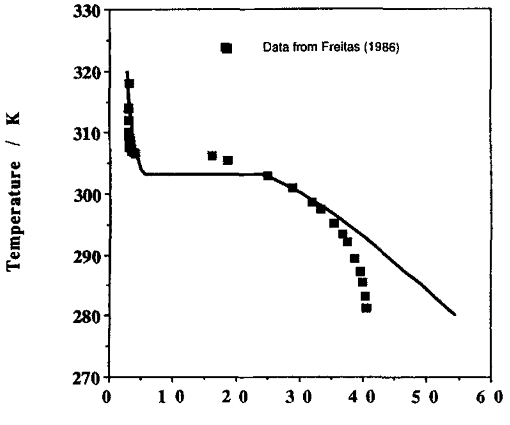

Figure 5. Swelling equilibria for the system water/PIPAA(gel).

The solid line is predicted from the uncorrected model using energy parameters correlated to the uncrosslinked-PIPAA/water system (Figure 4c). V_o is the gel volume at high temperature.

Conclusions

We have used an oriented quasichemical model to correlate phase equilibria for aqueous solutions of hydrophilic polymers and gels. By distinguishing between hydrogen-bonding and dispersion-force interactions, and without using temperature-dependent parameters, the model can predict the existence of lower critical solution temperatures that are caused by order-disorder transitions.

We have used the oriented quasichemical model to correlate VLE and LLE for aqueous systems containing small and large hydrogen-bonding solutes. Satisfactory representation is obtained for VLE and LLE in systems showing upper and lower critical solution temperatures. To represent quantitatively LLE near an upper or lower consolute point, we add to the model dePablo's fluctuation correction for the coexistence curve.

Encouraging results were obtained by applying the model to swelling equilibria for a gel/water system. Using energy parameters optimized to LLE data for the uncrosslinked poly(*N*-isopropylacrylamide)/water system, the model predicts swelling equilibria (and gel collapse) in semiquantitative agreement with experiment. Quantitative representation of swelling data will require a more realistic expression for the elastic contribution to the Gibbs energy.

Finally, it is important to note that all of the exchange energy parameters obtained from regressing experimental data have magnitudes and signs consistent with the physical premise of our model. The model appears to correctly represent the competition between hydrogen-bonding and dispersion-force interactions which leads to order-disorder transitions and lower critical solution behavior. These conclusions regarding parameter significance are necessarily qualitative in light of recent computer simulation studies (Madden et al., 1989). However, the (relatively) favorable comparison of quasichemical theory with simulation (Madden et al., 1989) lends support to these conclusions and to the simplifying assumptions made in applying our model to real systems.

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Notation

a = constant in de Pablo's function
A = Helmholtz energy

b = constant in de Pablo's function
E_{latt} = lattice energy
G = Gibbs energy
G^E = excess Gibbs energy
k = Boltzmann constant
K = constant in de Pablo's function
N_i = number of molecules of type i
$N_{ij}^{\alpha\beta}$ = number of ${}_{ij}^{\alpha\beta}$ contacts
m = number of components in a mixture
n_i = number of moles of component i
P = pressure
q = surface parameter
Q = partition function
r = size parameter
R = gas constant
T = temperature
$u_{ij}^{\alpha\beta}$ = interaction energy of ${}_{ij}^{\alpha\beta}$ contact
V = volume
v_1 = molar volume of solvent
v_u = molar volume of monomer unit
z_i^α = number of α sites per segment of component i
z_i^β = number of β sites per segment of component i
z = coordination number

Greek letters

$\Gamma_{ij}^{\alpha\beta}$ = nonrandom factor for ${}_{ij}^{\alpha\beta}$ contact
θ_i = surface fraction of component i
θ_i^α = contact-site fraction for α sites on component i
θ_i^β = contact-site fraction for β sites on component i
θ_i^D = contact-site fraction for D sites on component i
μ_i = chemical potential of component i
ρ = crosslink density (fraction of monomer units engaged in a crosslink)
ρ_t = fraction of terminated polymer chains
ϕ_i = volume fraction of component i
$\omega_{ij}^{\alpha\beta}$ = exchange energy for a ${}_{ij}^{\alpha\beta}$ contact

Superscripts

^{o} = standard state
$^\alpha$ = hydrogen-bond donating site
$^\beta$ = hydrogen-bond accepting site
^{D} = dispersion-force interaction site

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Appendix I: Calculation of Swelling Equilibria in Solvent/Gel Systems

In an isothermal and isobaric system containing a crosslinked polymer in equilibrium with pure solvent, swelling equilibria must fulfill the equilibrium condition

$$\mu_1' = \mu_1'' \tag{A1}$$

where ′ and ″ denote the pure solvent phase and the gel phase, respectively; subscript 1 refers to the solvent.

As the gel phase is in equilibrium with pure solvent, we can rewrite the equilibrium condition

$$\mu_1'' - \mu_1^\circ = \Delta\mu_1'' = 0 \tag{A2}$$

Here superscirpt ° refers to the standard state which is the pure liquid at system temperature and pressure.

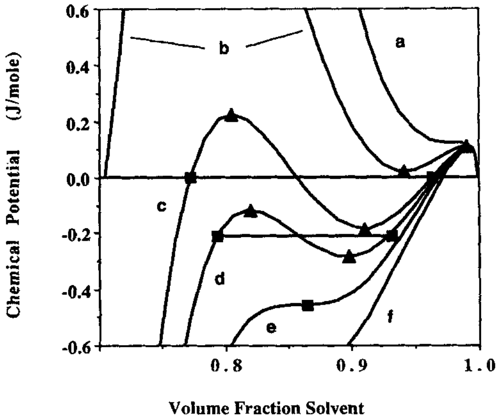
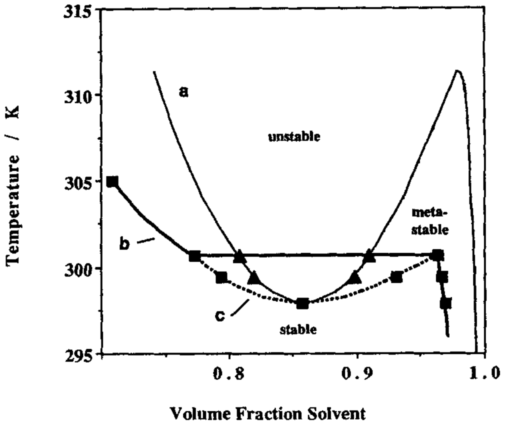


Figure A1. Isotherms of the chemical potential of the solvent ($\Delta\mu_1 = \mu_1 - \mu_1^\circ$) in a solvent/gel system for a gel showing a LCST: a) 311.3 K; b) 305 K; c) 300.6 K; d) 299.4 K; e) 297.2 K; and f) 295 K.

The phase transition temperature is 300.6 K [curve c]. The critical temperature is 297.2 K [curve e]. Squares represent calculated equilibrium compositions of coexisting gel phases. Triangles represent calculated limits of the stable region.



a) Spinodal curve for the coexistence of two gel phases
b) Coexistence curve for gel with pure solvent
c) Binodal curve for the coexistence of two gel phases

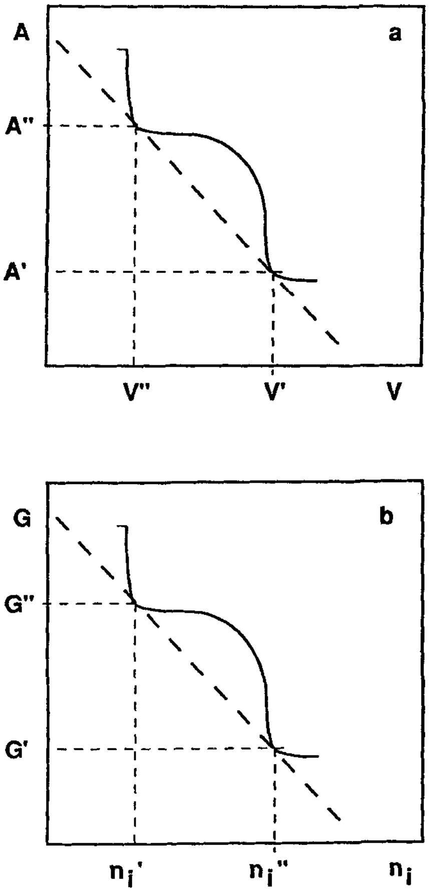
Figure A2. Phase diagram for a solvent/gel system that shows a LCST.

The squares represent calculated equilibrium compositions of coexisting gel phases. The triangles represent calculated limits of the stable region.

Figure A1 shows solvent chemical-potential isotherms for a gel/solvent system which exhibits a LCST, plotted vs. composition of gel phase. A distinguishing feature of phase equilibria for crosslinked polymers (gels) is an unstable region ($\partial\mu_1/\partial\phi_1 < 0$) at high concentration of solvent in the gel phase (high degree of

Table A1. Derivation of the Maxwell Condition for Equilibrium between Coexisting Phases ′ and ″ for a Pure Fluid and for a Binary Mixture

Pure Fluid	Binary Mixture
Equilibrium Conditions	
$P' = P''$	$\mu_i' = \mu_i''$, $i = 1$ or 2
$P = -\dfrac{\partial A}{\partial V}$	$\mu_i = \dfrac{\partial G}{\partial n_i}$
From Constructing the Common Tangents in a Plot of	
$A = f(V)$	$G = f(n_i)$, $i = 1$ or 2
Obtain New Equilibrium Conditions (Figure A3)	
$(A + PV)' = (A + PV)''$	$(G - \mu_i n_i)' = (G - \mu_i n_i)''$, $i = 1$ or 2
Forming the Total Differentials	
$d(A + PV) = -SdT + VdP$	$d(G - \mu_2 n_2) = -SdT + VdP$ $+ n_1 d\mu_1 - \mu_2 dn_2$
Integration Combined with Equilibrium Conditions Gives	
At constant T $(A + PV)' = (A + PV)''$ $= \int_{'}^{''} V dP = 0$	At constant T, P, n_2 $(G - \mu_2 n_2)' = (G - \mu_2 n_2)''$ $= \int_{'}^{''} n_1 \, d\mu_1 = 0$



a) Plot of Helmholtz energy v. volume in a pure fluid. The two coexisting phases ′ and ″ have to fulfill the equilibrium condition $P' = P''$ or $-[\partial A/\partial V]' = -[\partial A/\partial V]''$
b) Plot of Gibbs energy versus number of moles of component i in a mixture. The two coexisting phases ′ and ″ have to fulfill the equilibrium condition $\mu_i' = \mu_i''$ or $[\partial G/\partial n_i]' = [\partial G/\partial n_i]''$

Figure A3. Construction of the second step in Table A1.

swelling). This instability is caused by contributions of elastic forces to the chemical potential of the solvent which prevent the polymer from becoming completely soluble.

Figure A2 shows the coexistence and spinodal curves for the gel/solvent system. These curves can be obtained from the isotherms in Figure A1 by applying stability criteria and equilibrium conditions. The equilibrium composition of the gel phase is found from the solution of Eq. A2. At temperatures remote from the transition temperature T_t, Eq. A2 has only one root; only one gel phase can coexist with the pure solvent. Between T_c and T_s, however, we encounter a region where two gel phases can coexist with the solvent; T_s is the temperature at which the spinodal curve shows an extremum on the solvent-rich side (see Figure A2). Above this temperature only one gel phase can coexist with the solvent. Coexistence of two gel phases in equilibrium with pure solvent is encountered only in gels of those linear polymers that show partial miscibility with the solvent. The binodal curve for the coexistence of the two gel phases can be determined by applying the Maxwell condition to the chemical potential isotherms; in a solvent/gel system this condition is given by

$$\int_{\text{gel phase } S}^{\text{gel phase } C} \phi_1 \, d\Delta\mu_1'' = 0 \tag{A3}$$

Here S and C denote the swollen and the collapsed gel phases, respectively.

A general derivation of the Maxwell condition in a binary system is given in Table A1, augmented by Figure A3.

Points along the binodal curve are represented by squares in Figures A1 and A2. The triangles indicate points on the spinodal curve which represents the limit of stability. For a given pressure, the phase transition temperature is that temperature for which Eqs. A2 and A3 are satisfied. As the pressure changes, the phase transition can be shifted along the binodal curve until at some critical pressure, T_t and T_c coincide and the phase transition becomes continuous (Hirotsu, 1988; Lee et al., 1989). The critical point in a gel is analogous to the critical point of a pure solvent in the sense that at T_c discontinuous phase transitions become continuous.

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