CH.8 Polymers: Solutions, Blends, Membranes, and Gels

8.1 Properties of Polymers

Polymers are chain-like molecules.

- **Linear polymer**
- **Branched polymer**
- **Cross-linked polymer**

Polymers show little tendency to crystallize.

- **Semi-crystalline polymer**
  - **the extent of crystallinity in the range 30-80%**
  - **melts over a range of temperature 10-20 °C**
- **Amorphous polymer**
  - **The lower the temperature, the stiffer the polymers**
  - **Glass transition temperature T_g**
    - **(freezing without positional order, the second-order transition)**

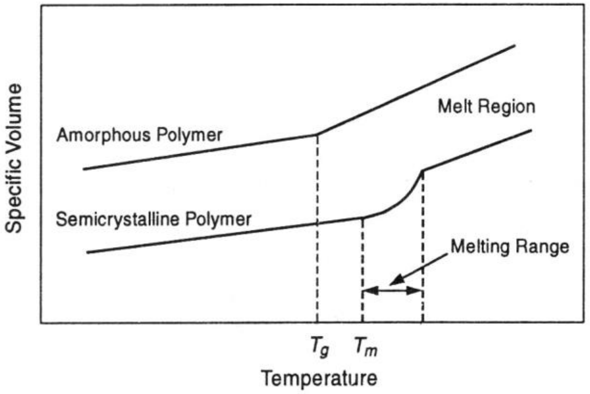

Figure 8-1 Schematic illustration of the variation of the specific volume of polymers with temperature.

At $T < T_g$, amorphous polymers are hard, stiff, glassy materials.

At $T > T_g$, amorphous polymers are in a rubbery or plastic state.

The formation of synthetic polymers is governed by random events, and thus the chains obtained vary in length.

The number average molecular weight is

$$\overline{M}_n = \frac{\sum N_i M_i}{\sum N_i} \qquad (8\text{-}1)$$

The number average molecular weight is

$$\overline{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} \qquad (8\text{-}2)$$

$$\overline{M}_w > \overline{M}_n$$

Polydispersity (or heterogeneity index)

$\overline{M}_w / \overline{M}_n$ **in the range 1.5 ~ 2.0 for many polymers**

8.2 Lattice Models: The Flory-Huggins Theory

We consider athermal solutions consisting of solvent and polymer.
Thermodynamic mixing properties is written as the sum of two parts:
(1) Combinatorial contribution (Entropy change)
(2) Residual contribution due to differences in intermolecular forces and in free volume

For the entropy of mixing

$$\Delta_{\text{mix}} S = \Delta S^C + S^R \qquad (8\text{-}3)$$

The combinatorial entropy of mixing was independently derived by Flory and by Huggins for flexible chains.

Consider a mixture of two liquids 1 and 2.
N_1 molecules of type 1 (solvent) are single spheres.
N_2 molecules of type 2 (polymer) are flexible chains consisting of r segments, each having the same size as that of a solvent molecule.
Flory and Huggins showed that if the amorphous polymer and the solvent in athermal condition, the change in Gibbs energy and entropy of mixing is given by

$$\boxed{-\frac{\Delta G^C}{RT} = \frac{\Delta S^C}{R} = -(N_1 \ln \Phi_1^* + N_2 \ln \Phi_2^*)} \qquad (8\text{-}5)$$

where

$$\Phi_1^* = \frac{N_1}{N_1 + rN_2} \quad \text{and} \quad \Phi_2^* = \frac{N_2}{N_1 + rN_2} \qquad (8\text{-}4)$$

(Derivation)

Assumptions

- **No vacant sites**
- **Each polymer molecule occupies *r* consequent sites**
- **Solvent molecule occupies a single site**
- **Total number of sites $M = N_1 + r N_2$**

Configurational degeneracy Ω: the number of possible arrangements

$$S = k \ln \Omega(N_1, N_2)$$

Entropy change of mixing is

$$\Delta_{mix} S = k \ln \frac{\Omega(N_1, N_2)}{\Omega(N_1, 0)\Omega(0, N_2)}$$

$\Omega(N_1, 0) = 1$ **for pure solvent**

$\Omega(0, N_2)$ **for pure polymer**

$$\Omega(N_1, N_2) = \frac{1}{N_2!}\prod_{i=1}^{N_2} \omega_i$$

where ω_i is the number of ways of placing *i*-th polymer provided that the previous *i*–1 polymers are already placed.

N_2! is taken into account because polymers are indistinguishable.

To obtain ω_{i+1}

Let the fraction of sites occupied at present $f_i = \dfrac{r\,i}{M}$

No. ways of placing 1st segment: $M - r\,i$

No. ways of placing 2nd segment: $z(1 - f_i)$

No. ways of placing 3rd segment: $(z-1)(1 - f_i)$

No. ways of placing 4th segment: $(z-1)(1-f_i)$

Thus

$$\omega_{i+1} = (M - r\,i)z(z-1)^{r-2}(1-f_i)^{r-1} = (M-ri)(z-1)^{r-1}\left(\frac{M-ri}{M}\right)^{r-1}$$

$$= (M - r\,i)^{r}\left(\frac{z-1}{M}\right)^{r-1}$$

$$\ln\prod_{i=1}^{N_2}\omega_i = \ln\prod_{i=1}^{N_2}\left(M - r\,(i-1)\right)^{r}\left(\frac{z-1}{M}\right)^{r-1}$$

$$= N_2(r-1)\ln\left(\frac{z-1}{M}\right) + r\sum_{i=0}^{N_2-1}\ln(M - r\,i)$$

$$\sum_{i=0}^{N_2-1}\ln(M - r\,i) \cong \int_0^{N_2}\ln(M - r\,i)di = -\frac{1}{r}\int_M^{M-rN_2}\ln u\,du = \frac{1}{r}\int_{N_1}^{M}\ln u\,du = \frac{1}{r}\left[u\ln u - u\right]_{N_1}^{M}$$

$$= \frac{1}{r}\left(M\ln M - M - N_1\ln N_1 + N_1\right)$$

Substituting

$$\ln\Omega(N_1, N_2) = \ln\frac{1}{N_2!}\prod_{i=1}^{N_2}\omega_i = -N_2\ln N_2 + N_2 + \ln\prod_{i=1}^{N_2}\omega_i$$

$$= -N_2\ln N_2 + N_2 + M\ln M - M - N_1\ln N_1 + N_1 + N_2(r-1)\ln\left(\frac{z-1}{M}\right)$$

for pure polymer $M = rN_2$

$$\ln\Omega(0,N_2)=-N_2\ln N_2+N_2+rN_2\ln rN_2-rN_2+N_2(r-1)\ln\left(\frac{z-1}{rN_2}\right)$$

Entropy change of mixing is

$$\Delta_{mix}S/k=\ln\frac{\Omega(N_1,N_2)}{\Omega(N_1,0)\Omega(0,N_2)}=\ln\Omega(N_1,N_2)-\ln\Omega(0,N_2)$$

$$=-N_1\ln\frac{N_1}{N_1+rN_2}-N_2\ln\frac{rN_2}{N_1+rN_2}$$

For the special case of $r = 1$, (8-5) reduces to

$$\boxed{\frac{\Delta_{\text{mix}} s}{R} = -\frac{1}{R}\left(\frac{\partial \Delta_{\text{mix}} a}{\partial T}\right)_v = -x_1 \ln x_1 - x_2 \ln x_2} \qquad (7\text{-}80)$$

(ideal entropy of mixing)

Eq (8-5) always gives a combinatorial entropy larger than Eq (7-80).

Various modifications have been suggested by Huggins, Guggenheim, Staverman, Tompa, and Lichtenthaler.

The excess entropy per mole of mixture is

$$\frac{s^E}{R} = -x_1 \ln\left[1 - \Phi_2^*\left(1 - \frac{1}{r}\right)\right] - x_2 \ln\left[r - \Phi_2^*(r-1)\right] \qquad (8\text{-}6)$$

S^E is positive for all $r > 1$. Therefore, the Flory-Huggins theory predicts negative deviation from Raoult's law:

$$\frac{g^E}{RT} = \frac{h^E}{RT} - \frac{s^E}{R} = 0 - \frac{s^E}{R} < 0 \qquad (8\text{-}7)$$

The activity of solvent is

$$\boxed{\ln a_1 = \ln(1 - \Phi_2^*) + \left(1 - \frac{1}{r}\right)\Phi_2^*} \qquad (8\text{-}8)$$

The activity coefficient of solvent based on mole fractions is

$$\boxed{\ln \gamma_1 = \ln\left[1 - \left(1 - \frac{1}{r}\right)\Phi_2^*\right] + \left(1 - \frac{1}{r}\right)\Phi_2^*} \qquad (8\text{-}9)$$

The activity coefficient of solvent

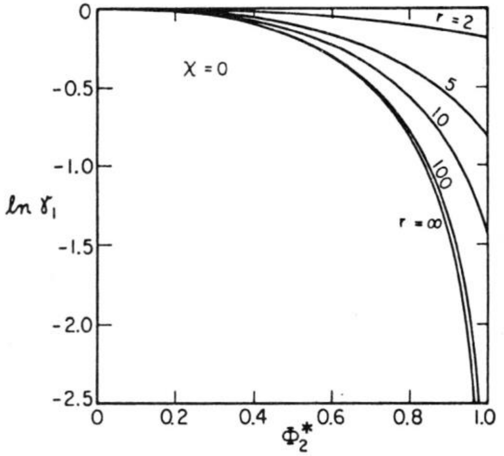

Figure 8-3 Solvent activity coefficient in an athermal polymer solution according to the equation of Flory and Huggins. Parameter *r* gives the number of segments in the polymer molecule.

The solvent activity coefficient γ_1 is a strong function of *r* for small values, But for *r* > 100, it is essentially independent of *r*.

For real polymer solutions, we add a term given by the enthalpy of mixing similar as in the regular solution theory.

$$\frac{\Delta_{\text{mix}}G}{RT} = \frac{\Delta G^C}{RT} + \frac{G^R}{RT} = N_1 \ln \Phi_1^* + N_2 \ln \Phi_2^* + \chi \Phi_1^* \Phi_2^* (N_1 + rN_2) \qquad (8\text{-}10)$$

where χ is the Flory-Huggins interaction parameter (dimensionless).

c.f.) the enthalpy of mixing from the regular solution theory

$$u^E = (c_{11} + c_{22} - 2c_{12})\Phi_1\Phi_2(x_1v_1 + x_2v_2) \qquad (7\text{-}30)$$

The activity of solvent and the corresponding activity coefficient of solvent based on mole fractions are

$$\boxed{\ln a_1 = \ln(1-\Phi_2^*) + \left(1-\frac{1}{r}\right)\Phi_2^* + \chi\Phi_2^{*2}} \qquad (8\text{-}11)$$

$$\boxed{\ln\gamma_1 = \ln\left[1-\left(1-\frac{1}{r}\right)\Phi_2^*\right] + \left(1-\frac{1}{r}\right)\Phi_2^* + \chi\Phi_2^{*2}} \qquad (8\text{-}12)$$

The parameter χ is assumed to be independent of composition. In terms of the interchange energy,

$$\chi = \frac{w}{kT} \qquad (8\text{-}13)$$

> 0 for nonpolar systems

recalling that

$$\frac{a^E}{RT} = \frac{w}{kT}x_1x_2 \qquad (7\text{-}79)$$

Assuming *w* is constant, Flory parameter χ is inversely proportional to temperature.

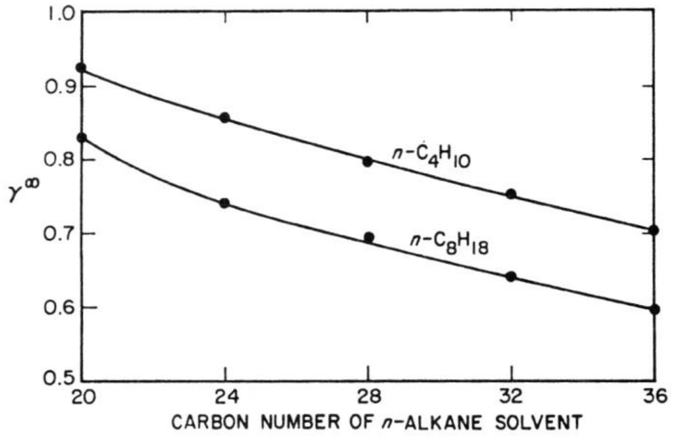

Figure 8-5 Activity coefficients at infinite dilution for *n*-butane and *n*-octane in *n*-alkane solvents near 100°C. Negative deviations from Raoult's law are due to the difference in molecular size.

χ is small as the components are chemically similar. The negative deviations from ideal-solution behavior are mainly from differences in molecular size.

Another example

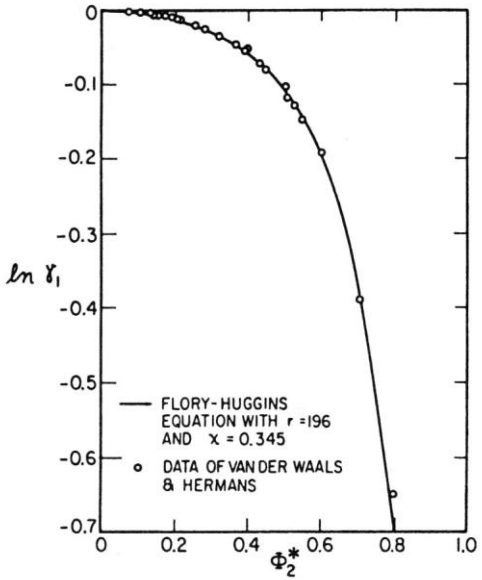

Figure 8-6 Activity coefficients of heptane in the *n*-heptane (1)/polyethylene (2) system at 109°C.

Experimental determination of χ parameter using Eq (8-11)

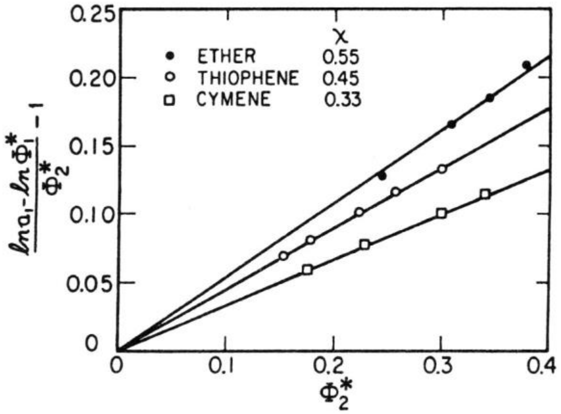

Figure 8-7 Data reduction using the equation of Flory and Huggins. Data are for solutions of rubber near room temperature. Interaction parameters χ are given by the slopes of the lines.

But for many other systems, χ varies with polymer concentration!

Calorimetric enthalpy-of-mixing often give a value of χ significantly different from that obtained from activities.

The temperature dependence of χ is not a simple proportionality to inverse temperature.

Connection with Scatchard-Hildebrand (regular solution) theory

In terms of solubility parameter, χ is given by

$$\chi = \frac{v_1}{RT}(\delta_1 - \delta_2)^2 \qquad (8\text{-}14)$$

where v_1 is the molar volume of the solvent, and δ_1 are δ_2 the solubility parameters of solvent and polymer.

Not an accurate description, but a good guide for a qualitative consideration of polymer solubility.

A criterion of a good solvent for a given polymer is

$$\delta_1 \approx \delta_2 \qquad (8\text{-}15)$$

Table 8-1 Solubility parameters for some amorphous polymers near 25°C (Grulke, 1989

Polymer	δ (J cm^{-3})$^{1/2}$
Teflon	12.7
Poly(dimethyl siloxane)	14.9
Polyethylene	16.2
Polyisobutylene	16.4
Polybutadiene	17.4
Polystyrene	18.6
Poly(methyl methacrylate)	19.4
Poly(vinyl chloride)	19.8
Cellulose diacetate	22.3
Poly(vinylidene chloride)	25.0
Polyacrylonitrile	25.3

For example, polyisobutylene (δ=16.8) should be readily soluble in cyclohexane (δ=16.4), but only sparingly soluble in carbon disulfide (δ=20.5)

Liquid-liquid equilibria

Flory-Huggins theory can represent partial miscibility of polymer/solvent systems at low temperatures.

From the stability analysis (sec. 6.12)

$$\left(\frac{\partial^2 \Delta_{\text{mix}} g}{\partial x^2}\right)_{T,P} < 0 \qquad \text{(6-129)}$$

condition for instability

The condition for complete miscibility for polymer solution is given by

$$\chi \le \frac{1}{2}\left(1 + \frac{1}{\sqrt{r}}\right)^2 \qquad \text{(8-16)}$$

At critical condition (UCST)

$$\chi^c = \frac{1}{2}\left(1 + \frac{1}{\sqrt{r}}\right)^2$$

As $r \to \infty$**,** $\chi^c = \frac{1}{2}$ *and* $\Phi_2^{*c} \to 0$ **c.f.) when** $r = 1$**,** $\chi^c = 2$ *and* $\Phi_2^{*c} = x_2 = 0.5$ **(sec. 7.6)**

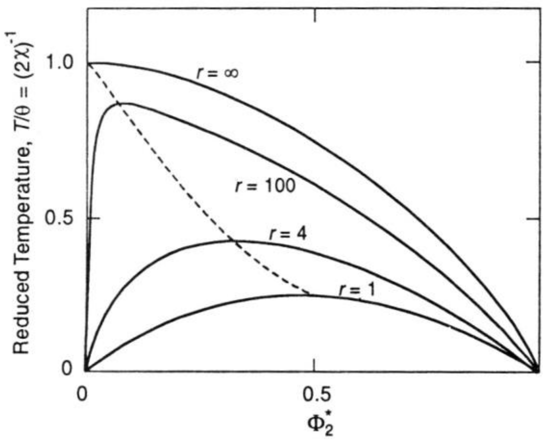

Figure 8-8 Calculated phase diagrams (cloud-point curves) for a binary mixture according to the Flory-Huggins theory. The dotted line shows the locus of upper critical solution temperatures.

θ temperature: the limiting UCST for a polymer of infinite molecular weight

As χ is inversely proportional to temperature,

$$\frac{\chi(T)}{\chi^{c}(T=\theta)} = 2\chi(T) = \frac{\theta}{T} \qquad (8\text{-}18)^{15}$$

Measured θ temperature for a polymer/solvent system gives χ(T)

LCST of polymer/solvent systems

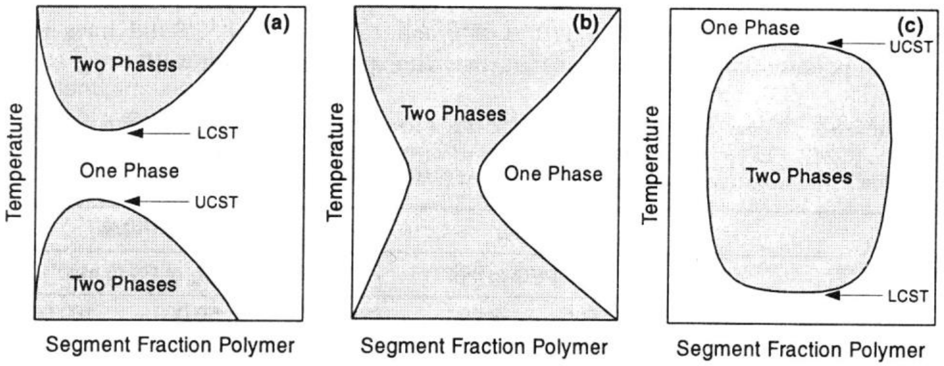

Figure 8-9 Schematic representation of phase stability in three binary polymer solutions. (a) UCST is below LCST; (b) hourglass; (c) closed loop, where LCST is below UCST.

The empirically extended Flory-Huggins model can represent these complicated phase behaviors but with no theoretical basis.

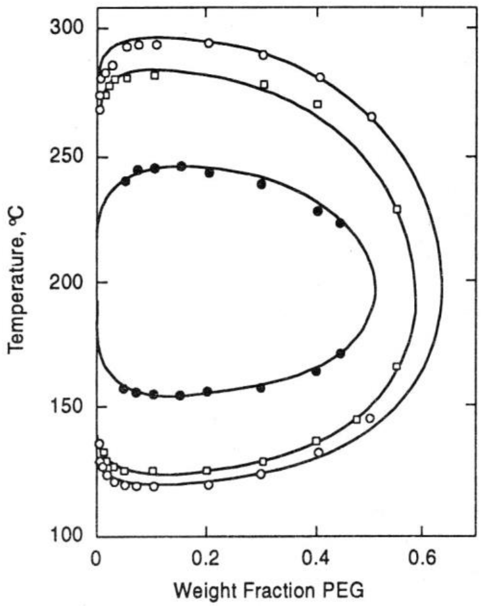

Figure 8-10 Phase diagrams for three PEG/water systems showing cl
temperatures as functions of PEG weight fractions. The molecular weigh
3,350 g mol^{-1} (●); 8,000 g mol^{-1} (□), and 15,000 g mol^{-1} (○). Solid lines
(Bae *et al.*, 1993).

$\chi(T,\Phi)$

8.3 Equation of State for Polymer Solutions

Prigogine-Flory-Patterson theory

A statistical-thermodynamic model

$$Q(T,V,N) = \frac{1}{N!}\left(\frac{V_f}{\Lambda^3}\right)^N [q_{\text{ext}}(V)]^N [q_{\text{int}}(T)]^N \left[\exp\left(\frac{-E_o}{2kT}\right)\right]^N \tag{8-39}$$

$$\frac{V_f}{\Lambda^3} q_{\text{ext}} = \left(\frac{V_f}{\Lambda^3}\right)^{rc} \qquad \text{for } rc \geq 1 \tag{8-40}$$

It uses Prigogine's suggestion for external degrees of freedom although this approximation is incorrect at low densities.

Equation of state in reduced form is given by

$$\boxed{\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{\tilde{v}^{1/3}}{\tilde{v}^{1/3}-1} - \frac{1}{\tilde{v}\tilde{T}}} \tag{8-45}$$

The residual part of the activity of solvent is

$$\begin{aligned}(\ln a_1)^R = \frac{(\mu_1-\mu_1^0)^R}{RT} = \frac{\Delta\mu^R}{RT} &= \frac{P_1^* V_1^*}{RT}\left[3\tilde{T}_1 \ln\frac{\tilde{v}_1^{1/3}-1}{\tilde{v}^{1/3}-1} + (\tilde{v}_1^{-1} - \tilde{v}^{-1})\right] \\ &+ \frac{V_1^*}{RT}\left(\frac{X_{12}}{\tilde{v}}\right)\theta_2^2 + \frac{P}{RT}\left(\frac{\partial \Delta_{\text{mix}} V}{\partial N_1}\right)_{T,P,N_2}\end{aligned} \tag{8-74}$$

Comparing with the Flory-Huggins theory

$$(\ln a_1)^R = \chi \Phi_2^{*2} \tag{8-75}$$

$$\chi \equiv \frac{\Delta\mu_1^R}{RT\Phi_2^{*2}} \qquad (8\text{-}76)$$

χ is identified as the reduced residual chemical potential.

χ now varies with composition, as found experimentally.

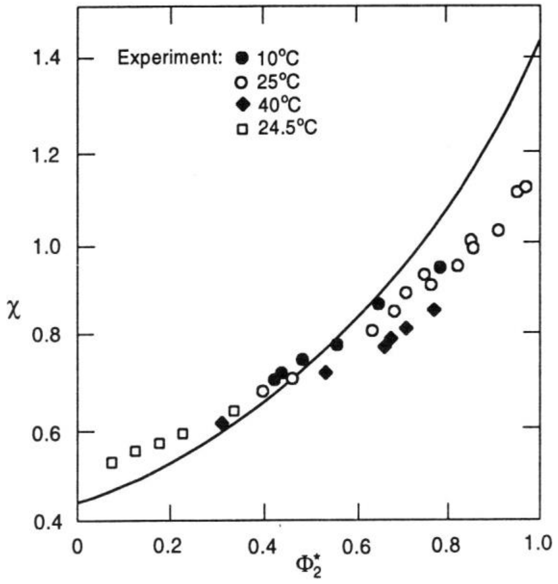

Figure 8-13 Reduced residual chemical potential χ [Eq. (8-76)] of benzene (1) in polyisobutylene (2) at 25°C. Solid curve calculated from Eq. (8-74) with $s_2/s_1 = 0.58$ and $X_{12} = 41.8$ J cm^{-3} (Eichinger and Flory, 1968). The experimental χ was obtained from solvent-activity data using Eq. (8-11).

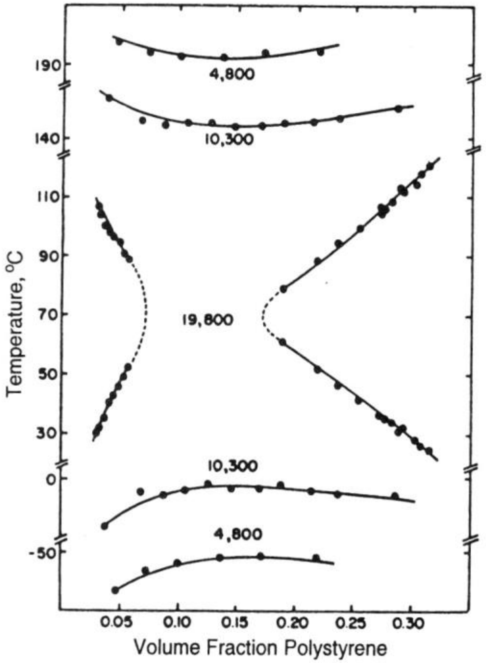

Figure 8-17 Phase diagram (temperature-volume fraction) for the polystyrene/acetone system for indicated polymer weight-average molecular weight (Siow *et al.*, 1972).

The Prigogine-Flory-Patterson EOS should be used in liquid-like density as it does not reduce to the equation of state for an ideal gas.

Lattice-Fluid Theory

Sanchez and Lacombe included empty lattice sites (holes) to account for volume changes on mixing.

For a pure component, the total number of lattice sites is

$$N_r = N_0 + rN \qquad (8\text{-}78)$$

where N_0 is the number of vacancies, N the number of molecules each with r segments.
The total volume of the system is

$$V = (N_0 + rN)v^* \qquad (8\text{-}79)$$

where v^* is the volume of a segment, equal to the volume of a lattice site.
The reduced density and the reduced volume are defined as

$$\tilde{\rho} = \frac{1}{\tilde{v}} = \rho v^* = \frac{v^*}{v} = \frac{rN}{N_0 + rN} \qquad (8\text{-}80)$$

where $\rho = Nr / V$ is the density of segments, $v = V / Nr$

The energy of the lattice is contributed by nearest-neighbor interactions. Assuming random mixing of vacancies and segments

$$E = -\frac{z}{2} N_r \varepsilon \left(\frac{rN}{N_0 + rN} \right)^2 = -N_r \tilde{\rho}^2 \frac{z\varepsilon}{2} \qquad (8\text{-}81)$$

$$= \frac{1}{2}(-\varepsilon) z N_r \left(\frac{rN}{N_0 + rN} \right)$$

The configurational partition function is

$$Q = Q^C \exp(-E / kT) \qquad (8\text{-}82)$$

$$Q^C = (\text{constant})^N \frac{(N_0 + rN)!}{N_0!N!} \frac{1}{(N_0 + rN)^{N(r-1)}} \qquad (8\text{-}83)$$

The combinatorial factor Q^c is identical to the Flory-Huggins theory, but with the solvent replaced by a vacancy. Therefore, Q^c contributes to the equation of state.

Differentiating the partition function with respect to volume gives the Sanchez-Lacombe lattice-fluid equation of state.

$$\boxed{\frac{\tilde{P}\tilde{v}}{\tilde{T}} = \frac{1}{r} - \left[1 + \tilde{v}\ln\left(1 - \frac{1}{\tilde{v}}\right)\right] - \frac{1}{\tilde{v}\tilde{T}}} \qquad (8\text{-}84)$$

where the reduced(~) and characteristic (*) temperature are

$$\tilde{P} = \frac{P}{P^*} = \frac{P}{z\varepsilon / 2v^*} \qquad \tilde{T} = \frac{T}{T^*} = \frac{T}{z\varepsilon / 2k}$$

$$P^* v^* = kT^*$$

A real fluid is characterized by three parameters, $z\varepsilon$, v^* and r.

For polymer, the 1/*r* term becomes insignificant, and Eq (8-84) suggests a corresponding-state behavior in the limit $r \to \infty$

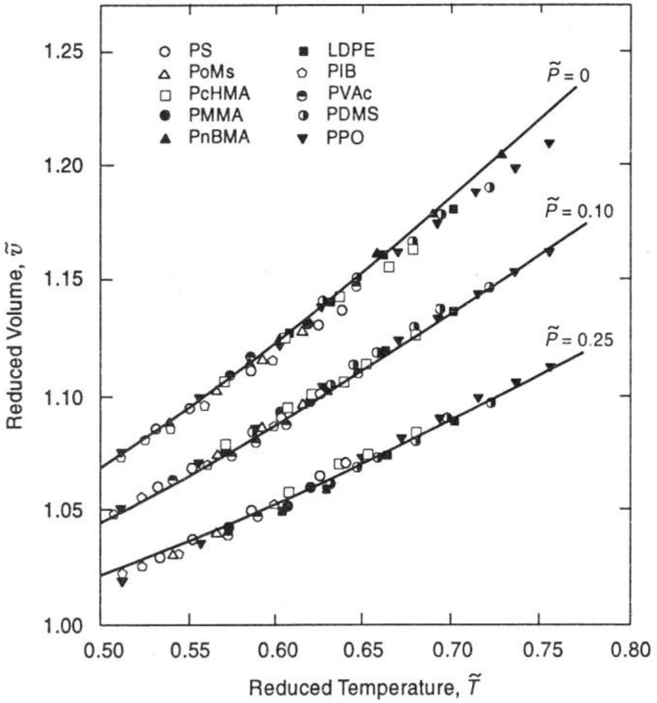

Figure 8-21 Corresponding-states behavior of polymer *P*-*V*-*T* data according to the Sanchez-Lacombe equation of state Points are experimental data and lines are calculated from Eq. (8-84) in the limit $r \to \infty$. PS, polystyrene; PoMS, poly(*o*-methyl styrene); PcHMA, poly(cyclohexyl methacrylate); PMMA, poly(methyl methacrylate); PnBMA, poly(*n*-butyl methacrylate); LDPE, low-density polyethylene; PIB, polyisobutylene; PVAc, poly(vinyl acetate); PDMS, poly(dimethyl siloxane); PPO, poly(propylene oxide) (Sanchez and Lacombe, 1978).

$\tilde{P} \approx 0$ **for atmospheric pressure**

$\tilde{P} = 0.25$ **is a pressure of the order 1,000 bar.**

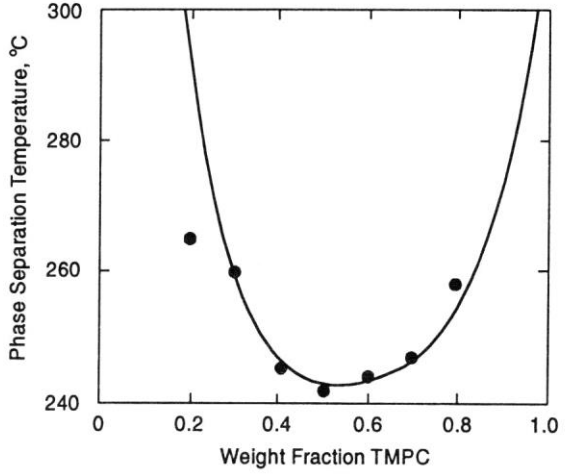

Figure 8-23 Comparison of experimental phase separation temperatures (●) obtained by differential scanning calorimetry with the spinodal curve (——) predicted by the lattice-fluid model (Kim and Paul, 1992).

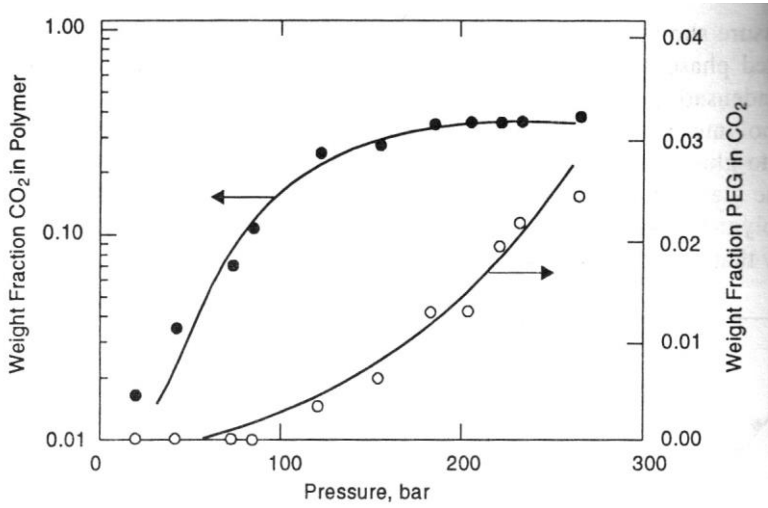

Figure 8-26 Compositions of coexisting phases for PEG/supercritical CO_2 mixtures at 323 K as a function of pressure. —— Calculated from the Panayiotou-Vera version of the lattice-fluid equation of state; ●, ○ experiment (Daneshvar *et al.*, 1990).

SAFT

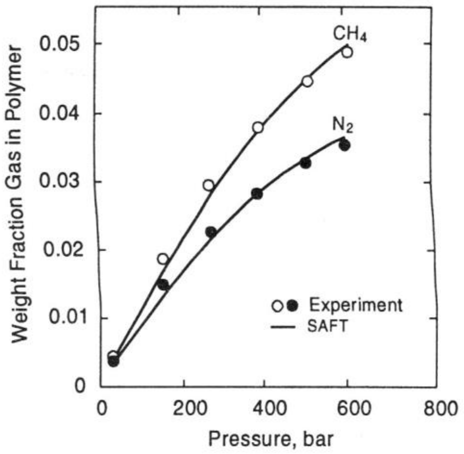

Figure 8-27 Solubilities of methane and nitrogen in polyethylene at 461.4 K. ●, ○ experiment. —— Calculated from SAFT equation of state. The binary parameter is calculated from a temperature-dependent correlation (Wu and Chen, 1994).

8.4 Nonporous Polymeric Membranes and Polymer Gels

[Nonporous Membranes]

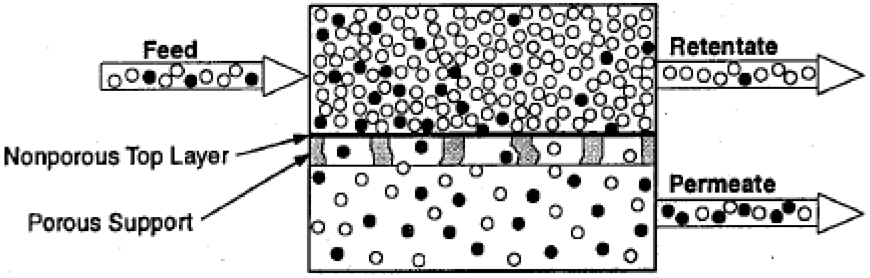

Figure 8-31 Schematic representation of a membrane-separation process using a composite membrane with a thin dense nonporous top layer and a thick porous support layer.

The driving force for any permeating component i = μ_i(feed) – μ_i(permeate)

The chemical potential of a liquid mixture in equilibrium with its vapor

$$\mu_i^G = \mu_i^{0G} + RT\ln(\varphi_i P_i) = \mu_i^L = \mu_i^{0L} + RT\ln(\gamma_i^L x_i^L) \qquad (8\text{-}99)$$

μ_i^{0G} = the st-st (1bar) chemical potential of the pure gas

φ_i = the fugacity coefficient

P_i = partial pressure

μ_i0L = the chemical potential of the pure liquid

at the same temp. and press. as those of the mixture.

γ_i^L = the activity coefficient

x_i^L = the mole fraction of i in the liquid mixture

The liquid mixture in equilibrium with the swollen polymer

$$\mu_i^L = \mu_i^M \qquad (8\text{-}100)$$

$$\mu_i^M = \mu_i^{0M} + RT\ln(\gamma_i^M x_i^M) \qquad (8\text{-}101)$$

where superscript M indicates the membrane phase.

At st-st chemical potential of the liquid phase and the membrane phase are identical.

$$\gamma_i^L x_i^L = \gamma_i^M x_i^M \qquad (8\text{-}102)$$

Eq. (8-102) rewrite as follow, (use molar concentration c_i^M)

$$\gamma_i^L x_i^L = \gamma_i^{c,M} c_i^M \qquad (8\text{-}103)$$

$$\boxed{c_i^M = \frac{\gamma_i^L}{\gamma_i^{c,M}} x_i^L = S_i^L x_i^L} \qquad (8\text{-}104)$$

where S_i^L = the liquid solubility coefficient of component i

Phase equilibrium between the gaseous (vapor) phase and the membrane phase.

$$\mu_i^G = \mu_i^M \qquad (8\text{-}105)$$

from Eqs. (8-99) and (8-103) we obtain

$$\mu_i^{0G} + RT\ln(\varphi_i P_i) = \mu_i^{0M} + RT\ln(\gamma_i^{c,M} c_i^M) \qquad (8\text{-}106)$$

or

$$\gamma_i^{c,M} c_i^M = P_i \varphi_i \exp\left(\frac{\mu_i^{0G} - \mu_i^{0M}}{RT}\right) \qquad (8\text{-}107)$$

or

$$\boxed{c_i^M = S_i^G P_i} \qquad (8\text{-}108)$$

where the gas solubility coefficient of component is

$$S_i^G = \frac{\varphi_i}{\gamma_i^{c,M}} \exp\left(\frac{\mu_i^{0G} - \mu_i^{0M}}{RT}\right) \qquad (8\text{-}109)$$

This equation is useful for the description of transmembrane fluxes of the solution-diffusion model.

In this model, the transport of each component i is divide into three steps.

1. **The components of the liquid or gaseous feed mixture are absorbed in the membrane. There is thermodynamic solubility equilibrium at the phase boundary.**
2. **The absorbed components diffuse across the membrane from the feed side to the permeate side according to Fick’s first law of diffusion.**
3. **The components are desorbed at the phase boundary between the membrane and the liquid or gaseous permeate.**

The case of pervaporation.

Inside the membrane, flux J_i of component i is given by Fick's law,

$$J_i = -D_i \frac{dc_i^M}{d\ell} \qquad (8\text{-}110)$$

where D_i = the diffusion coefficient, and l = the length coordinate perpendicular to the top layer of the membrane with thickness $\delta_M (0 \le l \le \delta_M)$.

Integration of Eq.(8-110) (Heinz and Stephan, 1994) gives

$$J_i = \frac{D_i}{\delta_M}(c_{iF}^M - c_{iP}^M) \qquad (8\text{-}111)$$

where c_{iF}^M and c_{iP}^M are the concentration in the membrane boundaries at the feed side(index F) and the permeate side(index P), respectively.

The solubility equilibrium conditions at both phase boundaries justifies substitution of c_{iF}^M from Eq. (8-104) and c_{iP}^M from Eq.(8-108) into Eq. (8-111).

$$\boxed{J_i = \frac{D_i}{\delta_M}(S_i^L x_i^L - S_i^G P_i)} \qquad (8\text{-}112)$$

At steady state, the mole fraction y_i of the gaseous permeate is obtained from

$$\frac{J_i}{\sum_i J_i} = \frac{P_i}{\sum_i P_i} = y_i \qquad (8\text{-}113)$$

For binary mixture, substitution of Eq.(8-112) into (8-113) gives

$$y_1 = \frac{P_1}{P_1 + P_2} = \frac{D_1(S_1^L x_1^L - S_1^G P_1)}{D_1(S_1^L x_1^L - S_1^G P_1) + D_2(S_2^L x_2^L - S_2^G P_2)} \qquad (8\text{-}114)$$

If the pressure P in the permeate side is about P ≈ 0, Eq.(8-114) then simplifies to

$$y_1 = \frac{D_1 S_1^L x_1^L}{D_1 S_1^L x_1^L + D_2 S_2^L x_2^L} \qquad (8\text{-}115)$$

A plot of the permeate mole fraction y_1 against L-L feed mole fraction x_1^L is called a separation diagram.

The separation factor is defined as follow.

$$\alpha \equiv \frac{x_1^L / y_1}{x_2^L / y_2} \qquad (8\text{-}116)$$

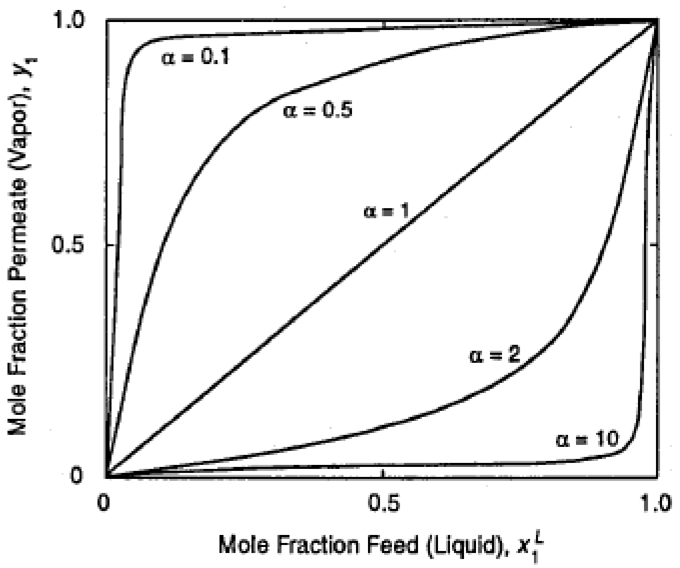

Figure 8-32 Separation diagram in pervaporation calculated from Eq. (8-115) for different values of the separation factor α.

α > 1, component 2 is enriched in the permeate.

α = 1, no separation effect is observed.

α < 1, component 1 is enriched in the permeate.

In gas separation, the flux Ji inside the membrane is also given by Eq.(8-111), with C_{iF}^{M} and C_{iP}^{M} from Eq. (8-108);

$$J_i = \frac{D_i}{\delta_M}(S_{iF}^{G} P_{iF} - S_{iP}^{G} P_{iP}) \qquad (8\text{-}118)$$

where P_{iF} and P_{iP} are the partial pressure of component i in the pressurized gaseous feed mixture(index F) and in the permeate mixture(index P), respectively.

Assume that, $S_{iF}^{G} \approx S_{iP}^{G} = S_{i}^{G}$, Eq. (8-118) simplifies to

$$\boxed{J_i = \frac{D_i S_i^G}{\delta_M}(P_{iF} - P_{iP})} \qquad (8\text{-}119)$$

At binary mixture, ($P_{iP} << P_{iF}$),

$$y_1 = \frac{D_1 S_1^G P_{1F}}{D_1 S_1^G P_{1F} + D_2 S_2^G P_{2F}} \qquad (8\text{-}120)$$

The separation factor is

$$\alpha \equiv \frac{D_2 S_2^G}{D_1 S_1^G} \qquad (8\text{-}121)$$

The case of reverse osmosis

The high pressures are applied to the liquid feed side, so the pressure dependence add in the chemical potential.

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,x} = \bar{v}_i \qquad (8\text{-}122)$$

where $\bar{v}_i$ = the partial molar volume of component i in the mixture.

Integration of Eq.(8-122) from the standard pressure(P^0 = 1bar) to P_F and assuming that $\bar{v}_i$ is independent pressure.

$$\begin{aligned} \mu_{iF}^L &= \mu_{iF}^L(P^0 = 1\ \text{bar}) + \bar{v}_{iF}(P_F - P^0) \\ &= \mu_{iF}^{0L} + RT\ln(\gamma_{iF}^L x_{iF}^L) + \bar{v}_{iF}(P_F - P^0) \end{aligned} \qquad (8\text{-}123)$$

The chemical potential of membrane,

$$\mu_i^M = \mu_i^{0M} + RT\ln(\gamma_i^{c,M} c_i^M) + \bar{v}_i^M(P_F - P^0) \qquad (8\text{-}124)$$

In reverse osmosis, equality of the chemical potentials requires

$$RT\ln(\gamma_i^{c,M} c_i^M) + \bar{v}_i^M(P_F - P^0) = RT\ln(\gamma_{iP}^L x_{iP}^L) + \bar{v}_i(P_P - P^0) \qquad (8\text{-}125)$$

or

$$\gamma_{iP}^L x_{iP}^L \exp\left[-\frac{\bar{v}_i(P_F - P_P)}{RT}\right] = \gamma_i^{c,M} c_i^M \qquad (8\text{-}126)$$

where P_P is the pressure in the liquid permeate (usually 1bar) and subscript P denotes the permeate. Again, assuming that Fick's law is valid inside the membrane,

$$J_i = \frac{D_{iM}}{\delta_M}(c_{iF}^M - c_{iP}^M) = \frac{D_{iM}}{\delta_M}\{S_{iF}^L x_{iL}^L - S_{iP}^L x_{iP}^L \exp[-\overline{\upsilon}_i(P_F - P_P)/RT]\} \qquad (8\text{-}127)$$

If $S_{iF}^L \approx S_{iP}^L = S_i^L$,

$$J_i = \frac{D_{iM} S_i^L}{\delta_M}\{x_{iF}^L - x_{iP}^L \exp[-\overline{\upsilon}_i(P_F - P_P)/RT]\} \qquad (8\text{-}128)$$

Reverse osmosis is applied mostly to dilute aqueous solutions. For solvent water, assuming that $\overline{v_i} \approx v_w$ Eq. (8-128) can be rewritten as

$$\boxed{J_w = \frac{D_w}{\delta_M} S_w^L x_{wF}^L \{1 - \exp[-\upsilon_w(P_F - P_P - \Delta\pi)/RT]\}} \qquad (8\text{-}130)$$

where $\Delta\pi$ is given by

$$\Delta\pi = \frac{RT}{\upsilon_w} \ln \frac{x_{wP}^L}{x_{wF}^L} \qquad (8\text{-}131)$$

- **$(P_F - P_P) > \Delta\pi$, $J_w > 0$**
- **$(P_F - P_P) = \Delta\pi$, $J_w = 0$**
- **$(P_F - P_P) < \Delta\pi$, $J_w < 0$**

<u>The binary mixture outside the membrane</u>.

Vapor sorption and the solubilities of liquids and liquids mixtures can be described well with the UNIQUAC model.

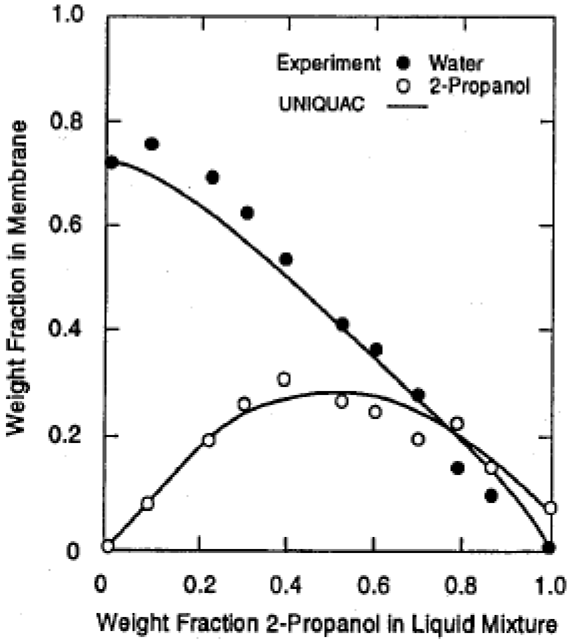

Figure 8-34 Experimental and calculated solubilities for the 2-propanol/water mixture in cross-linked poly(vinyl alcohol) at 333 K. (Heintz and Stephan, 1994). Calculations based on binary data only.

The solubility curve for 2-propanol has a maximum, indicating a higher solubility for propanol in the mixture than for pure alcohol. Synergistic solubility effects are evident.

The mixture 2-propanol/water with the poly(vinyl alcohol) membrane (VLE) system.

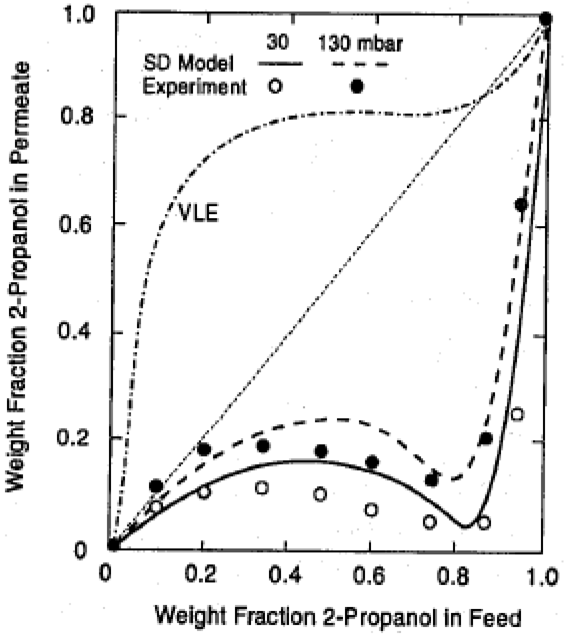

Figure 8-35 Separation diagram for the system 2-propanol/water/poly(vinyl alcohol) at 333 K. ○, ● Pervaporation data (Wesslein *et al.*, 1990) at two permeate pressures; ——, – – – extended solution-diffusion (SD) model (Heintz and Stephan, 1994); – · – · – vapor-liquid equilibrium (VLE) for 2-propanol/water.

- **These data are calculated from UNIQUAC, and using the Maxwell-Stefan theory to account for coupling of the diffusion of the two components.**
- **Water can be removed with high selectivity at fee weight fractions of 0.8-0.9. Within this composition range, the VLE curve shows the azeotropic point, i.e. pervaporation is effective where distillation is not.**
- **The lower permeate pressure increase the selectivity for water.**

[Polymer Gels]

Polymer gels are three-dimensional elastic-network materials. The heterogeneous system containing a gel consist of three different homogeneous phase.

- **The fluid surrounding the gel.**
- **The elastic structure forming the gel.**
- **The fluid inside the gel.**

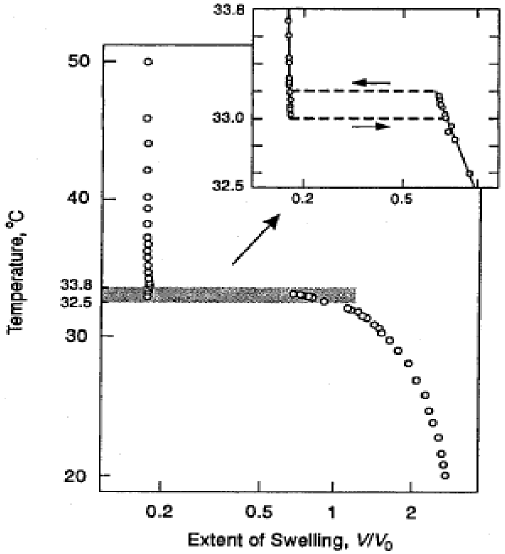

Figure 8-36 Effect of temperature on the volume of a poly(*N*-isopropylacrylamide) hydrogel in pure water. The expanded graph shows that, when the direction of transition is reversed, some hysteresis may be observed (Hirokawa and Tanaka, 1984).

This figure illustrates a hydrogel undergoing such a phase transition.

- **The temperature below 35°C : The hydrogel coexists with pure water in swollen state.**
- **The temperature upper 35°C : Collapses the hydrogel.**
- **The temperature about 33°C: A phase transition between the shrunken (collapsed) and the swollen state associated with a discontinuous change in volume.**

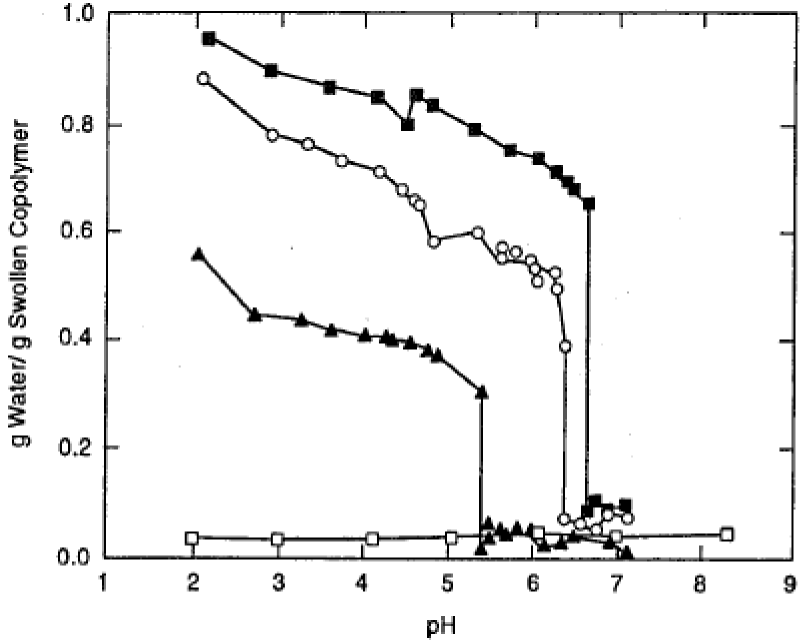

Figure 8-37 Swelling isotherms for the MMA/DMA copolymers of various comonomer composition, determined as a function of pH at 25°C and a total ionic strength of 0.1 M. ■ 70/30 mol/mol, ○ 78/22 mol/mol, ▲ 86/14 mol/mol, □ 93/7 mol/mol (Siegel and Firestone, 1988). MMA = methyl methacrylate (no charge); DMA = dimethylaminoethyl methacrylate (positive charge at low pH).

▪ pH > 6.6 : All gels studied here are collapsed, i.e. compact and hydrophobic, regardless of comonomer composition.

▪ pH ≤ 6.6 : A critical value of pH is reached where the equilibrium content of water abruptly increases, giving rise to a highly swollen gel. At still lower pH values, the water content continues to increase but at a more gradual rate.

▪ The water content in th low-pH range changes from about 90 to 40 weight%.

▪ The 93/7 mol/mol gel remains compact at all pH ; no volume transition occurs.

Hino′s semi-empirical model

Consider a binary polymer solution : solvent (component 1, represent by sphere) and linear polymer (component 2, polymer molecules by freely-jointed chains)

Use extened Flory-Huggins lattice theory to calculate the Helmholtz energy of mixing $\Delta_{mix}A$:

$$\frac{\Delta_{\text{mix}}A}{kT} = N_1 \ln(1-\Phi_2) + N_2 \ln(\Phi_2) + N_1\Phi_2\, g(T,\Phi_2) \qquad (8\text{-}138)$$

where k is Boltzmann′s constant, T is the absolute temperature, N_i is the number of molecules of component i, Φ_2 is the volume fraction of the polymer, and g(T, Φ_2) is an empirical function that replaces the customary Flory segmental interaction parameter.

Next, a polymer gel containing solvent (component 1) and a large cross-linked polymer molecule (component 2) having a small number of ionizable segments.

The Helmholtz energy of swelling is given by,

$$\Delta A^{\text{swe}} = \Delta_{\text{mix}}A + \Delta A^{\text{elas}} + \Delta A^{\text{ion}} \qquad (8\text{-}139)$$

where $\Delta_{mix}A$, ΔA^{elas} and ΔA^{ion} represent mixing, elastic, and electrostatic contributions.

The mixing contribution is,

$$\frac{\Delta_{\text{mix}}A}{kT} = N_1 \ln(1-\Phi_2) + N_1\Phi_2\, g(T,\Phi_2) \qquad (8\text{-}140)$$

For the Helmholtz energy change due to elastic deformation, Hino uses an expression given by Birshtein and Pryamitsyn and Grosberg and Kuznetsov :

$$\frac{\Delta A^{\text{elas}}}{kT} = \frac{3}{2}\nu\left(\alpha^2 + \frac{1}{\alpha^2} - 2\right) + \frac{1}{2}\nu \ln\alpha^3 \qquad (8\text{-}141)$$

where α is the expansion factor and v is the total number of chains.

The expansion factor is given by :

$$\alpha = \left(\frac{\Phi_0}{\Phi_2}\right)^{1/3} \qquad (8\text{-}142)$$

where Φ_0 is usually approximated by the volume fraction of polymer at preparation of the gel.

Finally, for a small charge density, Hino expresses the electrostatic effect using the van't Hoff equation :

$$\frac{\Delta A^{\mathrm{ion}}}{kT} = -m\nu \ln(N_1 + \nu r_n) \qquad (8\text{-}143)$$

where m is the number of charged segments per network chain between points of cross-linking and r_n is the number of segments per network chain.

For phase equilibrium calculations, the Flory χ parameter, defined by the product of two empirical functions :

$$\chi \equiv g - \left(\frac{\partial g}{\partial \Phi_2}\right)_T = D(T)B(\Phi) \qquad (8\text{-}144)$$

where B(Φ) is a function of composition and D(T) is a function of temperature.

The reduced temperature and interchange energy ε is defined as follows,

$$\tilde{T} \equiv \frac{kT}{\varepsilon} \qquad (8\text{-}145)$$

$$\varepsilon \equiv 2\varepsilon_{12} - \varepsilon_{11} - \varepsilon_{22} \qquad (8\text{-}146)$$

where ε_{ij}(i, j = 1, 2) is the segmental interaction energy for non-spectific interactions between components i and j.

The B(Φ) and D(T) is,

$$D(T)=\frac{z}{2}\left[\left(1+2\delta\varepsilon_{12}/\varepsilon\right)\left(\frac{1}{\tilde{T}}\right)+2\ln\left(\frac{1+s_{12}}{1+s_{12}\exp\left(\frac{\delta\varepsilon_{12}}{\varepsilon\tilde{T}}\right)}\right)\right] \tag{8-147}$$

$$B(\Phi)=\frac{1}{1-b\Phi_2} \tag{8-148}$$

where z is the lattice coordination number, $\delta\varepsilon_{12}$ is the difference between the segmental interaction energy for specific interactions and that for non-specific interactions, s_{12} is the ratio of degeneracy of non-spectific interactions to that of specific interactions and b is an empirical parameter, all obtained from independent polymer-solution data.

At equilibrium, μ_1 (surrounding pure solvent) is equal to μ_1 (in the gel). The chemical potential of the solvent in the gel is found from differentiation of ΔA^{swe} with respect to N_1.

$$\begin{aligned}\Delta\mu_1(\Phi_e)=\left(\frac{\partial\Delta A^{swe}}{\partial N_1}\right)_{T,V,N_2=1}&=\ln(1-\Phi_e)+\Phi_e+\chi\Phi_e^2\\&+\frac{\Phi_0}{r_n}\left[\left(\frac{\Phi_e}{\Phi_0}\right)^{1/3}-\left(\frac{\Phi_e}{\Phi_0}\right)^{5/3}-\left(m-\frac{1}{2}\right)\left(\frac{\Phi_e}{\Phi_0}\right)\right]=0\end{aligned} \tag{8-149}$$

where $\Delta\mu 1$ is the change in chemical potential of solvent upon mixing, and V is the volume of the gel.

Under the specific conditions where two gel phases can coexist at one temperature, a polymer gel exhibits a discontinuous volume change. The conditions for coexistence of the two gel phases are

$$\mu_1(\Phi_e') = \mu_1(\Phi_e'') \qquad (8\text{-}150)$$

and

$$\mu_2(\Phi_e') = \mu_2(\Phi_e'') \qquad (8\text{-}151)$$

where superscripts ‘ and “ denote coexisting phase.

From the Gibbs-Duhem equation, Eq. (8-1510 can be replaced by

$$\int_{\Phi_e'}^{\Phi_e''} \Delta\mu_1 \Phi_2^{-2} d\Phi_2 = 0 \qquad (8\text{-}152)$$

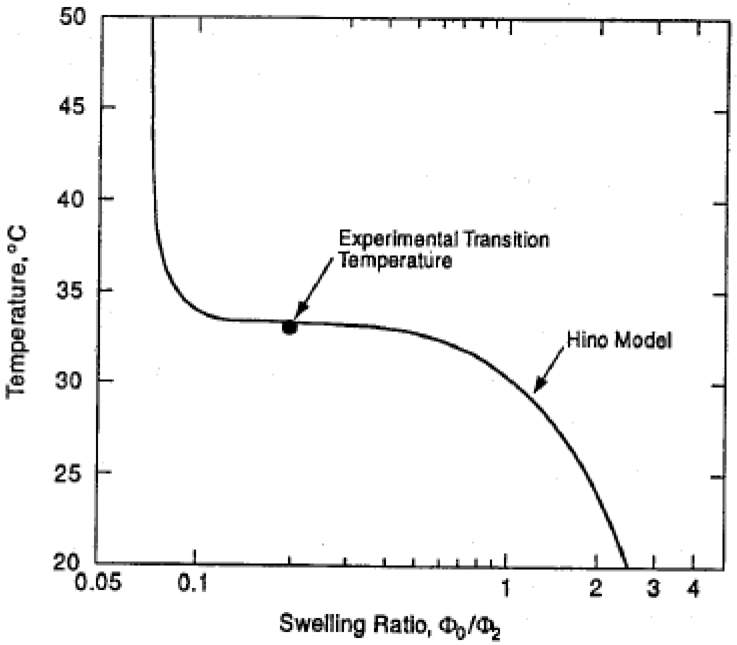

Figure 8-38 Swelling-ratio curve for neutral PNIPAAm gel in water calculated with the model of Hino (1998). Experimental transition temperature range is 32.5-33.8°C (Hirotsu *et al.*, 1987).