*Macromolecules* **1995,** *28,* 6579–6585

# Calculation of the Phase Diagrams of Polymeric Gels in a Two-Component Mixture

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*Received September 21, 1994; Revised Manuscript Received June 2, 1995*[⊗]

ABSTRACT: The swelling equilibrium of an ionic polymer gel soaked in a solution of two components has been investigated in terms of a modified Flory–Huggins model. A variety of phase diagrams are calculated for gel systems of liquid 1/liquid 2/polymer network for different values of the model parameters. It can be anticipated that gels can change their volume discontinuously even in a mixture of partially miscible liquids. In some systems, there is no critical point though a discontinuous change does take place. For gel systems of solvent/electrolyte/polymer network, calculation shows that the concentration of electrolyte inside the gel will change discontinuously at a point of discontinuous volume change. Calculation of transition points under a uniaxial swelling condition successfully explains the composition hysteresis between swelling and shrinking transitions.

## 1. Introduction

Swelling phenomena of polymers in a liquid mixture are closely related to the separation performance of polymeric membranes.[1] The composition of a liquid mixture inside the membrane is different from that on the outside, and this difference is one of the key factors determining separation performance of membranes. On the other hand, volume transitions of gels in binary liquid mixtures have often been explained by a single-liquid approximation, where the composition of the liquid mixture is assumed to be identical inside and outside of the gel. We expect that such phase transitions can be described more accurately by taking the difference of liquid compositions into account. Such a treatment will also be of use to an actual application of the phase transition of gels for controlled drug delivery systems.[2]

The authors have previously introduced a Flory–Huggins mean-field equation of the free energy in order to represent the swelling of an ionic gel in a liquid mixture.[3] The derived equations are simpler than the ones found by other researchers[4] and are based on the equality of the chemical potentials of each liquid component inside and outside of the gel. Numerical analysis of the equations enables one to estimate absorption quantities of the liquids into the gel. This method gives more detailed information than the single liquid approximation;[5] not only the volume but also the internal liquid composition can be calculated as a function of the external liquid composition.[3,6] It was shown that the internal liquid composition changes discontinuously at the point of discontinuous volume change. This conclusion provides a qualitative explanation for the experimental results reported by several researchers.[4,6]

In the present paper, on the basis of our previous model free energy, we develop a general treatment for the conditions of equilibrium, bulk instability, and critical points; then numerical calculations are carried out for several varieties of gel systems individually. We display in this way the characteristic features of phase diagrams of polymeric gels soaked in a solution of two components.

## 2. Equations

**Free Energy.** We first consider a gel system which comprises three components $i$ ($i = 1-3$): two liquid components ($i = 1, 2$) and a polymer segment ($i = 3$). Let the molar volume of component $i$ be $V_i$. The affinity of component $i$ for component $j$ ($i \neq j$) is represented by the interaction parameter[7] $\chi_{ij}$ in the Flory–Huggins model. For the structure of the polymer network, we employ the following conditions: (1) A unit volume of the polymer network consists of $\nu$ moles of polymer chains at the reference state in which the network was formed.[7,8] (2) Each polymer chain has $f$ moles of substituents[8] which are assumed to dissociate completely in any composition of the mixture of three components to yield $f$ moles of mobile counterion $X^+$. (3) The solution of dissociated counterions is dilute so that the electrostatic interaction between the charged ions is neglected. On those assumptions, we consider a thermodynamic process in which the network is immersed into an infinite amount of liquid mixture and isotropically swells, absorbing $n_1$ moles of liquid 1 and $n_2$ moles of liquid 2 from the external solution. Because of the infinite amount of external solution, its composition can be considered fixed. The free energy change $G$ in this process is expressed as follows:[3]

$$G = G_M + G_E + G_I + G_S \qquad (1)$$

where $G_M$ is the free energy change of mixing three pure components.[7] $G_E$ and $G_I$ originate from the entropy change of the polymer configuration and mobile ions, respectively.[7-9] $G_S$ is the free energy change upon separating $n_1$ moles of liquid 1 and $n_2$ moles of liquid 2 from the external solution into their pure states.[3,6] The terms in eq 1 are given by eqs 2–5.

$$G_M = RT(n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi_{12} n_1 \phi_2 + \chi_{13} n_1 \phi_3 + \chi_{23} n_2 \phi_3) \qquad (2)$$

$$G_E = (RT\nu V_0/2)(3\alpha^2 - 3 - \ln \alpha^3) \qquad (3)$$

$$G_I = -RT\nu V_0 f \ln \alpha^3 \qquad (4)$$

$$G_S = -(n_1 \Delta\mu_1 + n_2 \Delta\mu_2) \qquad (5)$$

where $R$ is the gas constant and $T$ is the absolute temperature. Neglecting the change of the total volume upon mixing of components, the volume fraction $\phi_i$ of component $i$ in the gel is related to $n_i$ by $\phi_i = V_i n_i / V$, where $V = V_1 n_1 + V_2 n_2 + V_3 n_3$ is the volume of the gel.

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[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1995.

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$\alpha$ is the one-dimensional elongation ratio of the gel, which is related to $\phi_3$ as[7,8,10] $\alpha^3 = V/V_0 = \phi_0/\phi_3$, where $V_0$ and $\phi_0$ are the volume of the gel and the volume fraction of polymer inside the gel at the reference state, respectively. $\Delta\mu_i$ is the difference of the chemical potential of liquid $i$ in the external solution and that of pure liquid $i$ at the same temperature. Since we need the free energy change of mixing polymer network with the liquid mixture of fixed composition, not with pure liquid 1 and pure liquid 2, $G_S$ should be subtracted as is written in eq 1. In the free energy change $G$, we have neglected the contributions of both non-Gaussian effects of polymer configuration and electrostatic interaction between charges,[11,12] although more elaborate models should contain those contributions.

**Swelling Equilibrium.** Bearing in mind that $\phi_i$ is a function of $n_i$ ($i = 1, 2$), we regard $G$ as a function of $n_i$ ($i = 1, 2$) under fixed values of $T$ and $\Delta\mu_i$. Swelling equilibrium is expressed by the simultaneous equations:

$$\partial G/\partial n_i = 0 \quad (i = 1, 2) \tag{6}$$

$\Delta\mu_i$ is equivalent to the change in chemical potential of liquid $i$ upon mixing the liquids to form the external solution and is given by the following equations on the basis of mean-field approximation:[13]

$$\Delta\mu_1/RT = \ln v_1 + (1 - s)v_2 + \chi_{12}{v_2}^2 \tag{7}$$

$$\Delta\mu_2/RT = \ln v_2 + (1 - s^{-1})v_1 + s^{-1}\chi_{12}{v_1}^2 \tag{8}$$

where $v_i$ is the volume fraction of liquid $i$ in the external liquid mixture ($v_1 + v_2 = 1$), and $s = V_1/V_2$. From eqs 1–8, we obtain the following equations which express the equality of chemical potential of each liquid inside and outside of the gel.

$$\begin{aligned}\ln v_1 + (1 - s)v_2 + \chi_{12}{v_2}^2 = \ln \phi_1 + (1 - s)\phi_2 +\\ \phi_3 + \chi_{12}{\phi_2}^2 + \chi_{13}{\phi_3}^2 + (\chi_{12} + \chi_{13} - s\chi_{23})\phi_2\phi_3 +\\ V_1\nu[(\phi_3/\phi_0)^{1/3} - (f + {}^1/_2)(\phi_3/\phi_0)]\end{aligned} \tag{9}$$

$$\begin{aligned}\ln v_2 + (1 - s^{-1})v_1 + s^{-1}\chi_{12}{v_1}^2 = \ln \phi_2 +\\ (1 - s^{-1})\phi_1 + \phi_3 + s^{-1}\chi_{12}{\phi_1}^2 + \chi_{23}{\phi_3}^2 +\\ (s^{-1}\chi_{12} + \chi_{23} - s^{-1}\chi_{13})\phi_1\phi_3 + V_2\nu[(\phi_3/\phi_0)^{1/3} -\\ (f + {}^1/_2)(\phi_3/\phi_0)]\end{aligned} \tag{10}$$

The equilibrium point can be obtained by solving eqs 9 and 10 for a given composition $v_1$ of the external liquid mixture. In the next section we shall regard the solution that gives the minimum value of $G$ in eq 1 as a stable point, when multiple sets of solutions are obtained for a given value of $v_1$. If two sets of solutions give the same value of $G$, the stable equilibrium curve changes discontinuously, implying that the gel will undergo a phase transition. This discontinuous point, however, is not exactly the point at which the gel undergoes a phase transition between a shrunken and a swollen phase in an experimental condition. Transition conditions have been discussed by several researchers.[14-17] Sekimoto indicated that the one-dimensional elongation ratio in a normal axis on the surface of the gel is different from that in horizontal axes at a transition point.[14] He determined such transition points considering the free energy for anisotropic swelling and gave a clear explanation for the temperature hysteresis observed in swelling and shrinking transitions of gels. In the present paper, a hysteresis curve caused by the change of the external liquid composition will be calculated on the basis of Sekimoto's formulation in section 4.

**Boundary of Bulk Instability.** The curvature of the free energy surface is proportional to $D$ defined as follows:[18,19]

$$D = \begin{vmatrix} \partial^2 G/\partial n_1\,\partial n_1 & \partial^2 G/\partial n_1\,\partial n_2 \\ \partial^2 G/\partial n_2\,\partial n_1 & \partial^2 G/\partial n_2\,\partial n_2 \end{vmatrix} \tag{11}$$

The condition $D = 0$ can be rewritten in the form

$$\begin{aligned}(1/\phi_1 - 2\chi_{13})(1/\phi_2 - 2\chi_{23}){\phi_3}^2 -\\ s^{-1}(\chi_{12} - \chi_{13} - s\chi_{23})^2{\phi_3}^2 -\\ (V_2/\phi_1 + V_1/\phi_2 - 2V_2\chi_{12})\nu[({}^1/_3)(\phi_3/\phi_0)^{1/3} -\\ (f + {}^1/_2)(\phi_3/\phi_0)] = 0\end{aligned} \tag{12}$$

The bulk modulus[20] $K$ of the polymer network is defined by $K^{-1} = -V^{-1}(\partial V/\partial P)$, where $P$ is the hydrostatic pressure imposed on the polymer network under an osmotic equilibrium condition. A straightforward calculation shows that the left-hand side of eq 12 is equal to $(V_2/\phi_1 + V_1/\phi_2 - 2V_2\chi_{12})K/RT$. Thus, the curve where $K$ is equal to zero under an equilibrium condition (boundary of bulk instability) can be calculated from eq 12 in addition to eqs 9 and 10.

**Critical Point.** The following equation[18,19,21] is necessary to hold at a critical point where a shrunken phase and a swollen phase coincide under an equilibrium condition.

$$\begin{vmatrix} \partial D/\partial n_1 & \partial D/\partial n_2 \\ \partial^2 G/\partial n_2\,\partial n_1 & \partial^2 G/\partial n_2\,\partial n_2 \end{vmatrix} = 0$$

This equation is simplified to

$$\begin{aligned}0 = -V_1(1 + 2\chi_1\Phi_1)^2\Phi_1 - V_2(1 + 2\chi_2\Phi_2)^2\Phi_2 -\\ (\Phi_1 + \Phi_2)^3\nu[({}^5/_9)(\phi_3/\phi_0)^{1/3} - (f + {}^1/_2)(\phi_3/\phi_0)]/{\phi_3}^3\end{aligned} \tag{13}$$

where $\Phi_i$ stands for $V_i\phi_i/(1 - 2V_i\chi_i\phi_i)$ and $2\chi_1 = \chi_{12}/V_1 + \chi_{13}/V_1 - \chi_{23}/V_2$ and $2\chi_2 = \chi_{12}/V_1 + \chi_{23}/V_2 - \chi_{13}/V_1$. At a critical point, eq 13 must be satisfied besides eqs 9, 10, and 12. Note that eqs 12 and 13 can be reduced to the expressions for the solution system of liquid 1/liquid 2/polymer[19] if $\nu$ equals zero (there is no cross-linking).

## 3. Calculation of Equilibrium Curves

**Discontinuity of Gels in a Liquid Mixture.** Equilibrium curves can be calculated taking the volume fraction of liquid 1 in the external solution, $v_1$, as a variable. The values of parameters are fixed as $V_1\nu/{\phi_0}^3 = 10$ and $V_1 = 20$ (cm$^3$/mol) throughout this paper; the value of $\phi_0$ is equal to 0.1 in this section. At first, interaction parameters between each liquid $i$ to the polymer are chosen to be identical as $\chi_{13} = \chi_{23} = 0.5$, $V_2 = 20$, and $\chi_{12} = -2$. It is not necessarily evident whether systems having those parameters are commonly encountered, because the negative sign of $\chi_{12}$ is not usual. We expect, however, that the following results of our model calculation will demonstrate some of characteristics of gels in a binary liquid mixture, especially concerning the number of critical points and the shape of the unstable region in the phase diagram.

The loci of the solution of eqs 9 and 10 are drawn in light dotted curves or solid curves in Figure 1a; solid

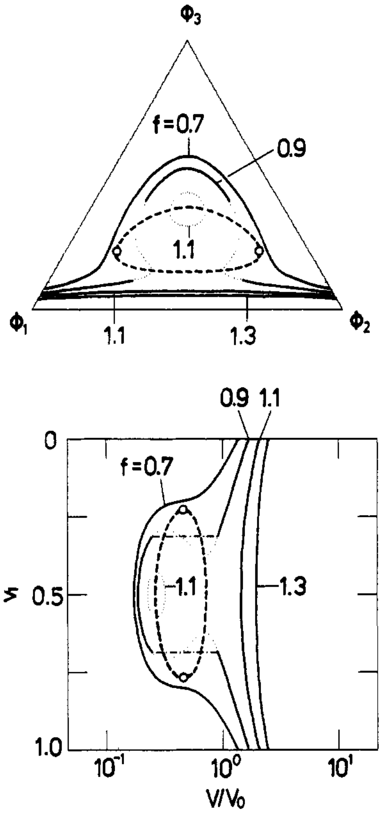

**Figure 1.** (a) Composition of the gel, $\phi_i$, in a binary liquid mixture. The equilibrium curve (—) and boundary of bulk instability (- - -) are shown. $V_1 = V_2 = 20$, $\chi_{12} = -2$, $\chi_{13} = 0.5$, and $\chi_{23} = 0.5$. (b) Volume of the gel, $V/V_0$, as a function of the composition of the external liquid mixture, $v_1$. $V_1 = V_2 = 20$, $\chi_{12} = -2$, $\chi_{13} = 0.5$, and $\chi_{23} = 0.5$.

ones are the stable equilibrium curves determined from the minimum value of $G$. Each apex of the triangle corresponds to the pure component $i$. The $\phi_2-\phi_3$ side of the triangle corresponds to mixtures of liquid 2 and the polymer network; that is, the external composition $v_1$ equals zero on this side. The stable equilibrium curve for $f = 0.9$ changes discontinuously twice when $v_1$ varies from 0 to 1. The portion surrounded by the broken curve is the region of bulk instability, where the bulk modulus $K$ has a negative value. It has been indicated that light scattering intensity does not diverge at $K = 0$ because shear modulus $M$ suppresses fluctuation of the polymer–network density.[17] The boundary of microscopic instability is defined by $K + (^4/_3)M = 0$.[17,22] Thus, a divergence does not occur at a critical point that is located on the boundary of bulk instability. Two critical points (○) are obtained in this system. They are

$$\begin{cases} \phi_1 = 0.160... \\ \phi_2 = 0.621... \\ \nu_1 = 0.231... \\ f\ = 0.767... \end{cases} \qquad \begin{cases} \phi_1 = 0.621... \\ \phi_2 = 0.160... \\ \nu_1 = 0.768... \\ f\ = 0.767... \end{cases}$$

In this system multiple solutions cannot be obtained unless the value of $f$ exceeds the critical value $f_c$(=0.767...). It should be noted, however, that there are gel systems[3] in which multiple solutions are obtained in the case of not only $f > f_c$ but also $f < f_c$.

Figure 1b shows the dependence of volume of the gel on the external composition $v_1$. Dry states ($\phi_3 = 1$) are to be located along the vertical line corresponding to $V/V_0 = 10^{-1}$. The discontinuous volume change has a shape of reentrant type. It can be pointed out that the boundary of bulk instability is constituted of points at which $dV/dv_1 = \infty$ holds on every locus of the solution calculated from eqs 9 and 10. Moreover, critical points are the points at which the condition $dV/dv_1 = \infty$ holds on the boundary of bulk instability. Since we can find out the points of $dV/dv_1 = \infty$ easily, it is not necessary to calculate eqs 12 and 13 for the schematic drawing of the boundary of bulk instability and critical points in the ($v_1$, $V/V_0$) plane. Figure 1b seems to be similar to the phase diagram obtained from a single liquid approximation[5] (SLA) in which liquid compositions inside and outside of the gel are supposed to be identical. On the other hand, in our treatment it is possible to estimate the difference in those liquid compositions as shown in the next subsection.[3] Thus we can expect that the present model is a more accurate approximation than the SLA to the volume as well as the internal liquid composition observed in real gel systems.

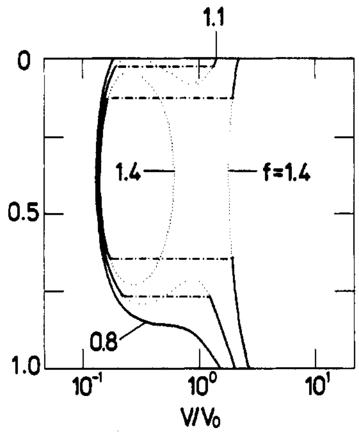

**Figure 2.** Volume of the gel, $V/V_0$, as a function of the composition of the external liquid mixture, $v_1$. $V_1 = V_2 = 20$, $\chi_{12} = -2$, $\chi_{13} = 0.5$, and $\chi_{23} = 1$.

The next two figures illustrate ternary systems having different values of $\chi_{i3}$ ($i = 1, 2$) from those of the system shown in Figure 1. As noted above concerning Figure 1b, the boundary of bulk instability and critical points is easily inspected in the ($v_1$, $V/V_0$) plane once the loci of solutions of eqs 9 and 10 for various values of $f$ are obtained. Consequently, they are not drawn from now on in this section aside from a special case.

Figure 2 shows the volume of the gel of which the parameters are $\chi_{13} = 0.5$ and $\chi_{23} = 1$. Volume curves that correspond to stable equilibrium for $f = 1.1$ and 1.4 change discontinuously twice. The region of bulk instability extends more than that of Figure 1b and reaches the axis of $v_1 = 0$. Thus, there is only one critical point in the region of lower $v_1$. The volume of the gel which has the interaction parameters $\chi_{13} = 1$ and $\chi_{23} = 1$ is shown in Figure 3. Since the boundary of bulk instability comes up to both axes of $v_1 = 0$ and $v_1 = 1$, there is no critical point in this system, while a discontinuous volume change takes place for gels with $f = 1.1$, 1.4, and 1.7.

**Discontinuity in a Mixture of Partially Miscible Liquids.** It is quite natural to anticipate a discontinuous volume change of the gel immersed in a mixture of partially miscible liquids. Let us examine a gel system characterized by the parameters of $V_1 = 20$, $V_2 = 40$, $\chi_{12} = 1.5$, $\chi_{13} = 0$, and $\chi_{23} = 1.5$. The following equations express the equality of the chemical potential of each liquid component between the two liquid phases a and b:

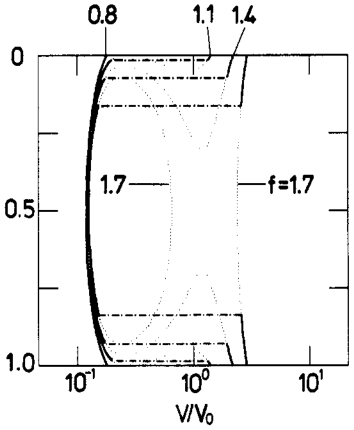

**Figure 3.** Volume of the gel, $V/V_0$, as a function of the composition of the external liquid mixture, $v_1$. $V_1 = V_2 = 20$, $\chi_{12} = -2$, $\chi_{13} = 1$, and $\chi_{23} = 1$.

$$\ln v_{a1} + (1 - s)v_{a2} + \chi_{12}(v_{a2})^2 = \ln v_{b1} + (1 - s)v_{b2} + \chi_{12}(v_{b2})^2$$

$$\ln v_{a2} + (1 - s^{-1})v_{a1} + s^{-1}\chi_{12}(v_{a1})^2 = \ln v_{b2} + (1 - s^{-1})v_{b1} + s^{-1}\chi_{12}(v_{b1})^2$$

where $v_{ai}$ and $v_{bi}$ are the volume fraction of liquid $i$ ($i$ = 1, 2) in phases a and b, respectively. Calculation of these equations gives values as $v_{a1} = 0.438...$ and $v_{b1} = 0.724...$. When $v_1$ lies in the range between $v_{a1}$ and $v_{b1}$, the external liquid mixture is immiscible and separates into two phases of which compositions are given by $v_{a1}$ and $v_{b1}$. In Figure 4a compositions of the gels with $f$ = 0, 1, and 2 are drawn in light dotted lines; each of them has a very small loop with two cusps. We denote the composition at the intersection point of a loop by $\phi_{iS}$ ($i$ = 1−3). This intersection point corresponds to the composition of a gel equilibrated in the liquid mixture of which composition is either $v_1 = v_{a1}$ or $v_1 = v_{b1}$, because the chemical potential of each liquid has an identical value in both phases a and b to yield an identical composition of the gel. In contrast to the gel systems shown in previous figures, the boundary of bulk instability seems to reach the bottom line of the triangle; this implies that there is no critical point in this system. Figure 4b shows volume of the gel versus the external liquid composition. The curves of $K = 0$ apparently cross each other in the ($v_1$, $V/V_0$) plane. In the miscible region, $v_1 < v_{a1}$, there is a discontinuous volume change for the gel with $f = 2$. In the immiscible range of $v_1$, the volume of the gel is given by $V_0\phi_0/\phi_{3S}$, whichever phase a or b the gel exists in upon the supposition of the constant value of $f$. Actually the value of $f$ depends on the compositions[6,23] of liquids and polymer, so that different swelling volumes may be observed experimentally in each phase.

For a measure of selective dissolution of liquid 1 into the gel, a selectivity $S$ is defined as[13] $S = (\phi_1/\phi_2)/(v_1/v_2)$. In this definition, the gel dissolves liquid 2 selectively when $0 < S < 1$. The selectivity of liquid 1, $S$, is shown in Figure 4c. In the immiscible range of $v_1$, $S$ has an alternative value of either

$$S_a = (\phi_{1S}/\phi_{2S})/(v_{a1}/v_{a2}) \quad \text{or} \quad S_b = (\phi_{1S}/\phi_{2S})/(v_{b1}/v_{b2})$$

according to which phase a or b the gel exists in.

**Discontinuity of Gels in an Electrolyte Solution.** Let us now consider a gel system of solvent/electrolyte/polymer network. A polymer network is soaked in a solvent in which a strong electrolyte XA is dissolved which dissociates completely as $XA \rightarrow X^+ + A^-$. The cation $X^+$ is taken to be identical with the one that is yielded by dissociation of the polymer.[7] Let the concentration of the electrolyte in the external solution be $c^0$ in molarity (mole/volume of the solution). The electrolyte solution is assumed to be dilute. Moreover, as supposed in the case of liquid mixture, we assume that the electrolyte concentration of the external solution does not change through the swelling process. The osmotic equilibrium for the solvent is expressed as follows:[7]

$$-V_1[2(c^0 - c^I)] = \ln \phi_1 + \phi_2 + \chi_{12}\phi_2^{\,2} + V_1\nu[(\phi_2/\phi_0)^{1/3} - (f + {}^1/_2)(\phi_2/\phi_0)] \quad (14)$$

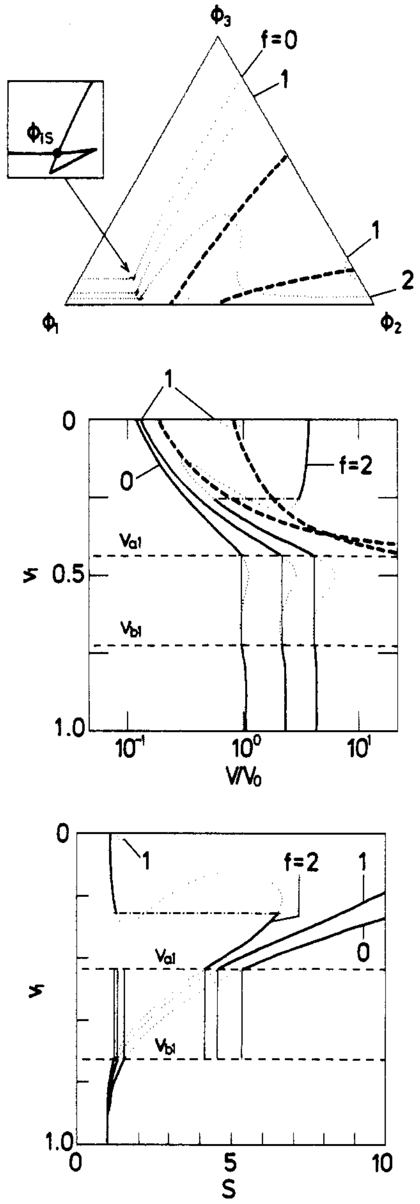

**Figure 4.** (a) Composition of the gel, $\phi_i$, in a binary liquid mixture. The solution of eqs 7 and 8 (···) and boundary of bulk instability (- - -) are shown. $V_1 = 20$, $V_2 = 40$, $\chi_{12} = 1.5$, $\chi_{13} = 0$, and $\chi_{23} = 1.5$. (b) Volume of the gel, $V/V_0$, as a function of the composition of the external liquid mixture, $v_1$. The boundary of bulk instability (- - -) is shown. $V_1 = 20$, $V_2 = 40$, $\chi_{12} = 1.5$, $\chi_{13} = 0$, and $\chi_{23} = 1.5$. (c) Dependence of the selectivity $S$ on the composition of the external liquid mixture, $v_1$. $V_1 = 20$, $V_2 = 40$, $\chi_{12} = 1.5$, $\chi_{13} = 0$, and $\chi_{23} = 1.5$.

where $c^I$ is the molarity of the electrolyte inside the gel. In this subsection, we shall denote by 1, 2, and E the solvent, polymer, and electrolyte, respectively. The left-hand side of eq 14 is osmotic pressure (divided by $RT$) exerted by the difference in the concentration of the electrolyte between the inside and outside of the gel.[7] On the other hand, the thermodynamic distribution of electrolyte is expressed by the Donnan equilibrium, which equates the product of activities of each mobile ion inside the gel to the product of activities outside the gel. Neglecting the electrostatic interactions between the dilute ions both in the solvent and in the gel, the Donnan equation is written as follows:

$$[n_E/V][(\nu V_0 f + n_E)/V] = (c^0)^2 \qquad (15)$$

where $n_E$ is the number of moles of electrolyte inside the gel. Note that $n_E/V$ is the molarity of the anion $A^-$ inside the gel, $c^I$, and $(\nu V_0 f + n_E)/V$ is that of the cation $X^+$, $\nu f(\phi_2/\phi_0) + c^I$, where the term $\nu f(\phi_2/\phi_0)$ arises from the counterions dissociated from the polymer. Equations 14 and 15 give[24,25] the volume of the gel, $V$, and the molarity of the electrolyte inside the gel, $c^I$, as a function of $c^0$.

Experimentally, Ricka et al. have found a volume transition of a gel by changing the concentration of the electrolyte in the surrounding water.[26] In order to examine such a transition, it is preferable to give an expression for the free energy from which eqs 14 and 15 are derived. It can be obtained in a manner similar to that for eqs 1–5. For this purpose, it is necessary to introduce the change in chemical potential of the solvent upon mixing, $\Delta\mu_1$, and that of the electrolyte, $\Delta\mu_E$, in the external solution. Besides, the entropy term of mobile ions inside the gel should be considered. Accordingly, the free energy change $G^{\text{elec.}}$ for the gel system of solvent/electrolyte/polymer network can be given by,

$$\begin{aligned} G^{\text{elec.}}/RT = {} & n_1 \ln \phi_1 + (\nu V_0 f + n_E)[\ln\{(\nu V_0 f + n_E)V_{X^+}/V\} - 1] + \\ & n_E[\ln(n_E V_{A^-}/V) - 1] + \chi_{12} n_1 \phi_2 + \\ & (\nu V_0/2)[3\alpha^2 - 3 - \ln \alpha^3] - (n_1 \Delta\mu_1 + n_E \Delta\mu_E)/RT \qquad (16) \end{aligned}$$

where $V_{X^+}$ and $V_{A^-}$ are the molar volumes of the cation and the anion, respectively. The second and third terms on the right-hand side are the contributions of the translational entropy of the cation and the anion[27] inside the gel, respectively. In the external solution, $c^0$ moles of dilute electrolyte yields $2c^0$ moles of mobile ions so that the changes in chemical potentials upon mixing are expressed as follows[27,28] on the basis of a dilute solution approximation:

$$\Delta\mu_1 = -RT(2V_1 c^0) \qquad (17)$$

$$\Delta\mu_E = RT \ln(V_{X^+} c^0) + RT \ln(V_{A^-} c^0) \qquad (18)$$

From eqs 16–18 and the expression for the gel volume, $V = V_1 n_1 + V_2 n_2$, the derivative of $G^{\text{elec.}}$ with respect to $n_1$ becomes

$$\begin{aligned} (1/RT)\, \partial G^{\text{elec.}}/\partial n_1 = {} & \ln \phi_1 + \phi_2 + \chi_{12}\phi_2{}^2 - \\ & V_1[(\nu V_0 f + n_E)/V + n_E/V] + V_1 \nu[(\phi_2/\phi_0)^{1/3} - \\ & (^1/_2)(\phi_2/\phi_0)] + 2V_1 c^0 \qquad (19) \end{aligned}$$

Substitution of $(\nu V_0 f + n_E)/V = \nu f(\phi_2/\phi_0) + c^I$ and $n_E/V = c^I$ into eq 19 makes it apparent that the condition $\partial G^{\text{elec.}}/\partial n_1 = 0$ is equivalent to eq 14. The other derivative becomes

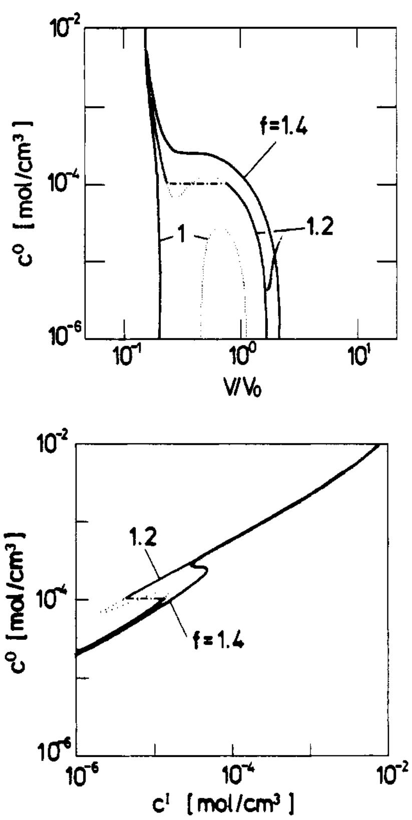

**Figure 5.** (a) Volume of the gel, $V/V_0$, as a function of the electrolyte concentration in the external solution, $c^0$. $V_1 = 20$ and $\chi_{12} = 1$. (b) Concentration of the electrolyte inside the gel, $c^I$, as a function of $c^0$.

$$\begin{aligned} (1/RT)\, \partial G^{\text{elec.}}/\partial n_E = {} & \ln[(\nu V_0 f + n_E)V_{X^+}/V] + \\ & \ln(n_E V_{A^-}/V) - [\ln(V_{X^+}c^0) + \ln(V_{A^-}c^0)] \qquad (20) \end{aligned}$$

This equation is equivalent to eq 15. Thus, we can calculate the expression of $K$ for this system, if necessary.

For comparison of the magnitude of free energy change $G^{\text{elec.}}$, values of $V_{X^+}$ and $V_{A^-}$ are not necessary; they are introduced solely to make the arguments of the logarithmic functions dimensionless. By use of eqs 14–16, equilibrium diagrams are calculated for the gel system having parameters $V_1 = 20$, $\chi_{12} = 1$, $\phi_0 = 0.1$, and $V_1\nu/\phi_0{}^3 = 10$. The volume $V$ is shown in Figure 5a, and the concentration of the electrolyte inside the gel, $c^I$, is shown in Figure 5b. It can be concluded that the discontinuous increase of the volume is accompanied by the discontinuous increase of $c^I$; this means that the number of electrolyte molecules inside the gel, $n_E = c^I V$, also increases discontinuously at this point.

## 4. Consideration

We have identified discontinuities by evaluating the free energy change $G$ expressed in eqs 1–5 in order to survey various phase diagrams of gel systems with their bulk instability regions and critical points. In this section we further consider rigorous conditions for transition points. In general, two phases coexist at a phase transition point (coexistence point). Particularly for gel systems, the skin layer of a new phase is generated on the surface of the original phase at a

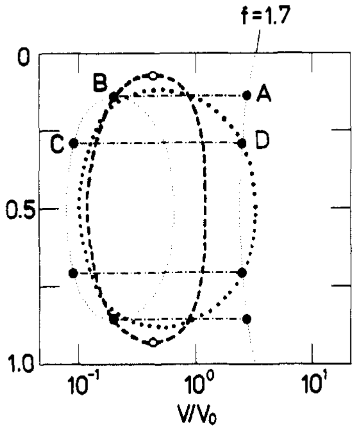

**Figure 6.** Hysteresis in volume change of the gel (···) shown as a function of the composition of the external liquid mixture, $v_1$. Transitions take place at the uniaxial transition curve (• • •) or at the boundary of bulk instability (- - -). $V_1 = V_2 = 20$, $\chi_{12} = -2$, $\chi_{13} = \chi_{23} = 0.5$, and $\phi_0 = 0.05$.

coexistence point. Let $\psi_i$ ($i = 1-3$) be the volume fractions of component $i$ in a new phase ($\psi_1 + \psi_2 + \psi_3 = 1$) and $\phi_i$ ($i = 1-3$) be those in an original phase. The free energy change of an original isotropic phase is expressed in eq 1, and thus each $\phi_i$ should satisfy eqs 9 and 10. On the other hand, a new phase is anisotropic; the one-dimensional elongation ratio $\beta$ of a new phase normal to the surface of the gel is different from horizontal ones ($\alpha$, $\alpha$). The free energy change $G^N$ of a new phase (skin layer) is expressed as

$$G^N/RT = m_1 \ln \psi_1 + m_2 \ln \psi_2 + \chi_{12}m_1\psi_2 + \chi_{13}m_1\psi_3 + \chi_{23}m_2\psi_3 + (\nu V_0/2)[2\alpha^2 + \beta^2 - 3 - (2f + 1) \ln(\alpha^2\beta)] - (m_1\Delta\mu_1 + m_2\Delta\mu_2)/RT \quad (21)$$

where $m_i$ is the number of moles of component $i$ ($i = 1-3$, $m_3 = n_3$) inside the anisotropic gel phase, and the condition of $\alpha^2\beta = \phi_0/\psi_3$ holds. The value of $\beta$ is smaller than $\alpha$ in a shrinking transition and larger than $\alpha$ in a swelling transition. Equilibrium of the skin layer is defined by

$$\partial G^N/\partial m_i = 0 \ (i = 1, 2) \quad (22)$$

under fixed values of $T$, $\Delta\mu_i$, and $\alpha$. Two phases expressed by eqs 9, 10, and 22 can coexist when both phases have an equivalent value of free energy change, $G = G^N$. This condition determines the value of $v_1$ at a coexistence point. The result will picturize the composition hysteresis in swelling and shrinking transition of gels when $v_1$ is changed with an infinitesimal rate. We shall adopt parameters as $V_1 = V_2 = 20$, $\chi_{12} = -2$, $\chi_{13} = \chi_{23} = 0.5$, $\phi_0 = 0.05$, and $V_1\nu/\phi_0^3 = 10$; note that we have chosen a smaller value of $\phi_0$ than that of previous systems. From $\phi_0 = 0.05$ and $V_1\nu/\phi_0^3 = 10$, we obtain $\nu = 6.25 \times 10^{-5}$ (mol/cm³), of which the magnitude is the same as the one obtained in mechanical experiments by Ilavský.[12] In Figure 6 a heavy dotted curve corresponds to the original phases at transition points determined from the coexistence condition $G = G^N$. This curve is named the "uniaxial transition curve",[14] of which the portion lying outside the closed heavy broken curve is accessible. The locus of solutions of eqs 9 and 10 for the gel of $f = 1.7$ is drawn in a light dotted curve. In a shrinking transition, the gel passes points in the order of A → D → C. The onset point of transition, D (original phase), is determined by the coexistence condition $G = G^N$ and is accompanied with formation of the skin layer of a new phase. This anisotropic skin layer shrinks toward the isotropic state C. As for a swelling transition, the uniaxial transition curve does not encounter the light dotted curve in its shrinking portion. Therefore, the transition is not dominated by the coexistence condition $G = G^N$. Instead, the gel passes through phase points in the order C → B → A. The point B lies at the boundary of bulk instability.

We can estimate the shapes of equilibrium curves with other values of $f$ by either direct calculation or by analogy with Figure 1b. These estimates lead to another feature of interest. An equilibrium curve does not encounter the accessible portion of the uniaxial transition curve if the value of $f$ is not larger than its critical value. Thus, for such values of $f$, swelling transitions as well as shrinking transitions take place at the boundary of bulk instability. Moreover, if the value of $f$ exceeds 1.7 so as not to encounter the accessible portion of the uniaxial transition curve, no shrinking transitions take place, whereas swelling transitions can take place when $v_1$ is changed. In this case, the gel remains swollen once a swelling transition has taken place.

The shear modulus[7] $M$ ($M = RT\nu\alpha^{-1}$ for an isotropic polymer network) also affects the transition characteristics through the parameter $\nu$. As the value of $\nu$ becomes larger toward the case shown in Figure 1b, in other words, the value of $\phi_0$ increases from 0.05 to 0.1, keeping the value of $V_1\nu/\phi_0^3$ (=10) constant, the region surrounded by the uniaxial transition curve diminishes, so that both transitions of shrinking and swelling tend to take place at the boundary of bulk instability.

## 5. Conclusion

A modified Flory–Huggins model is applied to the swelling of gels in a solution of two components. Numerical calculations using this model have shown a variety of discontinuities caused by changes in the composition of the external liquid phase. Discontinuities in phase diagrams imply the occurrence of phase transitions. In every phase diagram, we determine transition points in the manner demonstrated in section 4 using Sekimoto's formulation. Therefore, we assert that a "discontinuity" in a phase diagram is qualitatively called a "transition" as long as we have a prescription to determine transition points. Discontinuities in phase diagrams show four main characteristics of transitions. They are (1) composition of the electrolyte solution as well as that of the nonelectrolyte liquid mixture inside the gel changes discontinuously at a transition point, (2) gels can undergo transitions in a mixture of partially miscible liquids, (3) in some systems, there is no critical point whereas gels undergo transitions, and (4) in some systems, if the gel is initially conditioned in an appropriate shrunken state, the transition to be brought about is irreversible when the composition of external liquid is changed. Though a more quantitative model would include the effect of the gel composition on the value of $f$, conclusions obtained in the present paper will be of use both for description and for classification of a variety of transitions that have been observed for gels in a binary liquid mixture. Furthermore, our simple model will predict transitions which have not been found experimentally.

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MA946371F