A Four-Component Model for Volume Phase Transition

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NOTES

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ABSTRACT

By means of the Flory-Huggins and Iwatsubo theory for macro-molecules, a four-component model of a hydrogel, which consists of a copolymer network and a solution with two solvents, is given for discussing the "normal pattern" volume phase transition which was proposed by Katayama. Furthermore, the theoretical result shows that an ionic gel can also undergo a volume phase transition caused by the variation of the ratio of the two components in the copolymer network.

INTRODUCTION

A polymer gel swollen in a large amount of good solvent can undergo abrupt shrinking when the solvent quality becomes poor. This phenomenon is called polymer gel collapse. It was observed experimentally by Tanaka [1, 2] and explained by means of the Flory-Huggins theory [1-3]. This type of phenomenon is a critical behavior and named volume phase transition. As is well known, the volume phase transition of hydrogels has been attracting much more attention because of its technological and scientific importance [4, 5]. Not only can it be induced by

continuous change of surrounding conditions such as solvent composition, salt concentration, pH, and temperature, but also can be induced by continuous variation of the ratio of the components in the network [6].

Recently, Iwatsubo [7, 8] discussed convexo type volume phase transition by using the Flory-Huggins theory and brought forward a three-component model. Since some of the experiments for the polymer gel consist of a copolymer network and a solution with two solvents [4, 5], a four-component model is given in this paper as an extension of the treatment of the three-component one [7, 8]. By using this model, the "normal pattern" volume phase transition, which was observed experimentally by Katayama [9], is investigated. In order to prevent the present paper from becoming too long, the treatment of the "reverse pattern" and the "combined pattern" volume phase transitions will be reported in a consecutive paper. Furthermore, the theoretical result shows that an ionic gel may undergo a transition induced by the variation of the ratio of the two components in the copolymer network.

THEORETICAL SECTION

In this section, we shall present the volume phase transition theory of four-component model which is, in essence, an extension of the three-component theory of Iwatsubo [7,8]. For the four-component model, the indices 1 and 2 are used to denote the two solvents, whereas the indices 3 and 4 to denote the two components in the copolymer network. In order to make our discussion easier, some notations are introduced as follows,

$\Delta\mu_i$: the difference of the chemical potential of solvent i in the external solution and that of pure liquid i at the same temperature with $i = 1, 2$,

n_i: moles of the ith solvent in the gel with $i = 1, 2$,

α: one-dimensional shrinkage(expansion) factor of the network,

R: swelling ratio with $R = \alpha^3 = \dfrac{V}{V} = \dfrac{\phi_0}{\phi_3 + \phi_4}$,

V: volume of the gel,

V_0: volume of the gel when the constituent chains are in random configuration state,

ϕ_0: volume fraction of polymer network when the constituent chains are in random configuration state (is taken as 0.1 in this paper),

ϕ_i: volume fraction of component i in the gel with $\phi_1 + \phi_2 + \phi_3 + \phi_4 = 1$,

v_i: volume fraction of solvent i in surrounding mixture with $v_1 + v_2 = 1$,

V_i : molecular volume of solvent i with $i = 1, 2$ (V_1 is taken as unity in this paper),

s: the ratio of molecular volume of solvents 1 and 2, $s = V_1/V_2$ (s is taken as unity in this paper),

χ_{ij}: interaction parameter between component i and j,

f: average number of ionized group per chain,

v : number of constituent chains per unit volume of polymer network when $\phi_3 + \phi_4 = \phi_o$

W: the composition of the two components in the copolymer network, $W = P/(P+1)$

p: the ratio of ϕ_4 and ϕ_3, $= \phi_4/\phi_3$

Now let us discuss the free energy change of the four-component system in which a copolymer network and a solution with two solvents are involved. It is known that the free energy change ΔF can be divided into three parts [7, 8]

$$\Delta F = \Delta F_M + \Delta F_E + \Delta F_S$$

where ΔF_M caused by mixing the two solvents with the copolymer network) and ΔF_E (caused by the gel elasticity induced by shrinking or swelling of the network) were introduced by Flory and Huggins [10], and where ΔF_S, defined as the free energy change upon separating n_1 moles of solvent 1 and n_2 moles of solvent 2 from the external solution into their pure states, was proposed by Iwatsubo [7, 8].

For the four-component model, ΔF_M, ΔF_E and ΔF_S, and take the forms in Equation 1 is obtained by taking n_3 and n_4 as zero in Flory-Huggins theory due to the absence of individual polymer molecules in the network structure [10]; in Equation 2 is obtained by employing the following conditions: (a) a unit volume of the copolymer network consists of v moles of polymer chains at the reference state in which the network is formed; (b) each polymer chain has f moles of ions and yields f moles of mobile counterions X^+ and; (c) the solution of dissociated counterions is dilute so that the electrostatic interaction between the charged ions is neglected; ΔF_S in Equation 3 must be minus because we need the free energy change of mixing copolymer network with the solvent mixture of fixed composition, not with pure solvent 1 and pure solvent 2.

With respect to Equations 1-3, the conventional equilibrium condition can be written as

$$\Delta F_M = RT(n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1\chi_{12}\phi_2 + n_1\chi_{13}\phi_3 + n_1\chi_{14}\phi_4 + n_2\chi_{23}\phi_3 + n_2\chi_{24}\phi_4) \tag{1}$$

$$\Delta F_E = RT \frac{vV_0}{2}[3\alpha^2 - 3 - (2f+1)\ln\alpha^3] \tag{2}$$

$$\begin{aligned}
\Delta F_S &= -(n_1\Delta\mu_1 + n_2\Delta\mu_2) \\
&= -RT\{n_1[\ln v_1 + (1-s)v_2 + \chi_{12}v_2^2] + n_2[\ln v_2 + (1-s^{-1})v_1 + s^{-1}\chi_{12}v_1^2]\}
\end{aligned} \tag{3}$$

Equation 4 expresses the equality of chemical potential of each solvent inside and outside of the gel. Under the restrictions of $v_1 + v_2 = 1$ and $\phi_1 + \phi_2 + \phi_3 + \phi_4 = 1$, the two formulas in Equation 4 become

$$(\frac{\partial\Delta F}{\partial n_i})_{T,P} = (\frac{\partial\Delta F_M}{\partial n_i})_{T,P} + (\frac{\partial\Delta F_E}{\partial\alpha})_{T,P}(\frac{\partial\alpha}{\partial n_i})_{T,P} + (\frac{\partial\Delta F_S}{\partial n_i})_{T,P} = 0 \qquad (i=1,2) \tag{4}$$

$$\ln v_1 + \chi_{12}(1-v_1)^2 = \ln\phi_1 + 1 - \phi_1 - \phi_2 + \chi_{12}\phi_2^2 + \frac{(1-\phi_1-\phi_2)^2}{(p+1)^2} \times (\chi_{13} + \chi_{14}p^2)$$

$$+ \frac{\phi_2(1-\phi_1-\phi_2)}{p+1} \times [(\chi_{12} + \chi_{13} - \chi_{23}) + (\chi_{12} + \chi_{14} - \chi_{24})p]$$

By solving Equations 5 and 6 simultaneously, three equilibrium volume curves as shown in Figure 1 can be obtained and these curves are determined by a set of parameters χ_{ij}, f, p and v which are suitably chosen.

$$+ (\chi_{13} + \chi_{14})p\frac{(1-\phi_1-\phi_2)^2}{(p+1)^2} + vV_1[(\frac{1-\phi_1-\phi_2}{\phi_0})^{\frac{1}{3}} - (f+\frac{1}{2})(\frac{1-\phi_1-\phi_2}{\phi_0})] \tag{5}$$

$$\ln(1-v_1) + \chi_{12}v_1^2 = \ln\phi_2 + 1 - \phi_1 - \phi_2 + \chi_{12}\phi_1^2 + \frac{(1-\phi_1-\phi_2)^2}{(p+1)^2} \times (\chi_{23} + \chi_{24}p^2)$$

$$+ \frac{\phi_1(1-\phi_1-\phi_2)}{p+1} \times [(\chi_{12} - \chi_{13} + \chi_{23}) + (\chi_{12} - \chi_{14} + \chi_{24})p]$$

$$+ (\chi_{23} + \chi_{24})p\frac{(1-\phi_1-\phi_2)^2}{(p+1)^2} + vV_2[(\frac{1-\phi_1-\phi_2}{\phi_0})^{\frac{1}{3}} - (f+\frac{1}{2})(\frac{1-\phi_1-\phi_2}{\phi_0})] \tag{6}$$

Now let us turn our attention to the spinodal curve [7, 8] which is the boundary between the unstable and metastable regions. The stability of the system is determined by the sign of the curvature of the two-dimensional free energy surface which is proportional to the determinant D,

Notice that the determinant D holds true for the four-component system. Under the case where $D = 0$, we obtain, from Equation 7,
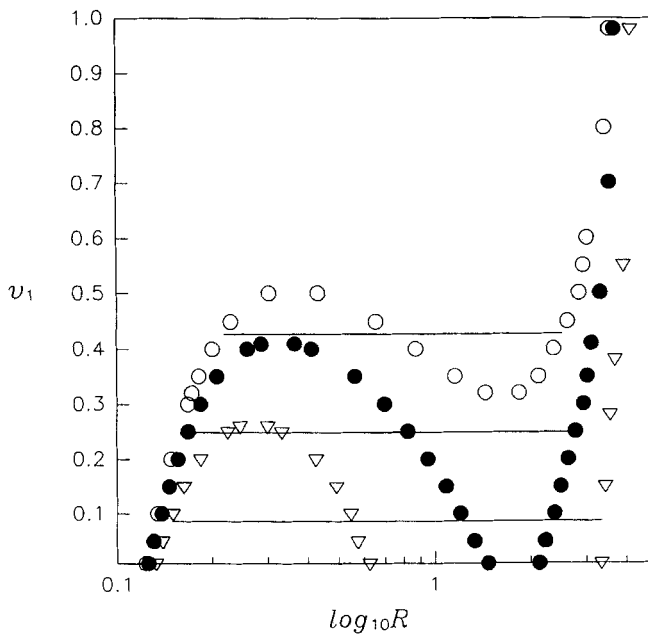
Figure 1. Equilibrium volume curves with $\log_{10} R$ (R is the swelling ratio) plotted against solvent volume fraction of surrounding mixture v_1. The three equilibrium volume curves possess the same paramters,

$\chi_{12} = 0.6$, $\chi_{13} = 0.6$, $\chi_{14} = 0.4$, $\chi_{23} = 1.5$, $\chi_{23} = 1.0$.

Open circle with the parameters $f = 1.9$, $p = 0.15$, $v = 0.04$.

Solid circle with the paramters $f = 2.0$, $p = 0.20$, $v = 0.05$.

Triangle with the paramters $f = 2.1$, $p = 0.30$, $v = 0.07$.

$$D = \det\left[\frac{\partial^2 \Delta F}{\partial n_i \partial n_j}\right]_{i,j=1,2} = \begin{vmatrix} \dfrac{\partial^2 \Delta F}{\partial n_1 \partial n_1} & \dfrac{\partial^2 \Delta F}{\partial n_1 \partial n_2} \\ \dfrac{\partial^2 \Delta F}{\partial n_2 \partial n_1} & \dfrac{\partial^2 \Delta F}{\partial n_2 \partial n_2} \end{vmatrix} \tag{7}$$

$$\frac{(1-\phi_1-\phi_2)^2}{\phi_1\phi_2} - \frac{2(1-\phi_1-\phi_2)^2}{p+1}\left(\frac{\chi_{13}+p\chi_{14}}{\phi_2} + \frac{\chi_{23}+p\chi_{24}}{\phi_1}\right) - \frac{(1-\phi_1-\phi_2)^2}{p+1}\{(\chi_{12}-\chi_{13}-\chi_{23})^2$$

$$+ p(\chi_{12}-\chi_{14}-\chi_{24})^2 - \frac{4}{(p+1)}(\chi_{13}\chi_{23}+p^2\chi_{14}\chi_{24}) - \frac{p}{p+1}\{(\chi_{13}-\chi_{14}+\chi_{23}-\chi_{24})^2$$

By solving Equations 5, 6 and 8 simultaneously, the spinodal curve can be obtained. For brevity, the calculated result is omitted here.

$$-4(\chi_{14}\chi_{23} + \chi_{13}\chi_{24})]\} - v(\frac{V_2}{\phi_1} + \frac{V_1}{\phi_2} - 2V_2\chi_{12})[\frac{1}{3}(\frac{1-\phi_1-\phi_2}{\phi_0})^{\frac{1}{3}} - (f + \frac{1}{2})(\frac{1-\phi_1-\phi_2}{\phi_0})] = 0 \quad (8)$$

When taking $\phi_4 = 0$, it is not difficult to find that Equations 5, 6 and 8 can be reduced to the three-component forms which were obtained by Iwatsubo [7, 8] , i.e., the Equations 9, 10 and 12 in Reference 8. Alternatively, when considering, and $\chi_{13} = \chi_{14}$, $\chi_{23} = \chi_{24}$ and replacing the term ϕ_3 and ϕ_4 as a whole by ϕ_3. Equations 5, 6 and 8 can also be reduced to the three-component forms. Furthermore, if the surrounding mixture is replaced by a pure solvent, Equation 5 or 6 can be directly reduced to the formula of Tanaka [1, 2].

RESULTS AND DISCUSSION

In this section, we shall deal with the "normal pattern" volume phase transition [9] and the transition caused by the variation of the ratio of the two components in the copolymer network. The "normal pattern" volume phase transition means that when one of two components in the copolymer network, which can offer ions and crosslinks simultaneously, increases, the volume change of the gel increases accordingly, and then the transition point moves downward to the lower solvent composition [9]. This solvent is assigned in this paper as solvent 1. It is easily seen that for the equilibrium volume curves in Figure 1, $\log_{10} R$ (R is the swelling ratio) is plotted against volume fraction of solvent 1 in the surrounding mixture v_1. In Figure 1, the three equilibrium volume curves keep the same interaction parameters $\{\chi_{ij}\}$, whereas the parameters p, f, and v are different for each of the curves. The details for building up the equilibrium volume curves have been reported in Reference 8. It should be noted that associated with the three equilibrium volume curves, there are three solid lines and these lines characterize, in essence, the volume phase transitions [1, 2, 7, 8]. In obtaining the solid lines, the spinodal curve technique [8] has been used by solving Equations 5, 6 and 8. When solvents 1 and 2 are taken as water and acetone, and the components 3 and 4 as acrylamide and 2-(acryloyloxy) ethyl acid phosphate, the three curves together with the three solid lines as shown in Figure 1, which describe the volume phase transition, are in harmony with the experimental "normal pattern" curves [9].

By using the similar procedure done for approaching the volume phase as shown in Figure 1, we can obtain the equilibrium volume curves A, B and C as shown in Figure 2. These three curves describe the volume phase transition of an
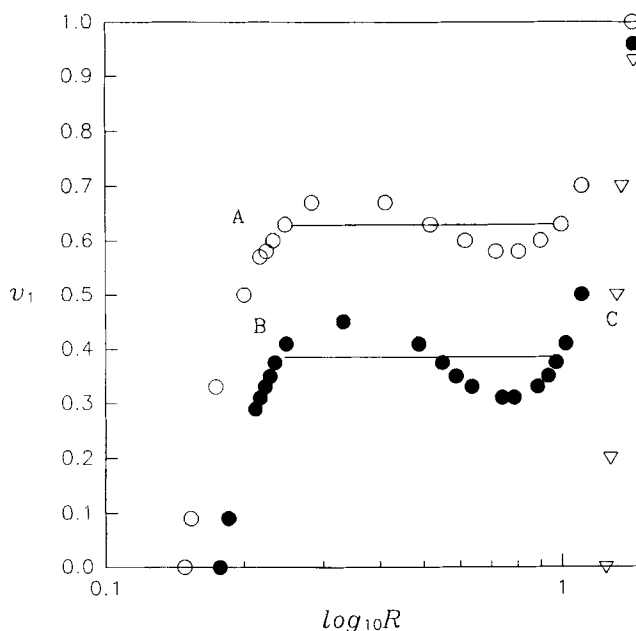
Figure 2. Equilibrium volume curves with $\log_{10} R$ (R is the swelling ratio) plotted against copolymer composition W. The three equilibrium volume curves possess the same paramters,

$\chi_{12} = 0.6$, $\chi_{13} = 0.6$, $\chi_{14} = 0.4$, $\chi_{24} = 1.0$, $f = 1.0$, $v = 0.1$, $v_I v = 0.2$.

A: the open circle with the paramter $\chi_{23} = 1.5$.

B: the solid circle with the paramter $\chi_{23} = 1.3$.

C: the triangle with the paramter $\chi_{23} = 1.1$.

ionic gel ($f \neq 0$) which arises from the variation of the ratio of the two components in the copolymer network.

In Figure 2, $\log_{10} R$ (R is the swelling ratio) is plotted against the composition of the two components W in the copolymer network. In obtaining the equilibrium volume curves, it is not difficult to find that when all of the five interactions χ_{12}, χ_{13}, χ_{14}, χ_{23}, and χ_{24}, are taken as variables or any one of them is taken as variable with the remaining ones which are fixed, it will lead us to the curves with similar features as the curves A, B and C shown in Figure 2. For brevity, we choose in this paper χ_{23} as variable, with the parameters χ_{12}, χ_{13}, χ_{14}, χ_{24}, f, v and v_I which are fixed, to obtain the curves A, B and C as shown in Figure 2. It implies that the three curves A, B and C may correspond to different

temperatures. When the temperature increases (the interaction χ_{23}, goes small), curve A approaches curve B, and consecutively, curve B to curve C. It means that the gel swells, as the temperature increases. It seems that this temperature-dependent behavior (curve A moves via curve B to curve C) can cover that behavior of the thermo-swelling gel which was observed experimentally [1, 2], if the crosslinking agent is regarded as the fourth component in the four-component model.

In order to keep this paper brief, the treatment of the "reverse pattern" and the "combined pattern" volume phase transtions will be reported in a consecutive paper.

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