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## **A FOUR-COMPONENT MODEL FOR VOLUME PHASE TRANSITION: DISCUSSION OF REVERSE PATTERN AND COMBINED PATTERN**

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### **ABSTRACT**

As an extension of “normal pattern” volume phase transition, the four-component model of a hydrogel, which consists of a copolymer network and a solution with two solvents, is further applied to the “reverse pattern” and “combined pattern” proposed by Katayama. It is shown that these two kinds of volume phase transitions can be explained by choosing interaction parameters suitably.

### **INTRODUCTION**

As is well known, a polymer gel can undergo an abrupt volume change when the environments, such as temperature, solvent composition and pH, change smoothly. This kind of phenomenon is a critical behavior and named volume phase transition. It was observed experimentally by Tanaka and explained by means of Flory-Huggins theory [1-3]. Recently, Iwatsubo discussed convex type volume phase transition and proposed a three-component model [5, 6]. As an extension, a four-component model was presented in a previous paper [7] to deal with the “normal pattern” volume phase transition of Katayama [8]. In this paper, an attempt is made to apply further the four-component model to the “reverse pattern” as well as “combined pattern” [8]. It is shown that by choosing the interaction parameters properly, the volume phase transitions in which the “reverse pattern” and “combined pattern” are involved can be explained.

## THEORETICAL SECTION

In order to make our discussion for the “reverse pattern” and “combined pattern” easier, let us write down some basic formulas for the four-component model of volume phase transition [7] which is, in essence, an extension of the three-component theory of Iwatsubo [6].

The conventional equilibrium conditions can be written as:

$$\begin{aligned}
 \ln v_1 + \chi_{12}(1 - v_1)^2 &= \ln \phi_1 + 1 - \phi_1 - \phi_2 + \chi_{12}\phi_2^2 \\
 &+ \frac{(1 - \phi_1 - \phi_2)^2}{(p+1)^2} \times (\chi_{13} + \chi_{14}p^2) \\
 &+ \frac{\phi_2(1 - \phi_1 - \phi_2)}{p+1} \times [(\chi_{12} + \chi_{13} - \chi_{23}) + (\chi_{12} + \chi_{14} - \chi_{24})p] \\
 &+ (\chi_{13} + \chi_{14})p \frac{(1 - \phi_1 - \phi_2)^2}{(p+1)^2} \\
 &+ vV_1 \left[ \left( \frac{1 - \phi_1 - \phi_2}{\phi_0} \right)^{\frac{1}{3}} - \left( f + \frac{1}{2} \right) \left( \frac{1 - \phi_1 - \phi_2}{\phi_0} \right) \right] \quad (1)
 \end{aligned}$$

$$\begin{aligned}
 \ln(1 - v_1) + \chi_{12}v_1^2 &= \ln \phi_2 + 1 - \phi_1 - \phi_2 + \chi_{12}\phi_1^2 + \frac{(1 - \phi_1 - \phi_2)^2}{(p+1)^2} \times (\chi_{23} + \chi_{24}p^2) \\
 &+ \frac{\phi_1(1 - \phi_1 - \phi_2)}{p+1} \times [(\chi_{12} - \chi_{13} + \chi_{23}) + (\chi_{12} - \chi_{14} + \chi_{24})p] \\
 &+ (\chi_{23} + \chi_{24})p \frac{(1 - \phi_1 - \phi_2)^2}{(p+1)^2} \\
 &+ vV_2 \left[ \left( \frac{1 - \phi_1 - \phi_2}{\phi_0} \right)^{\frac{1}{3}} - \left( f + \frac{1}{2} \right) \left( \frac{1 - \phi_1 - \phi_2}{\phi_0} \right) \right] \quad (2)
 \end{aligned}$$

Furthermore, the boundary between the unstable and metastable regions, which is called spinodal curve, takes the form

$$\begin{aligned}
 &\frac{(1 - \phi_1 - \phi_2)^2}{\phi_1\phi_2} - \frac{2(1 - \phi_1 - \phi_2)^2}{p+1} \left( \frac{\chi_{13} + p\chi_{14}}{\phi_2} + \frac{\chi_{23} + p\chi_{24}}{\phi_1} \right) \\
 &- \frac{(1 - \phi_1 - \phi_2)^2}{p+1} \{ (\chi_{12} - \chi_{13} - \chi_{23})^2 + p(\chi_{12} - \chi_{14} - \chi_{24})^2 \} \\
 &- \frac{4}{(p+1)} (\chi_{13}\chi_{23} + p^2\chi_{14}\chi_{24}) - \frac{p}{p+1} [(\chi_{13} - \chi_{14} + \chi_{23} - \chi_{24})^2]
 \end{aligned}$$

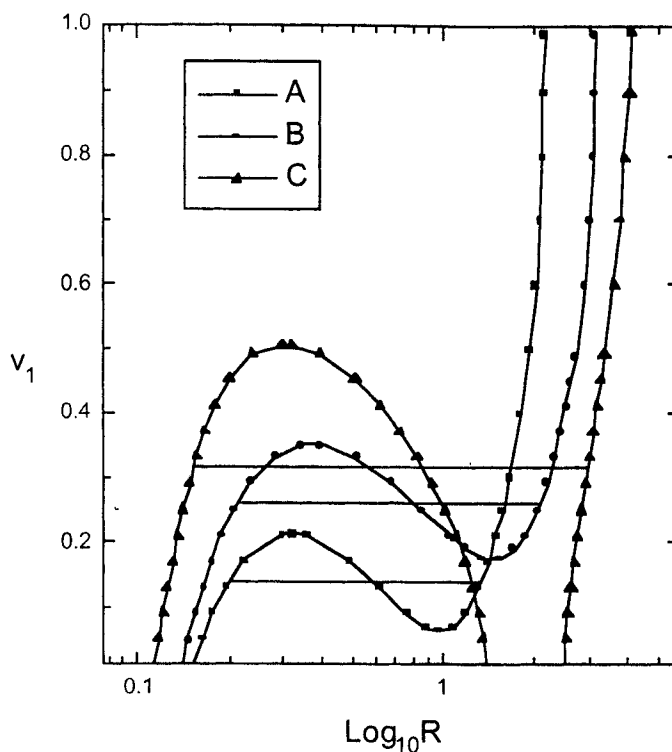
$$\begin{aligned}
 -4(\chi_{14}\chi_{23} + \chi_{13}\chi_{24}) \}} - v \left( \frac{V_2}{\phi_1} + \frac{V_1}{\phi_2} - 2V_2\chi_{12} \right) \\
 \left[ \frac{1}{3} \left( \frac{1 - \phi_1 - \phi_2}{\phi_0} \right)^{\frac{1}{3}} - \left( f + \frac{1}{2} \right) \left( \frac{1 - \phi_1 - \phi_2}{\phi_0}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

where  $v_i$  ( $i=1, 2$ ) is the volume fraction of solvent  $i$  in the surrounding mixture with  $v_1 + v_2 = 1$ ;  $\chi_{ij}$  ( $i=1, 2; j=1, 2, 3, 4; i < j$ ) is the interaction parameter between component  $i$  and  $j$ ;  $\phi_i$  ( $i=1, 2, 3, 4$ ) is the volume fraction of component  $i$  in the gel with  $\phi_1 + \phi_2 + \phi_3 + \phi_4 = 1$ ;  $\phi_0$  is the volume fraction of the polymer network when the constituent chains are in a random configuration state, ( $\phi_0$  is taken as 0.1 in this paper);  $p$  is the ratio of  $\phi_4$  and  $\phi_3$ ,  $p = \frac{\phi_4}{\phi_3}$ ;  $v$  is the number of constituent chains per unit volume of the polymer network when  $\phi_3 + \phi_4 = \phi_0$ ;  $V_i$  ( $i=1, 2$ ) is the molecular volume of solvent  $i$  ( $V_1$  is taken as unity in this paper);  $f$  is the average number of ionized group per constituent chain.

### RESULTS AND DISCUSSION

Let us give a brief discussion on the “reverse pattern” and the “combined pattern” [8]. “Reverse pattern” volume phase transition means that, when in the copolymer network, one of two components which can offer ions and crosslinks simultaneously (component 4), increases, the volume change of the gel increases accordingly, and then the transition threshold moves upward to the higher solvent composition. “Combined pattern” volume phase transition means that when component 4 increases, the volume change of the gel varies non-monotonically, and the transition threshold moves non-monotonically also.

The equilibrium volume curves for “reverse pattern” volume phase transition based on Equations 1 and 2 are shown in Figure 1, where  $\log_{10} R$  (the swelling ratio  $R$  is defined as  $R = \frac{\phi_0}{(\phi_3 + \phi_4)}$ ) is plotted against volume fraction of solvent 1 in surrounding mixture  $v_1$ . The parameters  $p, f, v$  and the interaction parameters  $\{\chi_{ij}\}$  are selected properly to get three equilibrium volume curves in Figure 1. It should be noted that unlike what we have done in Reference 7, where the interaction parameters  $\{\chi_{ij}\}$  were kept unchangeable for all curves, the interaction parameters  $\{\chi_{ij}\}$  in this paper can be changed for different curves. The reason is, that according to the Hirotsu and Tanaka theory [3, 9], the variations of interaction parameters  $\{\chi_{ij}\}$  may describe partly the hydrophobic effect. So, we can choose different  $\chi_{23}$  and  $\chi_{24}$  as parameters to get curves A, B and C as shown in Figure 1.



**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 parameters,

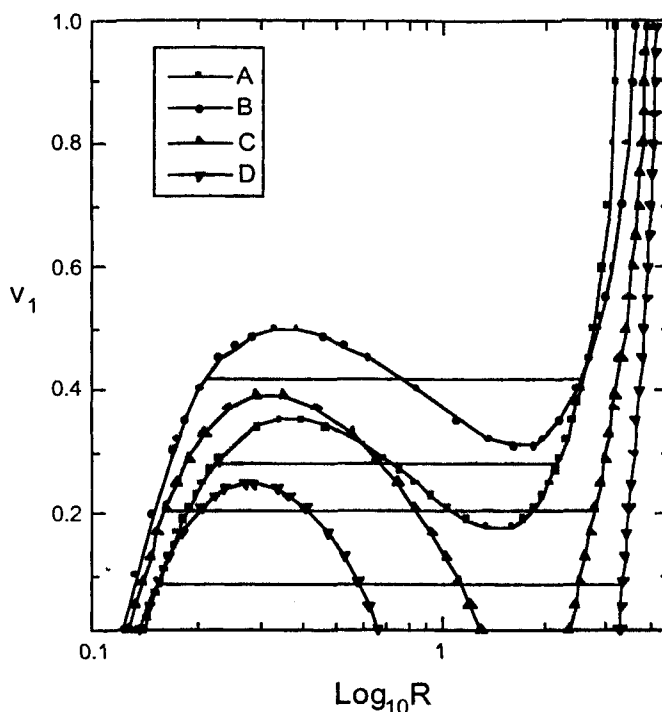
$$s = 1, \chi_{12} = 0.6, \chi_{13} = 0.6, \chi_{14} = 0.4.$$

Curve A with the parameters  $f=1.2, p=0.1, v = 0.008, \chi_{23} = 1.6, \chi_{24} = -3.5$ .

Curve B with the parameters  $f=1.7, p=0.15, v = 0.004, \chi_{23} = 1.5, \chi_{24} = -1$ .

Curve C with the parameters  $f=2.1, p=0.3, v = 0.007, \chi_{23} = 1.5, \chi_{24} = 3$ .

We can see from Figure 1 that curves A, B and C are in harmony with the “reverse pattern” volume phase transition in the experiment of Katayama [8]. Because  $\chi_{ij}$  is defined as  $\chi_{ij} = \frac{\Delta F_{ij}}{kT}$  in this paper, the increase of  $\chi_{ij}$  (for example, from  $\chi_{24} = -3.5$  in curve A, to  $\chi_{24} = 3$  in curve C of Figure 1) means that the interaction between component  $i$  and  $j$  increases, i.e., more positive  $\chi_{ij}$  is, the interaction between component  $i$  and  $j$  is more unfavorable. So the variations of  $\{\chi_{ij}\}$  can be depicted as considering some kind of interactions such as hydrophobic



**Figure 2.** Equilibrium volume curves with  $\log_{10}R$  ( $R$  is the swelling ratio) plotted against solvent volume fraction of surrounding mixture  $v_1$ .

The four equilibrium volume curves possess the same parameters,  
 $s = 1$ ,  $\chi_{12} = 0.6$ ,  $\chi_{13} = 0.6$ ,  $\chi_{14} = 0.4$ ,  $\chi_{23} = 1.5$ .

Curve A with the parameters  $f=1.7$ ,  $p=0.15$ ,  $\nu = 0.004$ ,  $\chi_{24} = -1$ .

Curve B with the parameters  $f=1.9$ ,  $p=0.17$ ,  $\nu = 0.004$ ,  $\chi_{24} = 1$ .

Curve C with the parameters  $f=2$ ,  $p=0.2$ ,  $\nu = 0.005$ ,  $\chi_{24} = 1$ .

Curve D with the parameters  $f=2.1$ ,  $p=0.3$ ,  $\nu = 0.007$ ,  $\chi_{24} = 1$ .

interaction and hydrogen bond effect. Hydrophobic interaction may affect  $\nu$  (number of constituent chains per unit volume of polymer network when  $\phi_3 + \phi_4 = \phi_0$ ) which is also changeable in Figure 1. This can be explained as follows: the variation of hydrophobic interaction may cause the formation or decomposition of some "pseudo cross-links" [10], so the number of constituent chains per unit volume  $\nu$  changes consequently.

By the similar procedure as we have done for approaching the volume phase transition as shown in Figure 1, we can obtain the equilibrium volume curves A, B, C, D in Figure 2 where  $\log_{10}R$  ( $R$  is the swelling ratio) is plotted against volume fraction of solvent 1 in surrounding mixture  $v_1$ .

It should be noted again that the interaction parameters  $\{\chi_{ij}\}$  and  $\nu$  were also changeable. When  $p$  and  $f$  increase,  $\chi_{23}$  and  $\nu$  were chosen properly to get the equilibrium volume curves from A to D. It can easily be seen in Figure 2 that the threshold of volume phase transition changes non-monotonically (from A through B to D) which is in harmony with the "combined pattern" volume phase transition in Reference 8. It is also due to hydrophobic interaction that this kind of non-monotonic change can be explained.

## CONCLUSION

When the  $\{\chi_{ij}\}$  and  $\nu$  are changeable due to the hydrophobic interaction, the "reverse pattern" and "combined pattern" volume phase transitions may be explained qualitatively in the present theory.

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