

QUANTITATIVE ANALYSIS ON SWELLING BEHAVIOR OF IONIC GELS IN THE MIXED SOLVENTS

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Abstract—Phase transition was observed in HSMA/PVA IPN gels having ionizable groups with 3-dimensional network structure in the mixed solvents such as water-methanol, water-acetone or water-ethanol. In order to analyze this phenomena quantitatively, two adjustable parameters related to gel properties were determined from the model based on Tanaka theory. One was the number of dissociated counterions per effective chain (f), the other was the interaction parameters (χ_{ij}) between gel and water. As increasing the composition of water, swelling of the gels occurs in the mixed solvent; the gel was shrunk instead when the water content was decreased, which was reversible regardless of the path of swelling and shrinking. A degree of swelling or shrinking of the gel was dependent upon these χ_{ij} and f of the gel. With smaller χ_{ij} and larger f , more rapid phase transition was observed. Additionally, swelling and shrinking behavior of the gel in system of two solvents and one polymer was influenced not only by χ_{ij} between gel and solvents but also by χ_{ij} between two solvents.

INTRODUCTION

As one of the advanced materials, polymer gels have been studied a lot because of their wide applicabilities for various industries. Especially soft contact lens, personal care products such as infant disposable diapers, femine pads, and medical sheets, agricultural items like soil conditioners have been already commercialized based on their absorbability. Generally speaking, these polymer gels are consisted of polymer chains having hydrophilic ionic groups in the 3-dimensional network structure, so that they can show the phase transition of rapid swelling-shrinking due to small change of external stimuli such as temperature [1-4], pH [5, 6], ionic strength or electrical potential [7]. Recently, several works have been focused on the possibility of polymer gels in the fields of drug delivery system, artificial muscle, separation membrane or switching sensors utilizing these properties [8, 9]. Therefore in order to accelerate the usage of these materials in newly developed areas, it is necessary to look into in details not only dynamic response of

polymer gels but also its relationship between the basic structure and property.

In this study swelling behaviors of HSMA/PVA IPN gels in the mixed solvents will be searched to see the phase transition according to the composition of the solvents in order to obtain the structure-related properties of polymer gels in the water such as the amount of polyions in the gel network, interaction parameter between gel and water.

Mixed solvents such as water-acetone, water-methanol, or water-ethanol, will be considered, where phase transition occurs when water composition is less than that of other solvent [5, 11]. Polymer gels with lots of ions have usually a broad range of phase transition. Tanaka has developed a theory to explain this phenomena qualitatively [10]. In order to investigate swelling behavior in the mixed solvents quantitatively, it is necessary to have several physical parameters such as interaction parameters between gel and solvents, ion content in the gel etc. in advance. Here we are trying to evaluate several parameters of new polymer gels synthesized by means of comparing the swelling data with a model based on Tanaka theory. Especially interaction parameters between solvent and

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solvent will be compared with other values reported elsewhere and effective polyion concentration and interaction parameter between gel and water will be used for the characterization of synthesized polymer gels, which may be useful in interpretation of electrical behavior of polymer gels in the water.

TANAKA THEORY

It is well known that polymer gels are soft compared with solid polymers, which swell or shrink according to the amount of liquid to exhibit various useful properties. Their properties are dependent not only upon the hydrophilic/hydrophobic nature of polymer itself of which the 3-dimensional network structure is composed, but also upon the solvent contained in the gel. Tanaka [10] has tried to explain the swelling and shrinking phenomena of the gel via the four osmotic forces based on Flory-Huggins theory [12]. Here, the sign of osmotic forces will be positive when the gel swells.

1. Elastic Pressure due to the Network

A polymer chain in vacuum will have a lot of conformation due to the thermal motion of the chain to exhibit a finite end-to-end distance depending upon its average conformation. Generally a polymer chain in equilibrium will tend to have the most stable conformation distribution with a finite end-to-end distance. Thus if one tries to stretch the chain from equilibrium, then a force is arising to lessen the distance. On the other hand if the chain is contracted, a force is apparent to stretch the chain to the equilibrium distance. Thermal effect can be considered similarly; at high temperature, vigorous thermal motion of the chain will tend to reduce the end-to-end distance. This force can be treated as an elastic pressure π_1 .

$$\pi_1 = \nu kT \left\{ \frac{\phi}{\phi_0} - \left(\frac{\phi}{\phi_0} \right)^{1/3} \right\} \quad (1)$$

Here, ν is the number of effective chains per unit volume at $\phi = \phi_0$; ϕ and ϕ_0 are the volume fraction of polymer chains of the network and that at random conformation respectively. And k and T denote the Boltzmann constant and absolute temperature respectively.

2. Pressure due to the Interaction between Gel and Solvent

Water soluble polymers such as polyacrylamide etc., dissolve in the water, and polystyrene dissolves in organic solvents such as benzene and toluene, when the interaction between a specific polymer and a solvent is stronger than that between polymer themselves. The interaction between polymer and solvent

will generate an osmotic pressure π_2 , which is given by Eq. (2).

$$\pi_2 = -\Delta F \phi^2 / \nu \quad (2)$$

Here, ΔF is the free energy change based on the interaction between polymer network and solvents, ν is the volume per unit mole of the liquid.

3. Pressure due to the Counter Ions in the Network

Pressure due to the counter ion in the gel network can be easily understood if one thinks of gas pressure in the balloon. Gas molecules in the balloon can move freely and they will generate the pressure due to the collision with the wall of balloon. Similarly counter ions in the gel structure with anionic carboxyl part will be confined in the gel in order to conserve the electrical neutrality. Thus counter ions can move freely only in the gel to produce the pressure π_3 , as shown in Eq. (3).

$$\pi_3 = f \nu kT (\phi / \phi_0) \quad (3)$$

Here, f is the number of counter ions per a polymer chain between crosslinking points in the gel structure.

4. Pressure due to the Mixing Entropy

Polymer gel and solvents are interacting each other; if gel does not exist, solvent will flow freely, and if solvent does not exist, gel cannot swell at all. Therefore the entropy of the mixture is different from simple average entropy of the gel and solvent, which will cause an osmotic pressure. If one has n mols of liquid, mixing entropy ΔS and gel volume V will be given by Eqs. (4) and (5).

$$\Delta S = n \ln(1 - \phi) \quad (4)$$

$$V = n \nu / (1 - \phi) \quad (5)$$

Thus the pressure π_4 can be derived as Eq. (6) on the basis of this entropy change.

$$\pi_4 = \delta(kT \Delta S) / \delta V = (kT/\nu) \{ \ln(1 - \phi) + \phi \} \quad (6)$$

Once above four types of pressures are given, an equation of state for polymer gel can be derived by the simple addition.

$$\pi = \pi_1 + \pi_2 + \pi_3 + \pi_4 \quad (7)$$

Here, π is the total pressure of the polymer gel, which will be zero at equilibrium. Then Eq. (7) becomes (8) as following:

$$\begin{aligned} \Delta F/kT = S_0 \phi_0^3 / \phi^2 \{ (2f+1)(\phi/\phi_0) - 2(\phi/\phi_0)^{1/3} \} \\ - 2/\phi - 2 \ln(1 - \phi) / \phi^2 \end{aligned} \quad (8)$$

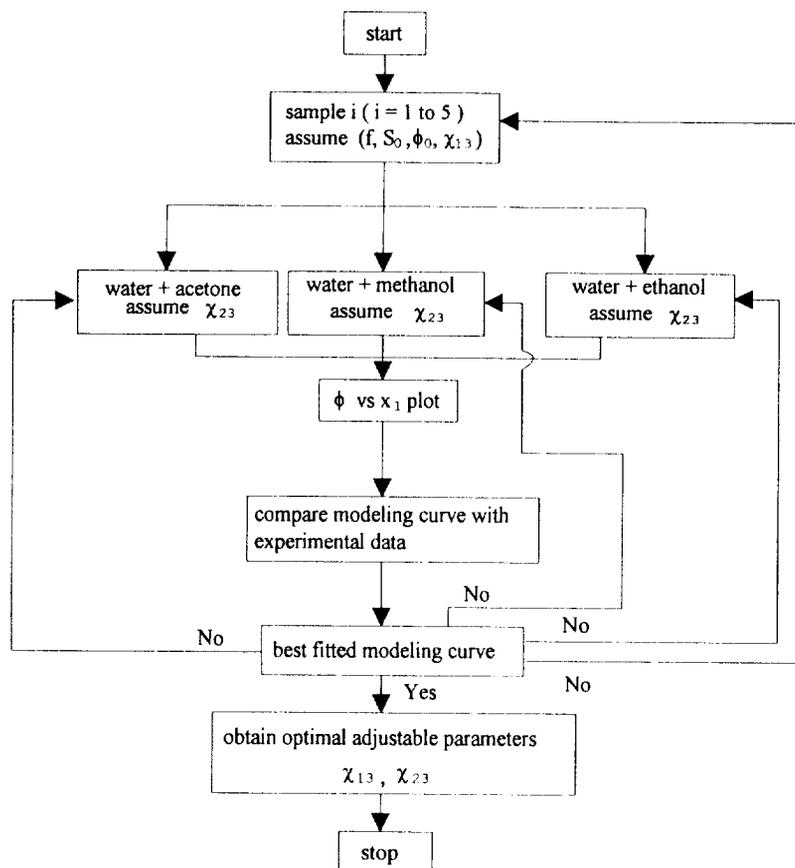


Fig. 1. Algorithm to obtain interaction parameters for several mixed solvent systems.

Here, S_0 denotes $v_0/\phi_0^3 N$, and ΔF is nothing but the excess free energy. f is the number of ions between crosslinking points. N is the Avogadro number. Thus this Eq. (8) can explain how the volume of polymer gels changes with temperature and composition of the mixed solvents quantitatively [13].

MODELLING AND ANALYSIS

If one adopts the single-liquid approximation to assume the mixed solvents as a single liquid to say that polymer gel does not have any selective adsorption for any solvent, then excess free energy ΔF can be expressed as a function of solvent compositions [14].

$$\Delta F = x_1 \Delta F_{13} + x_2 \Delta F_{23} - x_1 x_2 \Delta F_{12} \quad (9)$$

Here x_1 and x_2 ($= 1 - x_1$) are mole fractions of solvent 1 and solvent 2 respectively. And ΔF_{13} and ΔF_{23} are the changes of the free energy due to the interaction between solvent 1 and polymer gel 3, and interaction

between solvent 2 and polymer gel 3, ΔF_{12} is change of free energy between solvent 1 and solvent 2. Here it is also assumed that polymer gels have a homogeneous structure in the sense of interaction with solvents even though gels are IPN.

In this study solvent 1 is fixed as water, and solvent 2 is one of the three organic solvents such as acetone, methanol, and ethanol.

It is customary to use the following relationship between interaction parameter (χ_{ij}) and free energy change (ΔF_{ij}).

$$\chi_{ij} = \Delta F_{ij} / 2\kappa T \quad (10)$$

Now we would like to divide the parameters according to the dependence on solvent 2. First group such as f , S_0 , ϕ_0 , χ_{13} are independent of solvent 2, and second group such as χ_{12} , χ_{23} are dependent upon solvent 2. Last group will be ϕ as shown in (11).

$$x_1 = f(f, S_0, \phi_0, \chi_{13}, \chi_{12}, \chi_{23}, \phi) \quad (11)$$

Table 1. Preparation of HSMA/PVA IPN gels having ionic groups

Sample	HSMA ^a		CA ^b		H-PVA ^c	
	gr	mol*	gr	mol*	gr	mol*
1	3.2	1	1.07	0.1	0	0
2	3.2	1	1.07	0.1	0.16	0.1
3	3.2	1	1.07	0.1	0.32	0.2
4	3.2	1	1.07	0.1	0.48	0.3
5	3.2	1	2.14	0.2	0.16	0.1

a: Hydrolyzed styrene-maleic anhydride alternating copolymer, b: poly (ethylene glycol 600 diglycidyl ether) used as a crosslinking agent, c: 80%-hydrolyzed poly (vinyl alcohol), *denote the number of mole per repeating unit.

Once first group ($f, S_n, \phi_n, \chi_{13}$) is chosen, ϕ can be obtained as a function of x_1 if two interaction parameters (χ_{12}, χ_{23}) are known. Solvent-solvent interaction parameter will be chosen fixed, but interaction parameter between gel and solvent 2 will be adjusted to give the best fitting. Optimal values are going to be searched for three solvent systems, but if that is difficult, then parameters of gel will be adjusted to repeat the above algorithm, which is shown in Fig. 1.

EXPERIMENTS

1. HSMA/PVA IPN Cylindrical Gel

HSMA/PVA IPN gels used in this study have five different compositions as shown in Table 1. They were synthesized according to the following procedure, of which the details can be found in the separate report [15]. Here in Fig. 2 schematic method of synthesis and final structure are shown.

First 50 g of Styrene-Maleic Anhydride alternating copolymer (Aldrich) will be reacted with water in 325 cc of 1M-KOH aqueous solution for 2 days at room temperature with agitation, and then be precipitated by adding excess isopropyl alcohol. White colored HSMA (Hydrolyzed Styrene-Maleic Anhydride alternating copolymer) will be obtained after filtration followed by two day's drying. A specific amount of HSMA will be dissolved in the distilled water to give a transparent solution. And then the crosslinking agent and PVA are added into HSMA solution with vigorous agitation for 30 min. Air bubble in the mixture should be removed in the centrifuge. After putting the mixture free of air into glass tube of 2 mm inner diameter, it was crosslinked in the hot oven for 21 hours at 80°C followed by for 5 hours' reaction at 110°C. Finally after some time, cylindrical sample will be cutted from

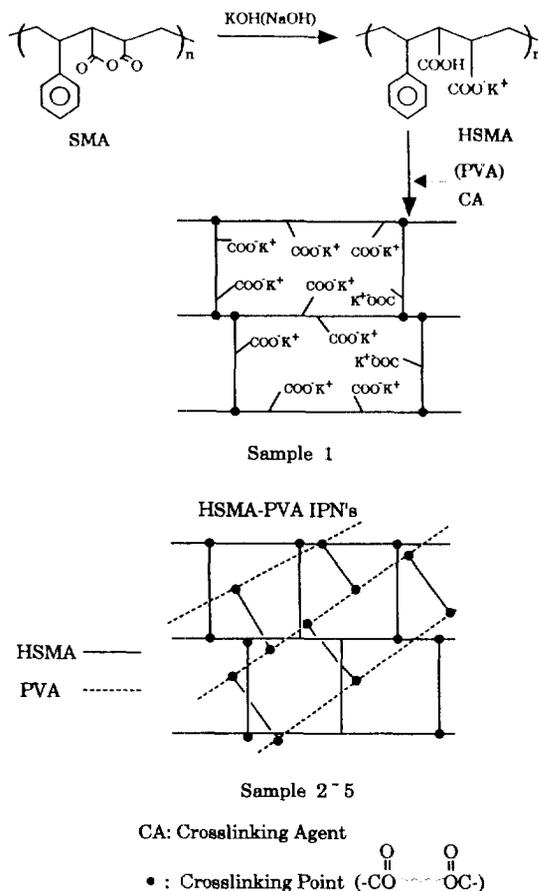


Fig. 2. Preparation and schematic structure of HSMA/PVA IPN gels.

the polymer gel about 2.0 cm in length.

2. Swelling Experiments

The principal purpose of swelling experiment is to estimate the ion concentration in the polymer gels and to examine the behavior of gels in the mixed solvents by measuring the swelling extents in the three sets of mixed solvent systems (water+acetone, water+methanol, water+ethanol) at room temperature. Detailed procedures are as follows:

Firstly, polymer gels synthesized were cut into 2 cm length and measure their weights (sample 1-sample 5). For the swelling experiments, they were put into 100% acetone and the weight were measured every hour after some time until the weight is unchanged. Similarly, the equilibrium weight were measured in from 90% acetone (10% water) to 0% acetone (pure water) successively. Swelling experiments were repeated using not only methanol instead of acetone but

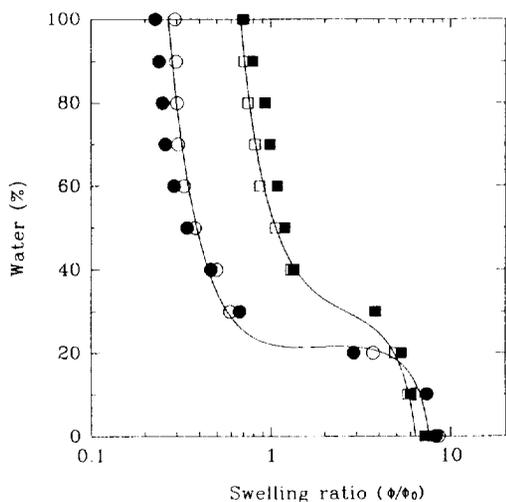


Fig. 3. Swelling behavior of HSMA/PVA IPN gels by the solvent composition of pure water and acetone. Solid lines were obtained from the modeling. Swelling in pure water first and then shrinking with adding acetone: (○; sample 3, □; sample 5); shrinking in pure acetone first and then swelling with adding waters (●; sample 3, ■; sample 5)

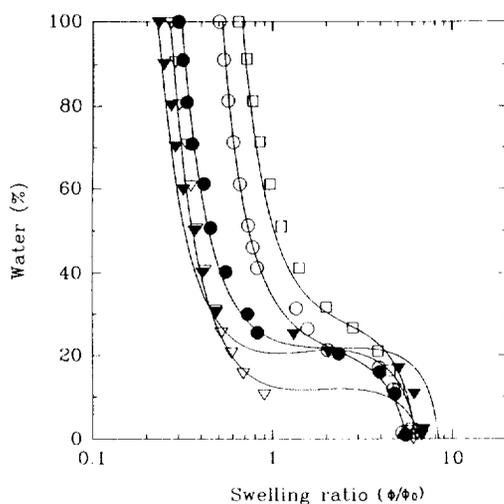


Fig. 4. Swelling behavior of HSMA/PVA IPN gels by the solvent composition of pure water and methanol. Solid lines were obtained from the modeling; sample 1 (○), sample 2 (●), sample 3 (▽), sample 4 (▼), sample 5 (□).

also ethanol.

RESULTS AND DISCUSSIONS

1. Swelling Behavior

Polymer gel in general can swell and shrink according to the composition of mixed solvents due to its network structure. This structure give a sharp change in volume with small change of composition of solvents, which is called a phase transition. Sometimes this transition occurs at different composition depending upon path of composition change. In other word, a certain polymer gel shows a rapid transition of swelling when adding the second component gradually after swelled in the water, however this gel does not show such a rapid change in swelling when adding water gradually after swelled in the second solvent such as acetone, methanol, or ethanol first. In this experiment, it shows a reversible phase transition regardless of the path of swelling as shown in Fig. 3, which may imply that our gels have reliable properties.

Solid lines in Fig. 3 are drawn from the mathematical model obtained by previously mentioned algorithm in order to explain the swelling behavior quantitatively. Experimental values are obtained via measuring the weight changes during swelling by assuming the

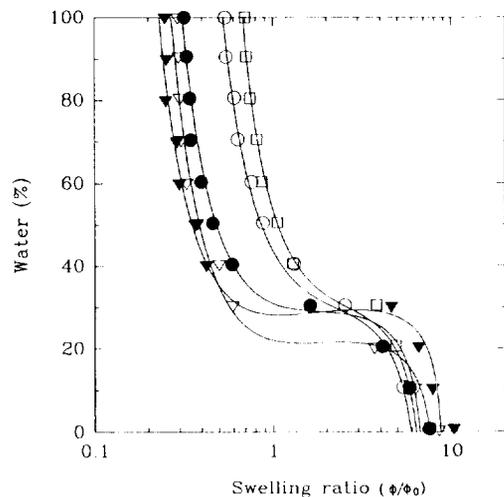


Fig. 5. Swelling behavior of HSMA/PVA IPN gels by the solvent composition of pure water and acetone. The solid lines and symbols are the same as in Figure 4.

constant density. The difference in density of IPN gels may be in the range of experimental errors.

2. Swelling Behaviors for Different Gels

Three different mixed solvent systems have been used for swelling experiment. Swelling ratios (ϕ/ϕ_0) are plotted against the composition of solvents x in Fig. 4 (methanol+water), Fig. 5 (acetone+water) and

Table 2. The adjustable parameters obtained from the modeling based on Tanaka theory

Sample	ϕ_0	S_0	f	water (1)+gel (3)	acetone (2)+gel (3)	methanol (2)+gel (3)	ethanol (2)+gel (3)
				χ_{13}	χ_{23}	χ_{23}	χ_{23}
1	0.145	7.0	0.400	-0.70	1.80	1.40	2.05
2	0.138	4.8	0.830	-1.28	2.00	1.65	2.20
3	0.120	6.0	0.950	-2.00	1.90	1.40	2.50
4	0.110	7.5	1.100	-2.30	2.55	2.00	2.85
5	0.140	2.0	0.315	-0.65	1.80	1.70	2.15

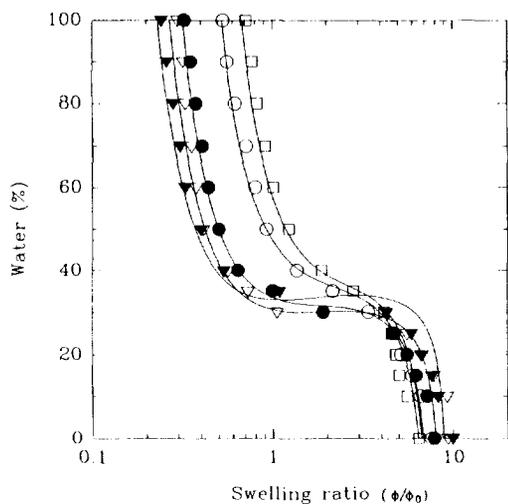


Fig. 6. Swelling behavior of HSMA/PVA IPN gels by the solvent composition of pure water and ethanol. The solid lines and symbols are the same as in Figure 4.

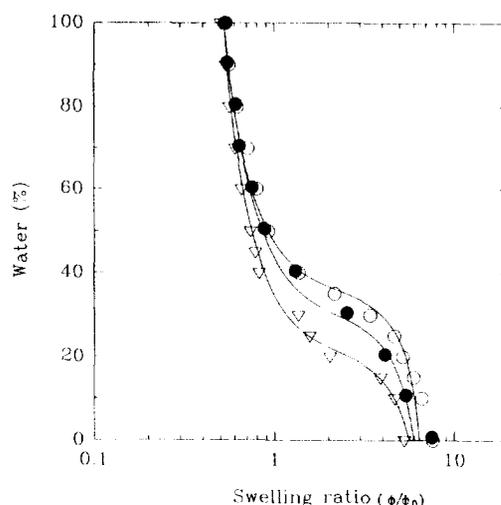


Fig. 7. Swelling behavior of sample 1 by the composition of mixed solvents: ethanol+water (\circ), acetone+water (\bullet), methanol+water (∇). The solid lines were obtained from the modeling.

Fig. 6 (ethanol+water). Solid lines in each plot were obtained according to modelling, of which the most appropriate values of parameters are tabulated in Table 2. The interaction parameters between solvent and solvent are fixed since they do not depend on gel's properties; 1.00 for water+acetone, 0.95 for water+methanol and 1.20 for water+ethanol. The values are not rigorously obtained but are chosen somewhat arbitrarily. As shown in Fig. 4, samples 1, 5 swell rather continuously in the mixed solvents, but samples 2, 3, 4 show a rather sudden change. And, as shown in Fig. 5 and 6, similar phenomena are observed for other sets of mixed solvents, which is consistent with the fact that these samples have more ions in the gel network [4]. The interaction parameters between water and gel show the same trend.

χ_i between two components is a physical parameter to show the extent of mixing or the possibility of mixing. Therefore it is useful to explain the swelling behavior of polymer gels. According to Flory-Huggins

theory if $\chi_i > 0.5$, then mixing is difficult and larger χ_i means that mixing is more difficult [17]. $\chi_i = 0.5$ is a starting point from which mixing can be possible, and smaller value means easier mixing. If $\chi_i < 0.5$, then interaction between polymer chains is weaker than that between solvent and polymer chain, so that smaller values of χ_i make it easier to be homogeneous solution with perfect mixing. For smaller χ_i , it is easily found that rather rapid swelling occurs when solvent composition is changed. Interaction parameters obtained in Table 2 are consistent with swelling behaviors of the gels, which means that our model is pretty accurate to predict the overall swelling patterns.

3. Swelling for Different Solvents

Sample 1 shows three different swelling curves according to the solvent systems as shown in Fig. 7 and results for sample 3 are shown in Fig. 8. The difference between Fig. 7 and 8 is mainly due to the number of ions in the gel structure. As shown in Table 1 sample 3 has more ions than sample 1, which results in

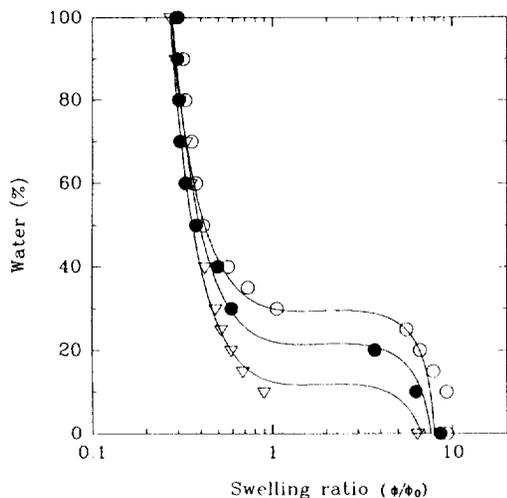


Fig. 8. Swelling behavior of sample 3 by the composition of mixed solvent: ethanol+water (○), acetone+water (●), methanol+water (▽). The solid lines were obtained from the modeling.

a rapid transition in swellings for all three solvent systems. In Fig. 8, the compositions at which phase transitions occur are nearly consistent with the order of interaction parameters between two solvents (water+methanol, water+acetone, water+ethanol). The interaction between component 2 and gels shows the order of methanol, acetone and ethanol, so that the transition in water+methanol occurs at less fraction of solvent 2 compared with other cases.

According to Butler, χ_{ij} between water and alcohol is positive and increases with the increasing number of carbons in alcohol molecules [16]. It is consistent with our estimations. Tirrell has obtained χ_{ij} as 1.1-1.7 for methanol+water case from gas-liquid equilibrium data [17]. It is also comparable with 0.95 used in this study.

CONCLUSIONS

Two major parameters to control the swelling characteristics of HSMA/PVA IPN gels are shown to be the number of effective ions in the network and interaction parameter between gel and water, which were successfully estimated by comparing Tanaka theory with experimental data in the mixed solvents.

Swelling behavior of the gel depends upon solvent systems and experimental data can be interpreted quantitatively via Tanaka theory to give us proper values of interaction parameters between solvent and solvent. These parameters obtained will be useful to

explain the electrical behavior of the polymer gels, which is undergoing in this laboratory.

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NOMENCLATURE

- f : the number of dissociated counter ions per effective chain
 ΔF : the excess free energy
 ΔF_{ij} : the free energy of the association between component i and j
 k : Boltzmann's constant
 N : Avogadro number
 S_{ij} : $= \nu \nu / \phi_0^3 N$
 T : absolute temperature
 x_i : mole fraction of component i

Greek Letters

- ν : the number of constituent chains per unit volume at $\phi = \phi_0$
 π_1, π_2 : the osmotic pressure arising from the rubber elasticity and the association between polymer segment and solvent respectively
 π_3, π_4 : the osmotic pressure arising from the polyion and the mixing entropy respectively
 v : the molar volume
 ϕ, ϕ_0 : the volume fraction of the network and at random-walk configurations respectively
 χ_{ij} : interaction parameter between component i and j

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