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Swelling equilibria of poly(N-isopropylacrylamide) gel in glucose and starch aqueous solution

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Abstract

Swelling equilibria of poly(*N*-isopropylacrylamide) (NIPA) gel in starch–water and glucose–water aqueous solutions were measured at 20, 25, 30 and 33°C. Furthermore, solvent concentrations inside and outside the gel were measured at 20°C. The gel exhibited continuous deswelling behavior in starch–water aqueous solution. A large amount of starch could hardly penetrate into the gel network. On the other hand, a volume phase transition of the gel was observed in glucose–water aqueous solution. A significant amount of glucose could penetrate into the gel network. A solution model, based on the Flory–Huggins formula coupled with osmotic pressure by rubber elasticity proposed by Flory, was adopted to correlate the phase behavior of the gel in starch–water and glucose–water aqueous solutions. The volume change behavior and the equilibrium concentrations inside and outside the gel were successfully correlated by using the model. © 1997 Elsevier Science B.V.

Keywords: Experiments; Data; Swelling equilibria; Polymeric gel; Starch; Glucose

1. Introduction

It has been shown that some polymeric gels undergo continuous [1] or discontinuous [2] volume changes depending on external conditions (e.g., temperature, pH and solvent concentration). Therefore, the gels are expected to be applied as a size-selective extraction solvent and other functional materials [3]. As an interesting application of the gels, immobilized enzyme reactions are considered. Recently, it is reported that the *N*-isopropylacrylamide (NIPA) gel with an entrapped enzyme shows a discontinuous volume change according to both substrate and product composition changes within the gel phase [4]. In immobilized enzyme (glucoamylase) reactions, the mass transfer rates of substrate

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(starch) and product (glucose) within the pores of the gel is changed by mesh sizes of the gel. To apply the gel as an immobilizer of enzymes, we should study the fundamentals such as volume change of the gel in binary mixtures (substrate–water and product–water) and concentrations inside and outside the gel [5–8]. Furthermore, the fundamental knowledge on mesh sizes of gel network and interaction between network and solvents have become very important [9].

In this work, the swelling ratios of NIPA gel in starch–water and glucose–water aqueous solutions were measured at 20, 25, 30 and 33°C. Furthermore, solvent concentrations inside and outside the gel were measured at 20°C. A solution model, based on the Flory–Huggins formula coupled with osmotic pressure by rubber elasticity proposed by Flory, was adopted to correlate the phase behavior of the gel in starch–water and glucose–water aqueous solutions.

2. Experimental

2.1. Materials

Soluble starch (Lot No. M4K30000) was purchased from Nakarai Chemical, Ltd. (Kyoto, Japan). Reagent-grade glucose was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). The weight-average molecular weight of starch (which is a mixture of amylose and amylopectin) and glucose are 30 000 and 180.2, respectively. NIPA gels were prepared by free radical polymerization in water at 0°C. Details of polymerization, purities and pretreatment of materials have been given elsewhere [10].

2.2. Experimental methods

The diameter of the gels, *D*, was measured by a calibrated microscope at swelling equilibrium condition. Assuming that the gel swells isotropically, the swelling ratio of the gel was calculated as

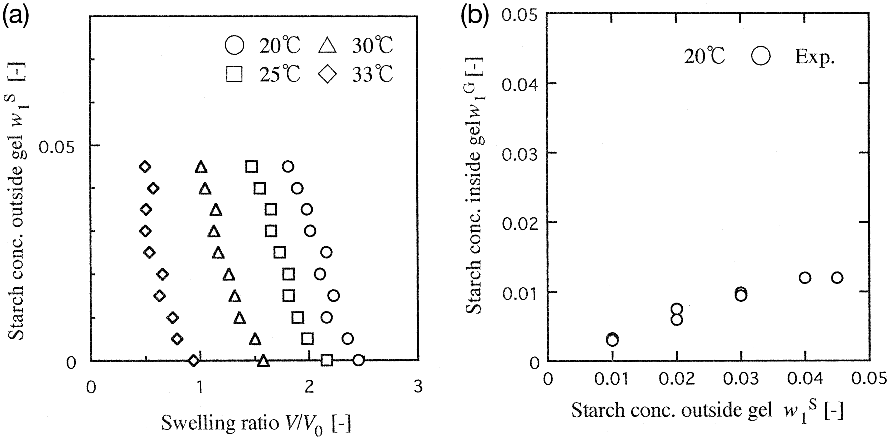

Fig. 1. (a) Swelling ratio V/V_0 of NIPA gels in starch(1)–water(2) solution: ○, 20°C; □, 25°C; △, 30°C; ◇, 33°C. (b) Concentration of starch(1) inside NIPA gels in starch(1)–water(2) solution at 20°C: ○, data.

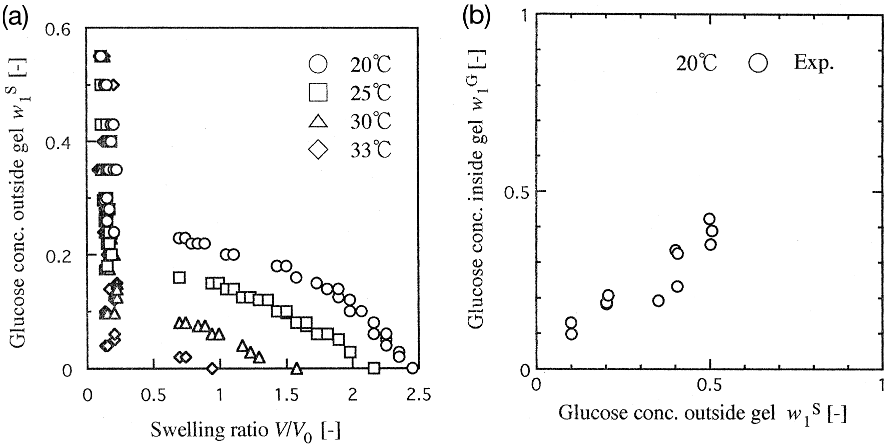

Fig. 2. (a) Swelling ratio V/V_0 of NIPA gels in glucose(1)–water(2) solution: ○, 20°C; □, 25°C; △, 30°C; ◇, 33°C. (b) Concentration of glucose(1) inside NIPA gels in glucose(1)–water(2) solution at 20°C: ○, data.

$V/V_0 = (D/D_0)^3$, where V and V_0 are the volumes of gel at equilibrium and reference conditions, respectively. Details of volume measurement have been given elsewhere [10]. The weight fraction of starch or glucose inside the NIPA gel, w_1^G, was determined by measuring the amount of water contained inside the gel. In starch–water system, the amount of water was determined by evaporation. The amount of starch remaining inside the gel was weighed by a balance. In glucose–water system, the amount of water was determined by the Karl Fischer method because glucose molecules might be evaporated. Details of weight fraction measurement have been given elsewhere [11]. The experimental accuracies for weight fraction inside and outside the gel are considered to be 10% and 1% respectively, based on reproducibility and mass balance.

3. Results

Swelling ratios of NIPA gel in starch–water and glucose–water aqueous solutions were measured at 20, 25, 30 and 33°C. The relationships between swelling ratio and solvent concentrations outside the gel are shown in Fig. 1a and Fig. 2a. Furthermore, solvent concentrations inside and outside the gel were measured at 20°C. The experimental results of the solvent concentrations inside and outside the NIPA gel are shown in Fig. 1b and Fig. 2b. As shown in these figures, the gel exhibited continuous deswelling behavior in starch–water aqueous solution. A large amount of soluble starch could hardly penetrate into the gel network. The deswelling of the gel depends mainly on the osmotic pressure of the solution outside the gel. On the other hand, a volume phase transition of the gel was observed in glucose–water aqueous solution. A significant amount of glucose could penetrate into the gel network. The jumpwise volume phase transition of the gel can be attributed to dehydration of water from the network.

4. Theory

4.1. Phase equilibrium

For swelling equilibrium of the solute(1)–water(2)–NIPA gel(3) system, the chemical potentials of component i ($i = 1, 2$) in both gel and solution phases should be identical [12].

$$\mu_i^{\mathrm{S}}(P = P^0) = \mu_i^{\mathrm{G}}(P = P^0 + \pi_{\mathrm{el}}) = \mu_i^{\mathrm{G}}(P = P^0) + \bar{v}_i^{\mathrm{G}}\pi_{\mathrm{el}} \tag{1}$$

where superscripts S and G denote solution and gel phases respectively, P^0 the atmospheric pressure, $\bar{v}_i^{\mathrm{G}}$ the partial molar volume of component i, and π_{el} the osmotic pressure caused by rubber elasticity. By assuming that the standard state is a pure component, one can obtain

$$\Delta\mu_i^{\mathrm{S}} = \Delta\mu_i^{\mathrm{G}} + v_i\pi_{\mathrm{el}} \tag{2}$$

where $\Delta\mu_i = \mu_i - \mu_i$ (pure) and the partial molar volume $\bar{v}_i^{\mathrm{G}}$ is assumed to be equal to the molar volume of pure component i, v_i. To quantitatively describe $\Delta\mu_i^{\mathrm{S}}$ and $\Delta\mu_i^{\mathrm{G}}$, the extended Flory–Huggins equation proposed by Tompa [13] can be applied. The free energy change of mixing ΔG_{mix} is given as

$$\frac{\Delta G_{\mathrm{mix}}}{RT} = \left(\sum_j \frac{\phi_j}{m_j}\ln\phi_j + \sum_j\sum_{k>j}\chi_{jk}\phi_j\phi_k\right)\sum_j n_j m_j \tag{3}$$

where n_i is the amount of component i in gel phase, ϕ_i the volume fraction of component i, m_i the molar volume ratio of component i to water ($m_i = v_i/v_2$), and χ_{ij} the Flory–Huggins interaction parameter. The chemical potential of component i and the osmotic pressure can be obtained by differentiating the free energy changes with respect to the amount of component i. For the free energy of elastic deformation of gel network ΔG_{el}, we adopt the rubber elasticity proposed by Flory [14]:

$$\frac{\Delta G_{\mathrm{el}}}{RT} = \frac{V_0\nu}{2N}\left\{3\left(\frac{V}{V_0}\right)^{\frac{2}{3}} - 3 - \ln\left(\frac{V}{V_0}\right)\right\} \tag{4}$$

where N is the Avogadro's number, ν is the number of elastically active network chains per unit volume when the volume of gel is V_0. It is considered that a volume phase transition of NIPA gel is due to a hydrogen bonding formed between water molecules and hydrophilic groups (–NH and –C = O) in NIPA. To consider the effect of hydrogen bonding, we assumed that the volume fraction of gel network should be separated as [11]:

$$\phi_3^{\mathrm{G}} = \phi_{\mathrm{M}}^{\mathrm{G}} + \phi_{\mathrm{S}}^{\mathrm{G}} \tag{5}$$

where subscripts M and S denote the main chain and side chain of network, respectively. Therefore, the chemical potential equations should be applied to the four components (1, 2, M and S) system in the gel phase. The effective volume fraction of side chain is approximated as follows by use of the volume of side chain in dried-gel, V_{S}.

$$\phi_S^G = \frac{V_S\beta}{V} \tag{6}$$

The parameter β was introduced as an adjustable parameter to distinguish the energy of hydrogen bonding between side chain and solute (starch or glucose). It was empirically expressed as a function of the solute concentration in gel phase and the gel volume because the contact fraction between side chains and solute molecules depends on the energy of their interaction and the gel volume.

$$\beta = \beta_0 + \exp\left(\beta_1 w_1^G + \beta_2 \frac{V}{V_0} + \beta_3\right) \tag{7}$$

The interactions between side chain and other species are assumed to be the same as those between main chain and other species for simplification, and the interaction between main chain and side chain is assumed to be negligible.

$$\chi_{1M} = \chi_{1S} = \chi_{13},\ \chi_{2M} = \chi_{2S} = \chi_{23},\ \chi_{MS} = 0 \tag{8}$$

As the molar volume ratio of polymer (main chain) to water m_M (v_M/v_2) is extremely large, one can ignore the term of ϕ_M/m_M. The expressions obtained here for the swelling equilibrium of a gel are shown below.

$$\begin{aligned}\ln \phi_1^S + \phi_2^S(1-m_1) + m_1\chi_{12}\left(\phi_2^S\right)^2 &= \ln\phi_1^G - \phi_1^G - m_1\phi_2^G - \left(\frac{m_1}{m_S}\right)\phi_S^G + m_1\left(\chi_{12}\phi_2^G + \chi_{13}\phi_3^G\right)\\ &\quad - m_1\left(\chi_{12}\phi_1^G\phi_2^G + \chi_{13}\phi_1^G\phi_3^G + \chi_{23}\phi_2^G\phi_3^G\right) + 1 - \frac{v_1\nu}{N}\left\{\frac{V_0}{2V} - \left(\frac{V_0}{V}\right)^{\frac{1}{3}}\right\}\end{aligned} \tag{9}$$

$$\begin{aligned}\ln \phi_2^S + \phi_1^S\left(1-\frac{1}{m_1}\right) + \chi_{12}\left(\phi_1^S\right)^2 &= \ln\phi_2^G - \left(\phi_2^G + \frac{\phi_1^G}{m_1} + \frac{\phi_S^G}{m_S}\right) + \chi_{12}\phi_1^G + \chi_{23}\phi_3^G\\ &\quad - \left(\chi_{12}\phi_1^G\phi_2^G + \chi_{13}\phi_1^G\phi_3^G + \chi_{23}\phi_2^G\phi_3^G\right) + 1 - \frac{v_2\nu}{N}\left\{\frac{V_0}{2V} - \left(\frac{V_0}{V}\right)^{\frac{1}{3}}\right\}\end{aligned} \tag{10}$$

where

$$\phi_1^S + \phi_2^S = 1 \tag{11}$$

$$\phi_1^G + \phi_2^G + \phi_3^G = 1 \tag{12}$$

4.2. Volume phase transition

The shrunk state (I) and swollen state (II) for a polymeric gel in the solvent(1)–water(2) mixture are considered here. For certain values of w_1^S, Eqs. (9)–(12) give three values of V corresponding to

Table 1
Parameters used in the model

Solution	χ_{12}	χ_{13}	β_0	β_1	β_2	β_3
Starch	0.47	0.18	−2.0902	−0.4559	0.0240	0.8078
Glucose	0.05	0.22	−2.5058	−0.1124	0.0165	0.9916

$\chi_{23} = 0.68$, $\nu / N = 1.4 \times 10^{-4}$ mol cm^{-3}.

one maximum (unstable state) and two minima (shrunk state or swollen state) of the free energy change of mixing. At the volume phase transition, the free energies of mixing for polymeric gel are identical at both shrunk and swollen states [12].

$$\left(\Delta G_{\mathrm{mix}}^{\mathrm{I}} + \Delta G_{\mathrm{el}}^{\mathrm{I}}\right) - n_1^{\mathrm{I}} \Delta \mu_1^{\mathrm{I}} - n_2^{\mathrm{I}} \Delta \mu_2^{\mathrm{I}} = \left(\Delta G_{\mathrm{mix}}^{\mathrm{II}} + \Delta G_{\mathrm{el}}^{\mathrm{II}}\right) - n_1^{\mathrm{II}} \Delta \mu_1^{\mathrm{II}} - n_2^{\mathrm{II}} \Delta \mu_2^{\mathrm{II}} \tag{13}$$

4.3. Correlation

The volume of gel and the equilibrium concentrations inside and outside gel can be calculated from Eqs. (2)–(7), and Eqs. (9)–(13). The molar volume of side chain (75.5 cm^3/mol) is calculated by the method proposed by Fedors [15]. The volume of dried-gel V_3 (4.30×10^{-5} cm^3), that of side chain in dried-gel V_S (3.26×10^{-5} cm^3) and gel volume in the reference state V_0 (6.14×10^{-4} cm^3) were experimentally determined under the preparation condition. The density of gel is assumed to be 1.00 g/cm^3 because the gel suspend in the water phase. The densities of starch and glucose are 1.461 g/cm^3 [16] and 1.562 g/cm^3 [17], respectively.

In Eqs. (9) and (10), there are eight parameters. All parameters were determined simultaneously using a nonlinear least-squares method to give the best fit for the experimental data of each system. They are given in Table 1. As shown in Figs. 3 and 4, the present correlation seems to be successful.

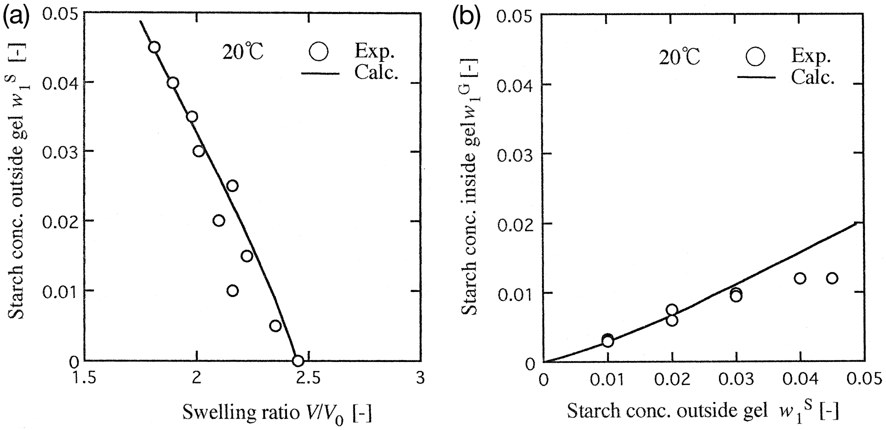

Fig. 3. (a) Swelling ratio V/V_0 of NIPA gels in starch(1)–water(2) solution at 20°C: ○, data; ————, model. (b) Concentration of starch(1) inside NIPA gels in starch(1)–water(2) solution at 20°C: ○, data; ————, model.

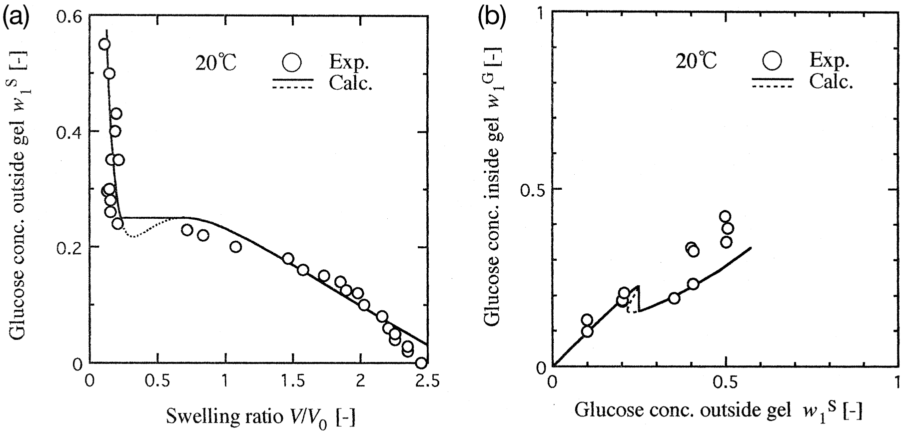

Fig. 4. (a) Swelling ratio V/V_0 of NIPA gels in glucose(1)–water(2) solution at 20°C: ○, data; ————, model. (b) Concentration of glucose(1) inside NIPA gels in glucose(1)–water(2) solution at 20°C: ○, data; ————, model.

However, the starch sample has a wide molecular weight distribution. The effect of the molecular weight distribution and the average molecular weight on swelling equilibria becomes very important. A quantitative correlation for these systems still remains to be studied in future work.

5. Conclusions

The phase equilibrium of a NIPA gel in starch–water and glucose–water mixtures were measured and correlated by a solution model. Both the volume phase transition and the concentrations inside and outside the gel were investigated. From the partition of starch and glucose, it was found that the NIPA gel can absorb low molecular weight glucose, but exclude high molecular weight starch in swollen state. This behavior may be due to the change in mesh sizes of the gel network and the interaction between glucose and gel network. It is shown that the extended Flory–Huggins formula can correlate the swelling equilibria by considering the solvent concentration dependence of volume fraction of the side chain in the gel phase.

6. List of symbols

G	Free energy
m_i	Molar volume ratio of component i to water (v_i/v_2)
n	Amount of solvent
N	Avogadro’s number
P	Pressure
P^0	Atmospheric pressure
R	Gas constant
T	Absolute temperature
v	Molar volume

$\bar{v}$	Partial molar volume
V	Apparent volume of gel
V_0	Volume of gel in the reference state
w	Weight fraction

Greek letters

β	Constant of Eq. (7)
μ	Chemical potential
ν	Number of elastically active network chains per unit volume in the reference state
π	Osmotic pressure
ϕ	Volume fraction
χ	Flory–Huggins interaction parameter

Subscripts

1	Starch or glucose
2	Water
3	Gel
el	Rubber elasticity
i,j,k	Components i,j,k
M	Main chain
mix	Mixture value
S	Side chain

Superscripts

G	Gel phase
S	Solution phase

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