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Short Communication

Solvent concentrations of dimethylsulfoxide–water and 1-propanol–water solutions inside and outside poly (*N*-isopropylacrylamide) gel

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Abstract: The volumes of poly (*N*-isopropylacrylamide) (NIPA) gel in both dimethylsulfoxide (DMSO)-water and 1-propanol–water solutions were measured at 25 °C. The solvent concentrations inside and outside the NIPA gel were also measured. The gel was swollen in water, shrunk according to increase in concentration of organic solvent, and reswollen in pure organic solvent. This phenomenon is typical reentrant swelling behavior. The DMSO concentrations inside the gel were almost equal to those outside the gel in the whole concentration range. On the other hand, the 1-propanol concentrations between inside and outside the gel were much different from each other in the shrunk state, though they were almost the same in the swollen state.

Key words: Polymeric gel – aqueous organic solution – swelling equilibrium – concentration inside gel

Introduction

Behaviors of gel in aqueous organic solution are very interesting [1–5]. Recently, Hirotsu [5] reported the differences in both enthalpy and entropy accompanied with solvation for poly (*N*-isopropylacrylamide) (NIPA) gel, and suggested that a large negative value of difference in enthalpy is due to a hydrogen bonding occurring between water molecules and hydrophilic groups (–NH and –C =O) in NIPA. Furthermore, Otake et al. [6, 7] suggested that both hydrophobic interaction and hydrophilic hydration play a main role in the volume-phase transition of gels. The mechanism in phase transition and phase equilibria of solvent between inside and outside the gel have become gradually clear by these considerable contributions.

On the other hand, to accurately understand the interaction between gel network and solvent, equilibrium concentrations of solution inside and outside the gel are also very important. Mukae et al. [8] have recently reported swelling volume of NIPA gel in alcohol (methanol through 2-methyl-2-propanol)–water mixtures and measured the ethanol concentration in aqueous ethanol solution inside and outside the gel by using isotope solutions. Moreover, they observed hydrogen bonding around the amide group in NIPA by using FT-IR. In our previous works [9–11], alcohol (methanol, ethanol or 1-propanol) concentrations inside and outside the gel (vinyl alcohol–sodium acrylate copolymer) in aqueous solutions were measured by using an apparatus based on evaporation and trap methods. These experimental results confirmed the mechanism in the volume-phase transition of gels.

In this paper, swelling behavior and solvent concentration inside and outside the NIPA gel will be reported in both dimethylsulfoxide (DMSO)–water and 1-propanol–water solutions.

Experimental part

Materials and synthesis

Dimethylsulfoxide (DMSO) and 1-propanol were purchased from Nakarai Chemical, Ltd. These reagents were all of special grade and used without further purification. Their purities are believed to be more than 99.8% and 99.7% for DMSO and 1-propanol, respectively. Water was

distilled, degassed and deionized using the Millipore Milli-Q water purification system.

NIPA gel was prepared by free radical polymerization of NIPA monomer (150 mmol) and *N,N'*-methylenebisacrylamide monomer (1.5 mmol) as a cross-linker in water (250 mL) at 0 °C. Full details of the preparation and materials have been given elsewhere [12]. The polymerization was carried out in glass tubes (0.85 mm in inner diameter and 50 mm in length) and polypropylene tubes (16 mm in inner diameter and 150 mm in length). The former (small gel samples) and the latter (large gel samples) were used for measurement of gel volume and solvent concentration inside the gel, respectively.

Measurement of gel volume

The NIPA gel samples (about 5 mm length chips) were immersed in glass tubes (15 mL) with water. The glass tubes were then set in a temperature-controlled water bath (25 ± 0.1 °C) for at least 2 h. After equilibrium had been reached, the diameters of the gels, D, were measured by a calibrated microscope at swelling equilibrium conditions. Assuming that the gel swells isotropically, the swelling ratio of the gel was calculated as $V/V_0 = (D/D_0)^3$, where V and V_0 are the volumes of the gel at equilibrium and initial conditions, respectively, and D_0 is the diameter of the gel at initial condition ($D_0 = 0.85$ mm). The concentrations were changed by adding solvent (DMSO or 1-propanol). The gel attained constant volume within 2 h after adding the organic solvent.

Measurement of solvent concentration outside gel

The solvent concentrations outside the gel, x_1^S, were measured by a gas chromatograph (Shimazu, KOR-70) equipped with a thermal-conductivity detector. A stainless steel column (2 m in length, 2 mm in inner diameter) was used to separate the peaks of solvents. Silicone SE-30 (80–100 mesh, dimethyl silicone gum) supplied by GL Science Co. was used as a packing material. Helium was used as carrier gas.

Measurement of solvent concentration inside gel

A few of the large gel samples (about 15 mm length chips) were immersed in vials (100 mL) filled with DMSO–water or 1-propanol–water solutions. The vials were then set in a temperature-controlled water bath for at least 3 days. After equilibrium had been reached, the gels were removed from the vials and were placed into centrifuge tubes with a hydrophobic filter to remove the solvent on the gel surface. The tubes were centrifuged for 10 min at 500 rpm.

The apparatus used in the measurement of solvent concentration inside the gel consists of an evaporation part and a trapping part. The gel chips prepared above were put into the drying cell. The solution inside the gel was evaporated at 110 °C and the vapor was carried with dried nitrogen through a stainless steel tubing (3 mm in inner diameter), and was trapped at − 40 °C. The velocity of the dried nitrogen was 1 mL/s. It took about 1 h to trap all solution contained inside the gel. The average absolute error in mass balance was less than 0.02%. The concentration of solution trapped, namely, the concentration inside the gel x_1^G, was analyzed by gas chromatography.

Results and discussion

Figure 1 shows the concentration dependence of the swelling ratios, V/V_0, for both DMSO–water and 1-propanol–water solutions. The gels were swollen in water, shrunk according to increase in concentration of organic solvent, and reswollen in pure organic solvent, that is, reentrant swelling behavior is shown. In both

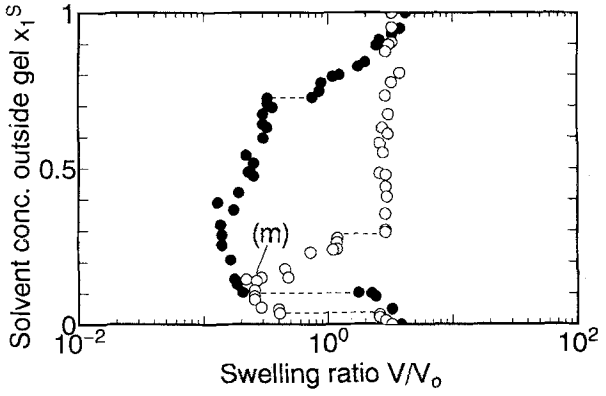

Fig. 1. Swelling ratio V/V_0 of NIPA gel in DMSO (1)-water (2) or 1-propanol (1)-water (2) mixtures with organic solvent (1) mole fraction x_1^S at 25 °C. ● DMSO, ○ 1-propanol

systems, discontinuous volume-phase transition was observed at $x_1^S = 0.102$, 0.725 in DMSO–water solution and $x_1^S = 0.034$, 0.28 in 1-propanol–water solution. These swelling behaviors are similar to the results obtained by Amiya et al. [4] and Mukae et al. [8]. A drastic change of gel volume was observed in the water-rich region. The organic solvents (alcohols, DMSO, acetone, etc.) are good solvents for uncross-linked NIPA polymer [13]. In such solvents the polymer behaves as a flexible coil. In water, however, the polymer is elongated and stiffer than in the organic solvents, because hydrogen bonding occurs between water molecules and amide groups in NIPA [14]. The jumpwise volume decrease in the water-rich region can be considered to be caused by dehydration of water from the amide groups.

Figure 2 shows the solvent concentration inside and outside the gels in both DMSO–water and 1-propanol–water solutions. It is noted that the DMSO concentrations inside the gel were almost equal to those outside the gel in the whole concentration range. On the other hand, the 1-propanol concentrations between inside and outside the gel were much different from each other in the shrunken state, though they were almost the same in the swollen state. The bulk phase volume inside the swelling gel is much larger than that inside the shrinking gel, therefore, the concentrations inside and outside the gel become very close. On the other hand, both concentrations in the shrunken state are considered to be different from each other in general.

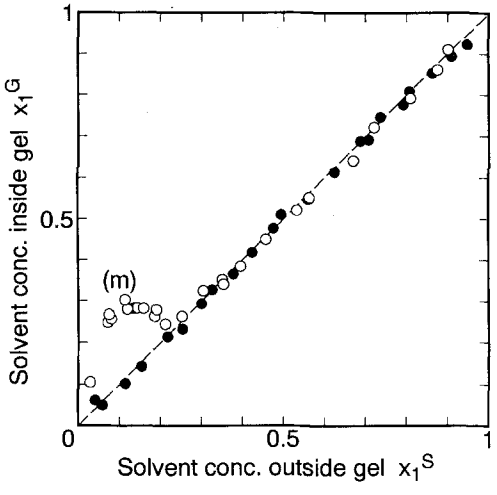

Fig. 2. Concentration of organic solvent inside NIPA gel x_1^G in DMSO (1)-water (2) or 1-propanol (1)-water (2) mixtures with organic solvent (1) mole fraction x_1^S at 25 °C. ● DMSO, ○ 1-propanol

Mukae et al. [8] have measured ethanol concentration inside the gel in aqueous ethanol solution by using isotope solution. They have reported that the ethanol molecules were selectively absorbed in the gel. Though the method of concentration measurement and alcohol (ethanol) used in their work is different from the present work, the experimental results (1-propanol–water system) obtained in this work are similar to their results. Namely, selective absorption of alcohol inside the gel was observed and a minimum in swelling curve (Fig. 1, (*m*)) corresponds to a maximum of the absorption (Fig. 2, (*m*)). They suggested that the swelling of the gel in water may be caused by a strong hydration around amide groups in polymer networks judging from measurement of FT-IR. Therefore, by addition of a small amount of organic solvent into water hydration shell is partly destroyed, and then dehydrated polymer chains associate to form a shrunken structure. Furthermore, by adding more ethanol, ethanol molecules adsorbed selectively upon the shrunk gel network, and the gel reswelled. It may be considered that a similar phenomenon arises inside the gel in this work.

Reentrant swelling behavior is shown in aqueous DMSO solution. The swelling mechanism in both pure solvents may be similar to that in 1-propanol or water. However, the degree of volume reduction is distinguished and the region of shrunk state is wide. Further, the DMSO concentrations inside the gel were almost equal to those outside the gel in the whole concentration range. The attractive interaction between DMSO and water molecules is quite strong compared to the alcohol–water interaction, so that water and DMSO molecules can associate to form a complex [15]. Therefore, DMSO and water molecules together penetrate into the gel network holding the same condition (concentration) as in the bulk phase (outside the gel). And, the hydration around amide groups is weakened by coexisting DMSO and water molecules because the DMSO–water interaction is stronger than the solvent–amide group interaction. The interesting behavior observed in aqueous DMSO solution may be due to this strong interaction between DMSO and water molecules.

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