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Isobars, the coexistence curve, and the critical exponent β of N-isopropylacrylamide gels obtained using a simple experimental method

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We have obtained "iso-osmobars," which refer to lines with constant osmotic pressures, and coexistence curve of the volume phase transition of N-isopropylacrylamide gel using a very simple method: hanging gels above NaCl solution having a given concentration in a sealed container that was placed in a temperature controlled bath. Since the chemical potential of the water molecules in the gel is equal to that of the water molecules in the NaCl solution, the osmotic pressure of the gel became the same value with that of the NaCl solution. Thus, air that separated the gel and the NaCl solution played a role of infinitely flexible semipermeable membrane. We have succeeded to obtain the coexistence curve and related critical exponent β from the series of the iso-osmobars of the gel. The value of β we obtained was 0.38(1.5).

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I. INTRODUCTION

Since the discovery of volume phase transition in ionic gel by Tanaka *et al.* [1], gel has attracted a wide range of interests from fundamental research on critical phenomena to application-oriented studies [2–9]. Many types of gels and cross-linkers have been developed to improve the fragile nature of the gels, improve their slow kinetic rate, and increase their volume change [10–13]. Numerous gel systems have been investigated by various techniques such as nuclear magnetic resonance [14], small-angle x-ray diffraction [15], microcalorimetry [16], Raman spectroscopy [17], and small-angle neutron scattering [18–20]. However, no phase diagram that can be directly and quantitatively compared with those of other critical phenomena, such as liquid-gas transition, has been obtained for the gel system, probably because of the complexity of such a system.

Tanaka *et al.* reported the phase transition of ionic gel induced not by temperature change but by the solvent composition, in their original work [1]. The discrete (first-order) transition was achieved by the positive osmotic pressure of the ions inside the gel due to the ionization of the gel network by hydrolysis of the side chain in poly-N-acrylamide molecules. Thus, the molecular structure of the gels that underwent a discrete volume phase transition was different from that of the gel showing a continuous volume change. Although their result revealed the existence of a volume phase transition in the gel, they failed to quantitatively characterize the volume phase transition by important quantities such as critical exponents. The simplest gel system that shows a phase transition is the N-isopropylacrylamide (NIPA) gel with pure water as the solvent, whose transition is induced by a temperature change. Although a study of the critical phenomenon for this type of system was reported by Hirokawa *et al.* [21], in that study, gel undergoing discrete (first-order) transition had a different composition (lower cross-linker fraction) from that of gel showing a continuous transition at $\Pi = 0$.

In 1988 Hirotsu applied osmotic pressure to NIPA gels by introducing large polymers in the solution surrounding the gels under assumption that the large polymers would not penetrate the gel network [22]. He demonstrated that the increase in osmotic pressure suppressed the discontinuous volume change. However, the molecular weight distribution of the large polymer and its penetration into the gel network made it extremely difficult to determine the osmotic pressure of the polymer solution; we postulate that these difficulties caused him to abandon the effort of determining the critical exponents.

In 1989 Li *et al.* classified the volume phase transition of gel by studying the critical exponents [23]. They varied the composition of gel and found a "critical gel," whose iso-osmobar at $\Pi = 0$ passed through the critical point; here "iso-osmobar" refers to a line with a constant osmotic pressure Π. They obtained the critical exponent δ related to the iso-osmobar using this "critical gel" and obtained the critical exponent α_π by the measurement of the divergence of the specific heat at the critical point along the $\Pi = 0$ iso-osmobar. By using these critical exponents and scaling relations, they also calculated the critical exponents of the NIPA gel. They estimated that $\gamma = 1.3(0.4)$, $\beta = 0.40(8)$. They classified the volume phase transition as three-dimensional (3D) Ising class. We must point out here that the critical exponents that they measured are the exponents along the equation of state (iso-osmobar at $\Pi = 0$), and scaling relations needed to be used in order to obtain the usual critical exponents for comparison with other systems such as the gas-liquid phase transition, Ising model, and 3D Heisenberg model. Moreover, as the exponent γ_π was observed on the iso-osmobar, even a small error in the observed value of the exponent δ caused considerable error in the calculation of the exponent γ. [See Fig. 2 and Eqs. (2.7)–(2.10) in Ref. [23].] Thus, it is highly essential to observe the other critical exponents directly in order to classify the critical phenomenon of the gel system. Shibayama *et al.* measured the γ of the NIPA system directly by using small-angle neutron scattering [18]. Their results demonstrated that the exponents for NIPA gels were close to the value for the 3D Ising model, while those for NIPA solutions were close to the value for the mean-field prediction.

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Onuki [24] and Golubovic and Lubensky [25] discussed the volume phase transition in gels within a general statistical mechanics treatment of gel density fluctuations. Their main result is that the shear modulus of gels induces a long-range interaction between density fluctuations and this effect prevents a true divergence of the correlation length. With approaching the critical point, the density-density correlation length only initially increases like for the zero shear modulus liquid-gas critical point, but then (close to the critical point) it saturates to a finite value, which is large if the shear modulus is small. Thus, in gel systems with a small shear modulus, the Ising-type behavior could be still seen in a crossover regime whereas the "ultimate critical behavior" of the gel volume transition turns out to be the same as in the mean-field theory (the so-called mean-field universality class) [24–26].

This theoretical finding is in accord with the experiments on the critical behavior of poly(methacrylic acid-co-dimethyl acrylamide) gel [26]. In this experimental system, the volume phase transition was found to belong to the mean-field universality class predicted in the theory of Refs. [24,25]. On the other side, experimental results on the NIPA gels, including our present results, have never shown the mean-field type critical behavior. The observed behavior might be explained as the Ising-type crossover regime discussed in Ref. [25]. By the theory of Ref. [25], in the systems with a small shear modulus, the ultimate mean-field-type behavior occurs only in a very small vicinity of the critical point, which may not be easy to capture in experiments. Note that more detailed experimental studies are needed for a NIPA gel system, since the comprehensive conclusion has not been obtained even in the last decade [27–29].

In the present work, we studied the volume phase transition of NIPA gels under various osmotic pressures using the exact same gel (i.e., synthesized in the same batch) and pure water as gel fluid. Furthermore, we induced the volume phase transition by changing the temperature, which made it possible to quantitatively compare the gel system with simple phase transition phenomena such as those in a gas-liquid system. We applied osmotic pressure to the gel network by placing gels in air above NaCl solution having a given concentration and kept in a sealed container. The positive osmotic pressure from the NaCl solution removed the water molecules from the gel, which had a lower osmotic pressure, until the osmotic pressure of the gel became equal to that of the NaCl solution; this resulted in the indirect application of osmotic pressure on the gel network. The role of the air in this system can be compared to that of an infinitely flexible semipermeable membrane, which is permeable to water molecules but impermeable to Na^+ and Cl^- ions, because the vapor pressure of Na and Cl or their ions is negligibly small as compared to that of water molecules.

II. EXPERIMENT

We had prepared the NIPA gels that undergo discrete volume phase transition at $\Pi = 0$ following the recipe presented in the work by Li *et al.* [23]. We obtained NIPA and other chemicals except cross-linker from Wako Pure Chemical Industries (Tokyo, Japan) and purified NIPA molecules by recrystallization in cyclohexane. Cross-linker, N,N'-methylene-bis-acrylamide (bis), was obtained from Sigma-Aldrich (St. Louis, MO, USA) and was used without purification. We used ammonium-peroxodisulfate (AP) as the initiator and tetramethylethylenediamine (TEMED) as a catalyst for the creation of free radicals for co-polymerization of NIPA and bis molecules. Solution of the NIPA and bis was de-oxygen-gased using dry N_2 gas and kept around 0 °C using ice and water. After the initiation of the free radical copolymerization by mixing initiator and catalyst, there was a short latent period before the beginning of the copolymerization. In this period, cylindrical glass pipettes (Vitrex, precalibrated pipettes 20 μl, 0.50 mm inner diameter) were put into the mixture to make cylindrical gel of fixed diameter. The solution was stored in a refrigerator overnight for the completion of the chemical reaction. The concentration of NIPA + BIS was 15 wt%, and the fraction of the cross-linkers, defined as $\frac{[\text{bis}]}{[\text{bis}]+[\text{NIPA}]}$ was 0.5%; here [bis] and [NIPA] are the weight concentrations of bis and NIPA molecules, respectively. After gels were taken out from the pipettes, gels were washed in a large amount of distilled water for a few days to remove residual chemicals. Washed gels were cut into small pieces (≈1 cm in length) and were hanged over large amount (≈10 cm^3) of NaCl solution of various concentrations and sealed in plastic bottles (Tissue Culture Flask 25 ml, BD Falcon, Franklin Lakes, NJ, USA). Plastic bottles were placed in temperature-controlled baths and the temperatures of the systems were controlled within the accuracy of ±0.01 °C using temperature-controlled bath circulators (Thermo Elite BH71 and modified Thermo Elite BH401, Yamato Scientific Co., Tokyo, Japan). The temperatures of two baths were calibrated using the same thermistor with a float. The number of gels used for this measurement was 12 × 2 (two gels in each bottle). The diameter of each gel was measured using a home-built video microscope that traveled on the rail guides with ball bearings. The image of the gel was captured by a personal computer, and the size (diameter) of the gel was measured using a software ("ruler" ver. 0.02 by Elm Bottega). Using the observed diameter d, swelling ratio d/d_0 and $V/V_0 = (d/d_0)^3$ were calculated, where d_0 is the diameter of the pipette that corresponds to the diameter of the gel when polymerized.

We found that it took about 10 hr for the gel to reach equilibrium size after the change of the temperature about +0.1 °C. So we set the shortest interval of the measurement to be 24 hr. Near the critical temperature and at the first-order transition, it sometimes took more than several days to reach equilibrium size. As we could not change the temperature of the bath till the gel at the transition had reached equilibrium, all the rest of the gels had to be kept at the same temperature for a long time, which made the sampling interval rather irregular.

When the gel reached the transition temperature, we could see the drastic changes in size and shape. Figure 1 shows the typical shape of the gels at the transition region or coexisting phase. The lower end of the coexisting temperature of an iso-osmobar was defined by the temperature at which such deformation was first observed at least one end of the gel, while the size of the gel at the temperature was given by that of the swollen phase. And the temperature at which the whole of the gel got shrunken was adopted as another end of the coexisting region. Thus, there was about 0.02 °C difference between the temperatures of the two ends of the transition.

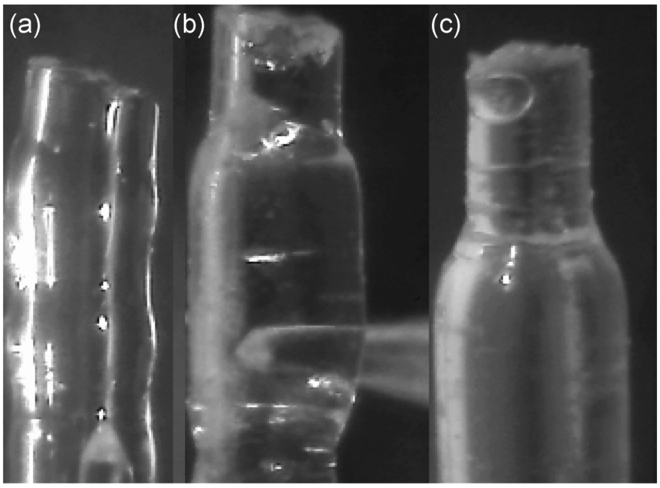

FIG. 1. Photographs of the gels at the coexisting phase. The osmotic pressure is highest (a) and lowest (c) among these three gels. When the width of the transition is large (at the lower osmotic pressure), we usually observe single swollen region with shrunken region at the both ends of the gel [see photos (b) and (c)]. However, when the system is close to the critical region where the width of the transition is small (at the higher osmotic pressure), we have observed multidomains of swollen phases and shrunken phases coexist in the gel [see photo (a)]. The horizontal spearhead in the photo (b) is the glass spike that holds the gel in position and part of glass spike is also seen in photo (a). We measured the widths of the gels away from these glass spikes.

As the osmotic pressure of strong electrolyte solution has the linear temperature dependence known as van't Hoff's law, the "iso-osmobar" observed by this measurement was not the iso-osmobars in the exact meaning. Thus we call the observed curve "semi-iso-osmobar." We deduced the true iso-osmobars from the observed $\frac{V}{V_0}$ vs [NaCl] curve at each temperature using the relation between NaCl concentration ([NaCl]) and osmotic pressure of the electrolyte solution given by van't Hoff's equation. It is very important to point out here that the coexistence curve obtained is exact in spite of the temperature dependence of the osmotic pressure of the electrolyte solution. All the measurements were performed with increasing temperature, the direction of the shrinkage of the gel. We discuss this point later.

III. RESULTS AND ANALYSIS

Figure 2(a) shows the observed semi-iso-osmobars of the NIPA gels. Here vertical axis is the temperature in degrees Celsius and horizontal axis is the swelling ratio V/V_0. Please note that the volume phase transition of the NIPA system is driven by the hydrophobic interaction and that the gel is shrunken at high temperatures and is swollen in the low-temperature range [21]. Thus, the critical point discussed here is the lower critical point. Using results shown in Fig. 2(a), we renormalized the semi-iso-osmobars to the osmotic pressure at the transition. If the transition was a continuous one, we used the temperature of the inflection point as the origin of the correction. As we know the temperature T_0 at the transition (or the inflection point), we can calculate the osmotic pressure Π_0 at T_0 as

$$\Pi_0 = 2RM_0T_0,$$

where R is the gas constant, M_0 [mol/L] is the concentration of the NaCl solution and 2 is the number of ions from NaCl. For $T_1 < T_0$, for an example, one can obtain the NaCl concentration M_1 where the osmotic pressure is $\Pi_0 = 2RM_1T_1$. From the data in Fig. 2(a), we can plot V/V_0 as the function of the concentration of the NaCl solution at constant temperature T_1. By interpolating the data by a quadratic function, we can get V/V_0 for M_1, which corresponds to Π_0. Since we have to extrapolate the points for 0.35 mol/L (under the highest osmotic pressure), the accuracy of the extrapolation may not be as good as the rest of the data obtained by interpolation. Inset of Fig. 2(b) shows the observed semi-iso-osmobar and corrected iso-osmobar. Using this simple procedure, we can get iso-osmobars of NIPA gel as shown in Fig. 2(b). It is

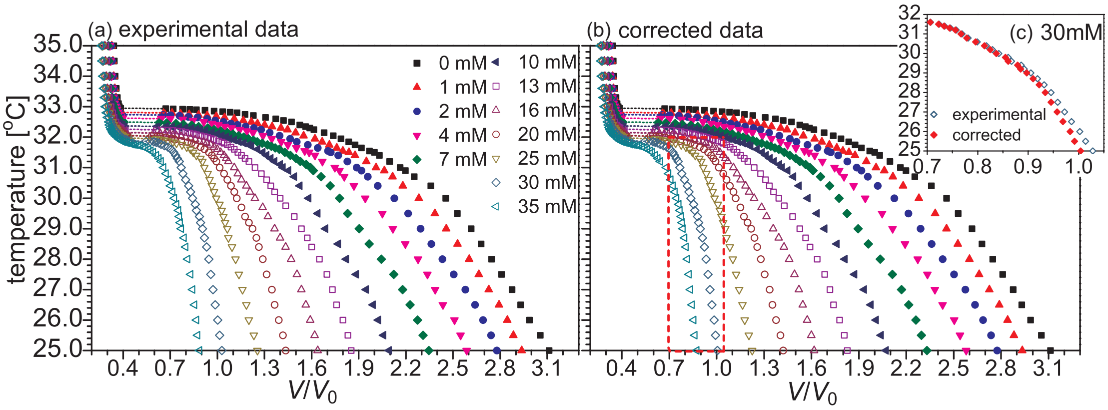

FIG. 2. (Color online) Observed semi-iso-osmobars from 25 °C to 35 °C (a). Molar fraction of the NaCl solution used in this study was 0 m*M* to 0.035 m*M*. The swelling ratio $\frac{V}{V_0}$ are plotted against the temperature. Dotted lines represent the discrete volume changes. The increase of the osmotic pressure suppressed the discontinuous volume phase transition and the transition became continuous transition at 35 m*M*. (b) The reconstructed iso-osmobars using a simple method described in the main text. The inset gives the difference between observed semi-iso-osmobar and reconstructed iso-osmobar for 0.03 Osm/L at the transition temperature. This inset is the expanded presentation of the iso-osmobar in the box of dotted line of (b).

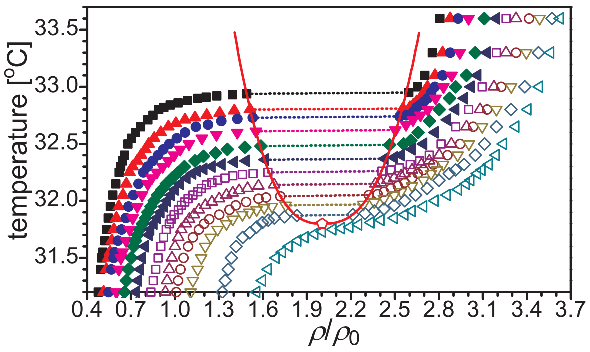

FIG. 3. (Color online) The horizontal axis of Fig. 2(b) is converted to normalized density $\frac{\rho}{\rho_0} = \frac{V_0}{V}$. The symbols are identical to the symbols in Fig. 2. The coexistence curve presented by the solid line was drawn using the parameters obtained by the analysis of the critical exponent β. An open pentagon at the bottom of the coexistence curve is the critical point given by $\frac{\rho_c}{\rho_0} = 2.005$ and $T_c = 31.80\,^\circ\mathrm{C} = 304.91$ K.

important to point out here that the coexistence curve is identical in Figs. 2(a) and 2(b). Figure 2(b) shows that the discrete transition (first-order transition) gradually changed to continuous one with increasing the osmotic pressure just like the case of gas-liquid phase transition. The transition temperature as well as the width of the first-order transition decreased with the increase of the osmotic pressure (Fig. 3).

A. Critical exponents

1. *Critical exponent β*

Figure 3 presents the density of the gel in the coexisting region as a function of the temperature. Here the horizontal axis is converted to $\frac{\rho}{\rho_0}$, where ρ_0 is the density of gel network when polymerized. In Fig. 3 the boundary of the coexistence region was drawn using the result of the analysis of critical exponent presented below. To obtain the critical exponent β, observed boundary point of the coexisting region $\frac{|\rho(\tau)-\rho_c|}{\rho_c}$ were plotted against reduced temperature $\tau = \frac{|T-T_c|}{T_c}$. Here $\rho(\tau)$ is the density of the gel network at the boundary of the coexisting region at τ, ρ_c is the critical density of the gel network, ρ_0 is the density of gel network when polymerized, and T_c is the critical temperature. Though we cannot directly determine the T_c and ρ_c from the results, we can give limits of both quantities as follows:

$$31.70\,^\circ\mathrm{C} < T_c < 31.85\,^\circ\mathrm{C}, \qquad 1.9 < \frac{\rho_c}{\rho_0} < 2.1.$$

We divided this region into 200×150 points of (T_c,ρ_c), and plotted $\log_{10}(\frac{|\rho-\rho_c|}{\rho_c})$ against $\log_{10}\tau = \log_{10}(\frac{|T-T_c|}{T_c})$, varying T_c and ρ_c for the both side of the coexistence curve. Fitting the 3.0×10^4 pair of curves, we obtained the set of (T_c,ρ_c) such that the both side of the coexistence curves fall on straight lines with the same slope. Figure 4 shows the best result where mean square error got minimum value, and the obtained values were

$$T_c = 31.80(1)\,^\circ\mathrm{C} = 304.95(1)\ \mathrm{K}, \quad \rho_c = 2.005(1.3), \quad \text{and}$$
$$\beta = 0.38(1.5)$$

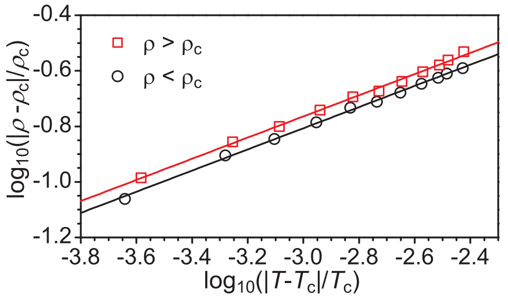

FIG. 4. (Color online) A log-log plot of the reduced density $\frac{|\rho-\rho_c|}{\rho_c}$ to the reduced temperature $\tau = \frac{|T-T_c|}{T_c}$. The solid line is the result of the least square fit by the parallel straight lines (see main text). The slope of this line is the critical exponent β. The slope here gives the value of $\beta = 0.38(1.5)$.

where numbers in brackets represent standard dispersions. This result coincides very well with the result of Li *et al.* [23]. Our result finally provided us three critical exponents of the gel system.

2. *Critical exponent δ*

The critical exponent δ is defined by

$$\frac{|\rho-\rho_c|}{\rho_c} \propto \left(\frac{|\Pi-\Pi_c|}{\Pi_c}\right)^{\frac{1}{\delta}}$$

at $T = T_c$, where Π_c is the critical osmotic pressure. As we could not vary the osmotic pressure with small interval in this experiment, we used the simple assumption

$$|\Pi-\Pi_c| \propto |T-T_c|$$

near the critical temperature. This assumption is based on the simple fact that $(\frac{\partial\pi}{\partial T})_\rho$ is an analytic function without singularity near T_c. This relation yields a relation

$$\frac{|\rho-\rho_c|}{\rho_c} \propto \left(\frac{|T-T_c|}{T_c}\right)^{\frac{1}{\delta}}.$$

Using this relation, we tried to obtain exponent δ using the iso-osmobar closest to the critical iso-osmobar. The plot at the bottom of Fig. 5 provides the $\log_{10}(\frac{|\rho-\rho_c|}{\rho_c})$ vs $\log_{10}(\frac{|T-T_0|}{T_0})$ plot for the iso-osmobar, where ρ_c is the critical density determined in the previous section, and T_0 is the transition temperature of this iso-osmobar. As this iso-osmobar is not the exact critical iso-osmobar, the plotted data deviate from the straight line when $\frac{|T-T_0|}{T_0}$ approaches 0. We calculated the slope of the most linear part of the plot where the slopes of both sides ($\rho > \rho_c$ and $\rho < \rho_c$) of the iso-osmobar coincide with each other. From this slope, we got the value $\delta = 4.1(1.2)$. This value of the exponent δ is in good agreement with the value provided by Li *et al.* ($\delta = 0.42 \pm 0.02$) [23].

3. *Other critical exponents α and γ*

Using the obtained values of two critical exponents $\beta = 0.38(1.5)$, $\delta = 4.1(1.2)$, Griffith's equation,

$$\alpha + 2\beta + \gamma = 2,$$

and Widom's equation

$$\gamma = \beta(\delta - 1),$$

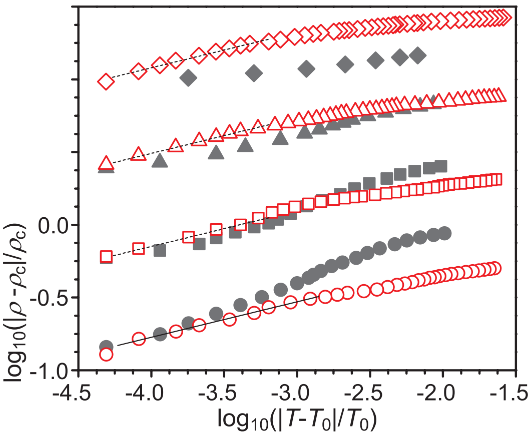

FIG. 5. (Color online) Using the iso-osmobars in Fig. 4, log$_{10}(\frac{|\rho-\rho_c|}{\rho_c})$ to log$_{10}(\frac{|T-T_0|}{T_0})$ are plotted to see the critical behavior of the iso-osmobars, where open symbols are for $\rho > \rho_c$, and filled symbols are for $\rho < \rho_c$. Each set of data plotted with an offset of 0.5 corresponds to the NaCl concentrations of 30 m*M* (circle), 20 m*M* (square), 10 m*M* (triangle), and 0 m*M* (diamond), from the bottom to the top. Here we adopted the transition temperature T_0 corresponding to each osmotic pressure instead of the critical temperature T_c, following the discussion of Li *et al.* [23]. The critical exponent δ was calculated using the plot which is closest to the critical iso-osmobar presented at the bottom of this figure. The solid line provides the slope of the log-log plot and the broken lines for plots above are the straight line with the same slope. The estimated value of δ was 4.15 (1.5), while the result of Ref. [23] was 4.2 (5).

we obtain the other exponents $\alpha = -0.06(12)$ and $\gamma = 1.28(15)$. Li *et al.* [23] had measured the exponent α along the critical iso-osmobar and determined that $\alpha = -0.08 \pm 0.19$ and $\delta = 0.42 \pm 0.5$. Table I presents the observed critical exponents and the other exponents calculated by the scaling relations for the polymer gel. In this table, experimentally observed critical exponents are presented with frame to distinguish them from the exponent obtained using scaling law. The critical exponents of 3D Ising model and those of gas-liquid transition of CO$_2$, which has very close values with those of the gel, are also presented in this table.

It is very important to point out here that the experiment by Li *et al.* [23] had used a "critical gel" having the total concentration of 143 mg/cm^3 (14.3 wt%) and the cross-linker fraction of 2.4%, while those parameters we employed were 15 wt% and 0.5%, respectively, which made the discrete transition wider at $\Pi = 0$. Both of the gels had almost the same total concentration of the polymer when polymerized, while the fractions of the cross-linkers were very different; the gel that undergoes discrete volume phase transition has less cross-link compared to the gel and undergoes second-order volume phase transition or continuous volume change at $\Pi = 0$. The gel with less cross-link is closer to the sol-gel boundary, where the correlation length diverges, than that with higher fraction of cross-linkers. Thus the inhomogeneity is believed to be larger for the former than the latter. It is very interesting and suggestive that the both gel systems have the same exponents within the experimental error, despite the difference of the composition of gels. We believe that the systematic study of the relation between the volume phase transition and inhomogeneity is of importance to understand not only the volume phase transition of the gels but also general phase transition phenomena.

IV. DISCUSSION

A. Inhomogeneity of the gel

In this report, we discuss the critical phenomena occurring in polymer gels. It is very important to note that this gel is a considerably inhomogeneous system as compared to ordinary liquid or gas phases. The most important inhomogeneity arises from the non-uniform distribution of cross-links. Such inhomogeneity plays a very important role in the swollen gel and creates built-in spatial density fluctuations in the system. For the shrunken state near the volume phase transition, however, the important length scale (correlation length) is

TABLE I. List of critical exponents of polymer gel and other systems. The exponents framed by a box are the experimentally determined values without using scaling law. This result indicates that three major critical exponents are determined experimentally for polymer gels. The critical exponents of a 3D Ising system and gas-liquid system, whose values are close to the gel system, are also provided for comparison. A set of exponents of mean-field theory is presented at the bottom.

Critical exponent		α	β	γ	δ
Polymer gel	This report	−0.06 (6)	$\boxed{0.38\ (1.5)}$	1.28 (2)	$\boxed{4.1\ (1.5)}$
	Method	Scaling	Experiment	Scaling	Experiment
	Li *et al.* [23]	$\boxed{-0.08\ (19)}$	0.40 (8)	1.3 (4)	$\boxed{4.2\ (5)}$
	Method	Experiment	Scaling	Scaling	Experiment
Other systems	3D Ising [30] (Simple cubic lattice)	0.110 (2)	0.3267 (10)	1.237 (2)	4.786 (14)
	CO$_2$ [31]	0.12	0.3447 (7)	1.2 (0.2)	4.2
	Mean field theory	0	1/2	1	3

determined not by chemical cross-links, but by the physical contact (entanglement) of the polymer network. If the correlation length associated with the volume phase transition is greater than this length scale, we can treat the gel as a homogeneous system. We also examined a gel system with more inhomogeneity than in the system considered in the present work, which revealed that the volume phase transition of the gel system is quite robust against inhomogeneity [32].

M. E. Fisher discussed the effects of such "hidden variables" on critical behavior and proposed the renormalization of the critical exponents to these effects [33]. As the critical exponent α plays an essential role in this renormalization, we did not attempt renormalization, because the error in the value of α is substantially large as compared to the other exponents. However, it might be of importance to note that the sign of the exponent α is changed by renormalization.

B. Reversibility

Air, as a semipermeable membrane, has a very interesting feature: Water from a gel in air can easily drip into NaCl solution when the gel shrinks. However, when the gel swells, it needs to absorb all the required water molecules from the air. We found that the swelling of the gel was "irreversibly" slow at the discrete volume phase transition. It required more than a month to reach the equilibrium state at the discrete transition. The experiment in which the swelling direction is considered is almost impossible to perform within a reasonable period of time. Thus, the data presented in this report were observed by raising the temperature, or in other words, the shrinking direction, as mentioned earlier.

C. Surface tension at the air-gel boundary

By using air as a semipermeable membrane, we introduced a new boundary in the system. We made measurements for the equation of the state at $\Pi = 0$ with the gel submerged in pure water. In this case, it was possible for the surface tension of the gel to be different from the case wherein a gel-air boundary existed. This fact indicates that further correction to the iso-osmobars might be required.

V. CONCLUSION

We experimentally determined the critical exponent β of a NIPA gel, for the first time, from a series of iso-osmobars obtained by a very simple method. The value of the critical exponent $\beta = 0.38(1.5)$ obtained here is very close to that of $\beta = 0.42(5)$ calculated from the measured values of α and δ using scaling law by Li *et al.* [23]. We have also obtained a very close value of critical exponent $\delta = 4.2(1.5)$, from the iso-osmobar closest to the critical iso-osmobar, to that experimentally obtained by Li *et al.* [23]. Thus, we can conclude that the three major critical exponents of the polymer gel system were obtained experimentally, and the results satisfied the scaling relation within the experimental error.

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