Interactions of a Dye and a Solvent with Poly(*N*-isopropylacrylamide) Gel in Relation to Its Phase-Transition Behavior

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The binding of a dyestuff and the sorption of a solvent to a polymer gel have been studied in relation to the phase-transition behavior of the gel. Binding or sorption isotherms of a dye (erythrosine B) and a solvent (benzyl alcohol) to a polymer gel (poly(*N*-isopropylacrylamide) : NIPA) were measured and found first to be Langmuir- and BET-type curves, respectively. A single Langmuir-type adsorption isotherm and the superposition of the two isotherms of the dye were fit for the collapsed (40 °C) and swollen states (25 °C) of the gel, respectively. The phase-transition behavior of the NIPA gel was not affected at all by binding of the dye, but was highly altered by the addition of benzyl alcohol. A reentrant-type phase transition of the NIPA gel was observed with increasing concentration of benzyl alcohol at 25 °C. It is quite interesting to note that the gel shrinks when the concentration of the solvent inside the gel attains its solubility limit (ca. 0.4 mol dm^{-3}), and swells again when it reaches the solubility in the bulk solution phase (outside the gel). At the stage of re-swelling, the solution in the gel interior consists of almost pure benzyl alcohol. These results indicate that the NIPA gel shows a selective sorption of benzyl alcohol, and separates it from its aqueous solutions.

Polymer gels have been extensively studied after their volume phase transition was discovered.[1,2] Studies on practical applications of the gels are also eagerly made.[3,4] Gel actuators,[5,6] which transform chemical or electric energy to mechanical energy, and drug delivery systems[7] are examples of the above.

Poly(*N*-isopropylacrylamide) (NIPA) gel is well known as a thermo-responsive hydrogel.[8] The NIPA gel shows a phase transition at about 34 °C, below which it is in a swollen state; however, at the transition point it shrinks to a collapsed one. This phase-transition behavior of the NIPA gel changes remarkably with some additives.[9—18] Surfactants[9—16] and organic solvents[9,17,18] are typical examples of such additives. The present authors previously studied the interactions between surfactants and the NIPA gel.[14,15] The phase-transition temperature was found to be dramatically elevated by the addition of a small amount of ionic surfactants.[10—15] Furthermore, the polymer chain network of gels very strongly affects the aggregation behaviors of surfactant molecules.[16] This work is an extension of the above-mentioned studies, and deals with the interactions of the gel with some amphiphilic compounds other than surfactants. We selected an anionic dye, erythrosine B, and an amphiphilic solvent, benzyl alcohol, as similar compounds to anionic and nonionic surfactants. The similarity and/or the difference between surfactants and the above-mentioned amphiphilic compounds are our main interest from the viewpoint of their interactions with the gel.

Experimental

Monomers and a reaction accelerator for the preparation of gel samples were *N*-isopropylacrylamide (Eastman Kodak Co.), *N*,*N*′-methylenebis(acrylamide) (a cross-linker; Wako Pure Chemical Industries Ltd.), and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (an accelerator of polymerization reaction; Wako Pure Chemical Industries Ltd.). A dye, erythrosine B (sodium salt of tetraiodofluorescein : Fig. 1), was purchased from Tokyo Chemical Industry Ltd. Benzyl alcohol and distilled water were obtained from Wako Pure Chemicals Industries Ltd. All of the samples were of guaranteed reagent grade, and were used without further purification.

Poly(*N*-isopropylacrylamide) (NIPA) gel was prepared by radical

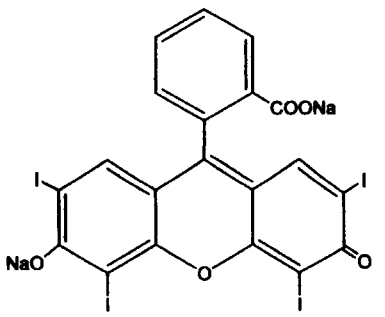

Fig. 1. Molecular structure of erythrosine B.

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polymerization. A mixture of 39.6 g (700 mM) (1 M = 1 mol dm^{-3}) of NIPA monomer, 0.65 g of *N,N'*-methylenebis(acrylamide) and 1.2 mL of *N,N,N',N'*-tetramethylethylenediamine was dissolved in pure water to be 500 mL of aqueous solution. Nitrogen gas was bubbled into this solution to purge oxygen for at least 30 min before polymerization. An aqueous solution of ammonium peroxodisulfate (4 wt%) was bubbled by N_2 gas, and a part of it (5 mL) was added to the above-mentioned monomer solution. A polymerization reaction was performed under a N_2 gas atmosphere in a thin capillary (inner diameter of 140 μm or 800 μm). The thus-obtained gel samples were thoroughly washed with a sufficient amount of pure water. Cylindrical gels of 140 and 800 μm diameter were employed for phase-transition measurements and to determine the binding isotherms, respectively.

The volume phase transition of NIPA gel was observed by measuring the diameter of the cylindrical gel (140 μm). The apparatus and the procedures of the phase-transition measurements have been described elsewhere.[14] The gel diameter was measured with a micrometer equipped with a charge coupled device (CCD) camera. Aqueous solutions having a certain concentration of erythrosine B were flowed continuously at a rate of 10 mL/min through a glass tube containing the sample gel. A large (at least 10^5 times greater) amount of the dye solution compared with the gel volume was used to obtain equilibrium. The temperature was kept constant (±0.1 °C) until an equilibrium diameter was obtained, and was then changed for the next measurement. Phase-transition experiments were performed in both heating and cooling processes. The swelling behavior of NIPA gel in benzyl alcohol solutions was observed by weighing the gel after being equilibrated with the solutions at constant temperature (25 and 40 °C).

Binding and sorption isotherms of erythrosine B and benzyl alcohol, respectively, were observed by the following procedure. Gel samples of 800 μm diameter (3—5 g) were put in a glass tube with a screw seal containing an erythrosine B or benzyl alcohol solution of 80 mL. Many such tubes with different dye or alcohol concentrations were allowed to stand at 25 and 40 °C (±1 °C) for 2 weeks. Equilibrium was assumed to be attained within 2 weeks, since no additional change in the binding amount was observed, even for a longer equilibration time. The binding or sorption amount of the dye or the alcohol to NIPA gel was calculated from the following equation after their concentration change in the solution outside the gel was determined:

$$A = \frac{W_0C_0 - C_1(W_0 + W_W)}{W_P/M_W}, \quad (1)$$

where A is the binding or sorption amount, expressed as the number of dye or benzyl alcohol molecules per one monomer unit of NIPA; C_0 and C_1 are the concentrations of the dye or the alcohol (mol kg^{-1}) of the solution outside the gel at the initial and final (equilibrated) state, respectively; W_0 is the mass (g) of the initial sample solution; W_P and W_W are the mass of the polymer and of water in the gel at the initial state (before immersed in the sample solution), respectively; and M_W is the molecular weight of the NIPA monomer. An excess amount of benzyl alcohol over its solubility was added to the initial solutions when its sorption amount was high. In such cases, the added amount of benzyl alcohol was, of course, corrected by putting one term ($+W_A$: moles of the added benzyl alcohol) in the numerator of the right-hand side of Eq. 1. In this equation, the concentration of erythrosine B or benzyl alcohol in the aqueous phase inside the gel is assumed to be equal to that of the solution outside the gel. The concentration of the erythrosine B and benzyl alcohol solutions was determined by visible-light absorption at 526 nm and a high-performance liquid chromatography (HPLC) technique, respectively. The HPLC was carried out with a UV (260 nm) detector and a column of Cica-Merck Hibar Lichrosorb RP-18 (5 μm) using an aqueous solution of 30 wt% methanol as an elusion solvent.

Results

Binding Isotherms of Erythrosine B or Sorption Isotherms of Benzyl Alcohol to NIPA Gel. Figure 2 shows the binding isotherms of erythrosine B onto NIPA gel at various temperatures. One can see from the figure that the binding amount is higher at 40 °C than those at 25, 28 and 30 °C, and should be a reminder of the phase-transition temperature (34 °C) of the gel. The collapsed phase of the NIPA gel may bind more of the dye molecules than the swollen phase in contrast to the case of ionic surfactants.[15] The shape of the binding curves seems to be a Langmuir-type, and is different from the sigmoidal one appearing in the binding isotherms of surfactants.[15]

The sorption isotherms of benzyl alcohol are shown in Fig. 3. The abscissa of the figure is expressed by the normalized concentration of benzyl alcohol (concentration/solubility limit (0.396 M at 25 °C and 0.430 M at 40 °C)). It is interesting to note that the sorption isotherms of the alcohol to the swollen state of NIPA at 25 °C and to the collapsed state at 40 °C are almost identical, and their shape is neither the type of erythrosine B nor that of surfactants.

Phase-Transition Behaviors of NIPA Gel on the Addition of Erythrosine B and Benzyl Alcohol. Figure 4 shows the swelling degree of the NIPA gel as a function of the temperature in the absence and presence of erythrosine B. The abscissa denotes the diameter (d) of the cylindrical gel normalized by the initial (as synthesized) diameter (d_0 = 140 μm). The swelling behavior of the NIPA gel does not change at all, even when the dye concentration changes.

The swelling degree of the NIPA gel is plotted against the concentration of benzyl alcohol at 25 and 40 °C in Fig. 5. The

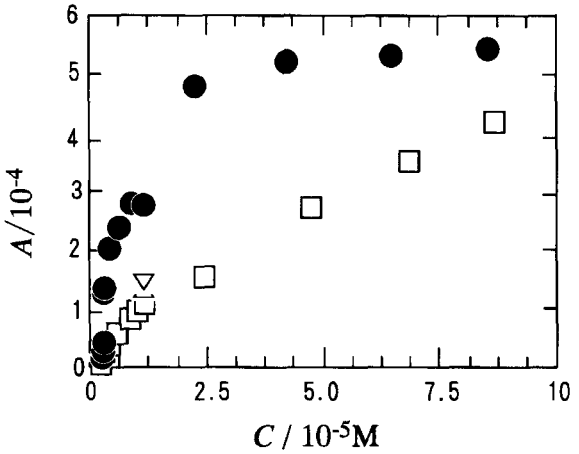

Fig. 2. Binding isotherms of erythrosine B onto NIPA gel at 25 °C (□), 28 °C (△), 30 °C (▽) and 40 °C (●). Open and filled symbols denote the swollen and the collapsed state of the gel. The data at 28 °C (△) and 30 °C (▽) were obtained only at 1.25×10^{-5} M.

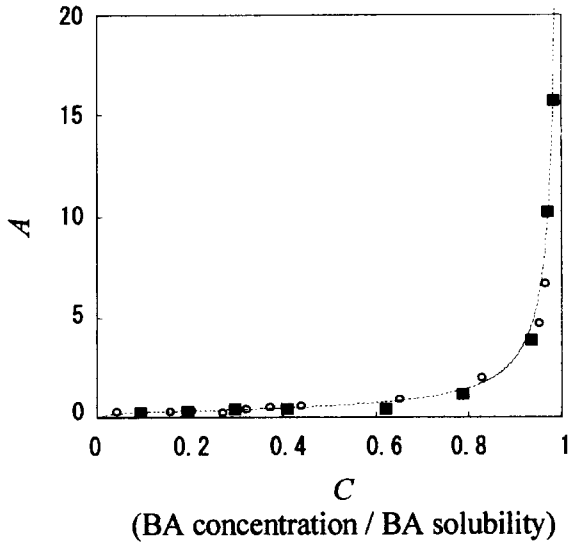

Fig. 3. Sorption isotherms of benzyl alcohol to NIPA gel at 25 °C (■) and 40 °C (○). Dotted line is the fitting curve for the BET equation.

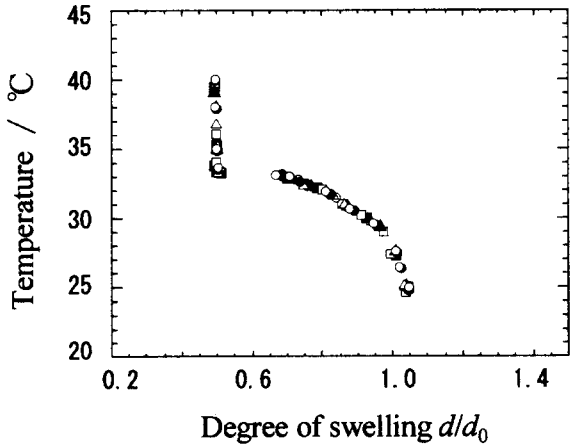

Fig. 4. Swelling behavior of NIPA gel as a function of temperature in the absence and the presence of erythrosine B. Erythrosine B concentrations are 0 (○, ●), 0.1 (□, ■) and 0.2 mM (△, ▲). Open and filled symbols denote the heating and the cooling processes, respectively, in the phase transition measurements.

ordinate (d/d_0) was calculated by extracting the cube root of the weight ratio of the gel, assuming the solution density to be unity. The abscissa is the same as that in Fig. 3. Although the NIPA gel exhibits a reentrant swelling behavior at 25 °C as a function of the benzyl alcohol concentration, simply transforms from the collapsed state to the swollen one at 40 °C. At both 25 and 40 °C, the gel swells at a benzyl alcohol concentration close to its solubility limit. It is particularly interesting to note in the phase-transition behavior at 25 °C that the NIPA gel shrinks at the concentration of benzyl alcohol solubility inside the gel. One can see from Fig. 5 that the gel collapses at about 0.3 normalized concentration of benzyl alcohol, i.e., at about 0.3×0.4 M = 0.12 M. The binding amount of the alcohol on the NIPA chain at this shrinking point can be estimated from Fig. 3 to be 0.39,

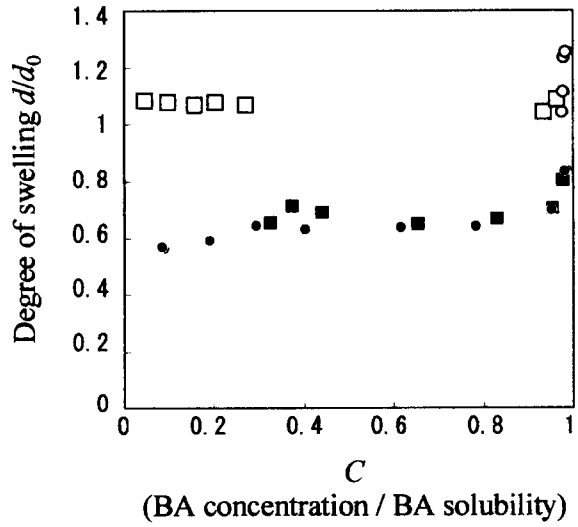

Fig. 5. Phase transition behaviors of NIPA gel as a function of benzyl alcohol concentration at 25 °C (□,■) and 40 °C (○,●). Open and filled symbols denote the swollen and the collapsed state of the gel, respectively.

i.e., 0.39×0.7 M (concentration of NIPA monomer) = 0.273 M. Consequently, the total concentration of benzyl alcohol inside the gel at the collapsed point is 0.393 M (= 0.12+0.273 M), which is very close to the solubility of benzyl alcohol in water at 25 °C (0.396 M).

Discussion

Type of Binding or Sorption Curves of Erythrosine B and Benzyl Alcohol. The binding or sorption curves shown in Figs. 2 and 3 are much different from those of surfactants onto NIPA gel reported previously.[15] In the case of surfactant binding, the sigmoidal shape is obtained below the phase-transition temperature (34 °C) of the gel. Above the transition temperature, the binding isotherms show a discontinuous jump due to the swelling transition by the surfactant binding.[15] The isotherms in Figs. 2 and 3 seem to be Langmuir- and BET-type, respectively, and were tried to be fitted to the Langmuir and BET equations.

The Langmuir adsorption isotherm can be expressed by the following equation:[19]

$$\frac{C}{A} = \frac{1}{KA_\infty} + \frac{C}{A_\infty}, \tag{2}$$

where A and C are the binding amount and the concentration of the dye, respectively, K the binding constant and A_∞ the saturated binding amount at infinite concentration. The data in Fig. 2 are re-plotted in Fig. 6 following Eq. 2. Although the values of C/A are well linearly related to C at 40 °C, as can be seen from the figure, the plot has a break point at 25 °C. These results indicate that although the binding of erythrosine B onto NIPA gel obeys the single Langmuir adsorption mechanism in the collapsed state of the gel, it obeys the superposition of the two mechanisms in the swollen state. The superposition may take place if two kinds of binding sites having different binding affinity are present in the swollen state of the gel. The values of K and A_∞ at

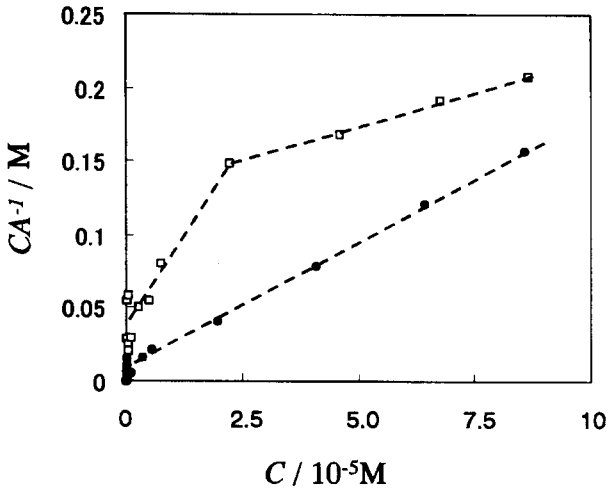

Fig. 6. The plots of C/A against C for the binding of erythrosine B onto NIPA gel at 25 °C (□) and 40 °C (●) to confirm the Langmuir-type adsorption mechanism. Data are taken from Fig. 1.

40 °C can be estimated to be 1.8×10^{5} M^{-1} and 5.8×10^{-4}, respectively, from the slope and the intercept of the straight lines in Fig. 6.

The following BET equation[20] seems to fit best to the data shown in Fig. 3:

$$\frac{C}{A(1-C)} = \frac{1}{KA_m} + \frac{(K-1)C}{KA_m}, \tag{3}$$

where A is the sorption amount of benzyl alcohol, C the concentration of the alcohol expressed as the normalized value, K the binding constant of the alcohol in the first layer (to the NIPA chain) and A_m the saturated adsorption amount in the first layer. Figure 7 shows plots of $C/A(1-C)$ against C using the data in Fig. 3. One can understand that benzyl alcohol molecules are bound onto NIPA gel in the fashion of the BET adsorption isotherm. The constants K and A_m were calculated to be 30 and 0.33, respectively. The value

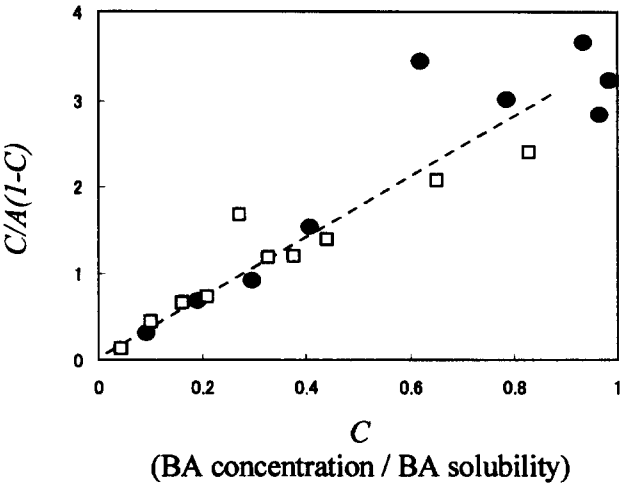

Fig. 7. The plots of $C/A(1-C)$ against C for the sorption of benzyl alcohol to NIPA gel at 25 °C (□) and 40 °C (●) to confirm the BET-type sorption mechanism. Data are taken from Fig. 3.

of A_m (0.33) should be compared with the saturated binding amount of anionic surfactants onto NIPA gel (0.2—0.5).

The Langmuir-type binding of erythrosine B and BET-type sorption of benzyl alcohol to NIPA gel was observed in this work. They are the first examples of Langmuir and BET curves found in the binding of small molecules to polymer chains of the gels, although sigmoidal curves have been known in the case of surfactants.[15]

Phase-Transition Behaviors of NIPA Gel upon the Addition of Erythrosine B and Benzyl Alcohol. The phase-transition behavior of NIPA gel is not affected at all by the binding of erythrosine B, as can be seen in Fig. 4. An anionic surfactant, e.g., sodium dodecyl sulfate, dramatically changes the phase-transition temperature of the NIPA gel.[14] A different effect between the dye and the surfactant on the NIPA gel phase-transition should be ascribed to their binding amount onto polymer chains of the gel, since the binding amount of erythrosine B is smaller by three orders of magnitude than that of the surfactants.[15]

As pointed out in the previous section, the NIPA gel transforms into a collapsed state when the benzyl alcohol concentration in the gel interior attains its solubility. Above the solubility limit, the phase separation of benzyl alcohol should occur inside the gel. Micro-phase-separation may take place along with the polymer chain, since the alcohol is condensed onto the chain due to its adsorption. Interfacial tension between the aqueous phase and the tiny separated-phase of benzyl alcohol might make the polymer chains come into contact with each other, and make the gel shrink. The interface mentioned above disappears when the separated benzyl alcohol phase also appears in the bulk aqueous phase (outside the gel). This may be the reason why the gel swells again at the solubility limit of benzyl alcohol in the bulk solution. One can understand the above mechanism by recognizing that the solution in the gel interior is almost pure benzyl alcohol when the gel swells again. As can be seen from Figs. 3 and 5, the binding amount of benzyl alcohol at the re-swelling point is about 15 (moles of the alcohol/mole of NIPA monomer). The concentration of the NIPA monomer is about 0.7 M. The concentration of benzyl alcohol is thus calculated to be ca. 10 M. The molar concentration of pure benzyl alcohol is also about 10. There is no longer any interface inside the gel, and no attractive force between the polymer chains.

One should pay much attention to the above result. Almost pure benzyl alcohol is present inside the gel when its concentration is about 0.4 M in bulk solution (outside the gel). This means that the NIPA gel shows selective sorption of benzyl alcohol and can strongly concentrate it in its interior.

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