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Volumetric Change and Surface Properties of Temperature-Sensitive Polyvinylalcohol (PVA) Hydrogel[1]

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Polyvinylalcohol (PVA) polymer gel is a temperature sensitive polymeric gel, with a critical transition temperature (with H_2O) of 310 K. At higher than 310 K, this temperature sensitive polymer gel shrinks because of discharging water, whereas at lower temperatures, the gel swelled because of absorbing water. The reversibility of the gel's volume change was confirmed by temperature swing. The adsorption behavior of an organic compound onto the PVA polymer gel in water was tested at various temperatures. The amount of adsorbed organic compound increased remarkably at temperatures higher than about 310 K. Then, it was confirmed that the organic compound in PVA polymer gel could be reversibly adsorbed and desorbed by a temperature change between 293 and 323 K. The mechanism of adsorption of the organic compound onto the PVA polymer gel could be explained by hydration and dehydration of polymer gel.

KEY WORDS: 1,2-dichloroethane; 1,2-dichloropropane; adsorption; chloroform; polyvinylalcohol; temperature sensitive gel; temperature swing; volumetric change.

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1. INTRODUCTION

Under appropriate control of chemical and cross-link structures, certain polymer gels exhibit property or molecular shape changes in response to slight changes in the external environment such as temperature, solvent composition, magnetic field, pH, or light [1–3]. These gels are called environmentally-sensitive polymer gels, or intelligent materials, and their application in artificial muscles and drug delivery systems has been investigated. The environmentally-sensitive polymer gels reported to date are poly-N-isopropylacrylamide (NIPA) and poly-vinylmethylether (PVME) [4–6] as shown in Table I. There are at least 3–4 other classes of polymeric gels reported in the literature.

The present authors' research group identified a polymer gel that is primarily composed of polyvinylalcohol (PVA), and which is partially cross-linked as a temperature sensitive polymer gel that expands or contracts according to temperature changes [7, 8]. The reversible phenomenon of volumetric contraction of up to 35% in response to a temperature rise from 280 to 310 K is confirmed in this work. The expansion and contraction behaviors of this polymer hydrogel have been explained in terms of hydration and dehydration of the gel.

The PVA polymeric gel adsorbed more organic substances in a contracted state (310 K or more) than in a expanded state (298 K) [9, 10]. This indicates that dehydration eliminates water easily from the surface of the gel in a contracted state. The PVA polymer gel presented in this study is shown to be a temperature-sensitive material. The polymeric gel is a high-function material that has potential application as a carrier for organic substance adsorption and in chemical substance transportation systems.

Table I. Chemical Structure of Temperature Sensitive Polymer Gels

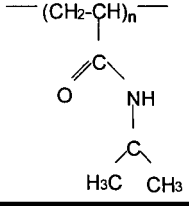
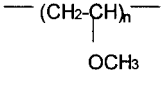
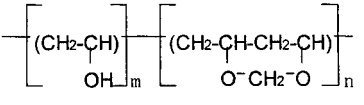
Poly-N-isopropylacrylamide (NIPA)	Polyvinylmethylether (PVME)	Polyvinylalcohol (bridging) (PVA)
		

Table II. Chemical Structure of Organic Compounds Used in this Experiment

Substance	Structure formula	Molecular weight	Purity (mass%)
Chloroform	$CHCl_3$	119.4	99.0
1.2-Dichloroethane	$ClCH_2CH_2Cl$	98.96	99.5
1.2-Dichloropropane	$CH_3CHClCH_2Cl$	113	98.0

2. MATERIALS

Polyvinylalcohol (PVA) was supplied by Krarey Co. Ltd. The degree of saponification was 99.8 mol%, and the degree of polymerization was 1700. The physical properties and molar mass of organic compounds used in this study are listed in Table II along with their purity. The reagent grade of organic compounds (chloroform, 1.2-dichloroethane, and 1,2-dichloropropane) were prepared from Wako Pure Chemicals Co., to be regent grade. Their purities were, according to the supplier, all higher than 99.9%.

3. EXPERIMENTAL METHOD

3.1. Synthesis of PVA Polymer Gel

Polyvinylalcohol (PVA) was initially generated from vinyl acetate. The degree of saponification was 99.8 mol%, and the degree of polymerization is 1700. Sodium alginate (1 mass%) and sodium hydrogen carbonate (0.3 mass%) were added to this PVA (8 mass%) to prepare a mixed solution. Using a roller pump with silicone tubing of 4 mm internal diameter and a nozzle with an internal diameter of 3 mm, the solution was added to a stirred calcium chloride solution ($0.1\ mol \cdot l^{-1}$) at $5\ ml \cdot min^{-1}$. In the solution, as the sodium alginate became calcium alginate, this mixture containing PVA became spherical solid beads in the solution. The spherical solids were soaked in a water solution of formaldehyde ($20\ g \cdot l^{-1}$), sulfuric acid ($200\ g \cdot l^{-1}$), and sodium sulfate ($100\ g \cdot l^{-1}$) for 60 min at 313 K. The solidified gel was treated with acetal, and the degree of cross-linking was about 50%. The degree of cross-linking was calculated from the concentration difference of formaldehyde in the solution before and after the acetal reaction. This value is mole ratio of PVA to used formaldehyde in this acetal reaction. Finally, synthesized PVA polymer gel was introduced into the sodium hydroxide solution ($1\ mol \cdot l^{-1}$) in order to remove the calcium alginate from the PVA polymer gel. In this reaction, the calcium alginate was removed from the PVA polymer gel as sodium alginate again. PVA

polymer gel with spherical solids was obtained by this synthesis procedure. Repeat-unit structure PVA polymer gel and other popular temperature-sensitive polymer gel are given in Table I.

3.2. Adsorption Test of Organic Compounds in Water

Experiments for adsorption of small amounts of organic compounds onto PVA polymer gel in water were carried out over the temperature range from 293 to 333 K. An initial concentration of organic compound in water is 200 ppm (10^3 mg·cm^{-3}). An aqueous solution of 100 cm^3 including organic compound and 50 gels were introduced into the flask of 300 cm^3 capacity at room temperature. The flask was shaken for 60 min in the constant temperature water bath. An adsorption test was carried out in the range of temperatures from 293 to 333 K. The amount of adsorption onto PVA polymer gel was determined from the difference between the initial and final concentrations of organic compound for each temperature. The concentration of organic compound in water was measured by capillary type gas chromatography. The effect of the vapor-liquid equilibrium of organic compounds on temperature swings was corrected by blank tests for each experiment.

4. RESULTS AND DISCUSSIONS

4.1. Volumetric Change of PVA Polymer Gel with Temperature Swings

Figure 1 shows the volumetric changes of PVA polymer gel with temperature and a photo of the gel in water at 275 and 323 K. The gel spheres, about 5 mm in diameter at water temperatures between 273 and 280 K, contracted with increasing temperature to about 4 mm in diameter at 310 K or higher. The average diameter was obtained from a digital image on a computer screen, and the volume was calculated assuming the PVA polymer gel to be perfectly spherical.

This demonstrates that the PVA polymer gel was temperature sensitive, contracting by about 30 to 40% in volume with water temperature. The reversibility of the volumetric change of the gel with water temperature was confirmed by five experimental trials. Figure 2 shows the repeated tests for the volumetric change of PVA polymer gel in water at 298 and 323 K.

4.2. Adsorption Behavior of Organic Compound in Water

In order to examine the change of surface properties of polymer gel with temperature swing, adsorption experiments of organic compounds in

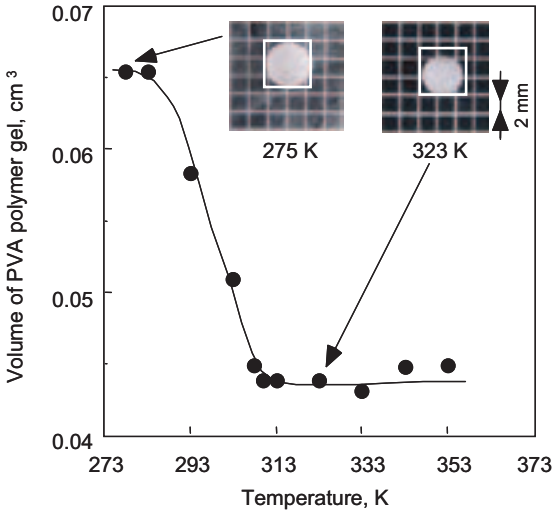


Fig. 1. Volumetric change of PVA polymer gel in water at various temperatures.

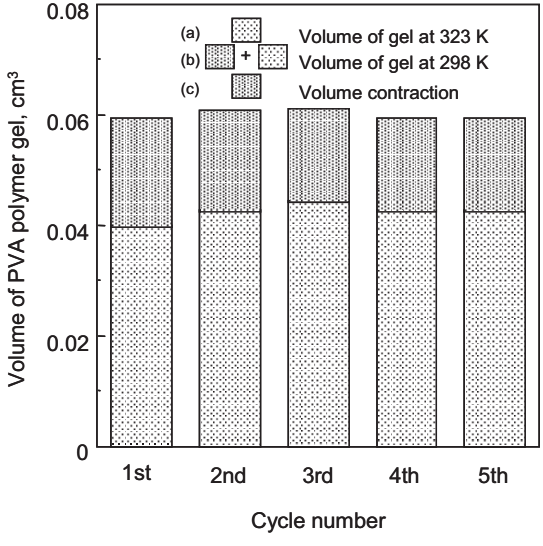


Fig. 2. Repeated tests for volumetric change of PVA polymer gel in sater at 298 and 323 K; volume is the average value for three gels; and equilibrium time is 3 h.

water were carried out for comparison of surface properties of PVA polymer gel between 298 and 323 K. Chloroform, 1.2-dichloroethane, and 1,2-dichloropropane were chosen as organic materials for the adsorption test. Figure 3 shows the amount of chloroform onto PVA polymer gel at different temperatures. The PVA polymer gel adsorbed more chloroform in a contracted state (310 K or more) than in an expanded state (298 K). The amount of adsorption of chloroform in aqueous solution at 323 K was 0.23 mmol/g-gel; this was a higher value than that at 298 K (0.02 mmol/g-gel). This indicates that dehydration eliminates water easily from the surface of the gel in a contracted state. The relation between the amount of adsorption of 1.2-dichloroethane and 1,2-dichloropropane onto PVA polymer gel with temperature is shown in Fig. 4. The amounts of adsorption of 1,2-dichloroethane and 1,2-dichloropropane in aqueous solution at 323 K were 0.32 and 0.44 mmol/g-gel, respectively; and they were significantly higher than those at 298 K (0.02 or 0.05 mmol/g-gel, respectively). This also indicates that dehydration eliminates water easily from the surface of the gel in a contracted state. The difference of the adsorption amount can be applied to the separation of organic compounds from water using temperature swing. Figure 5 shows an adsorption isotherm of

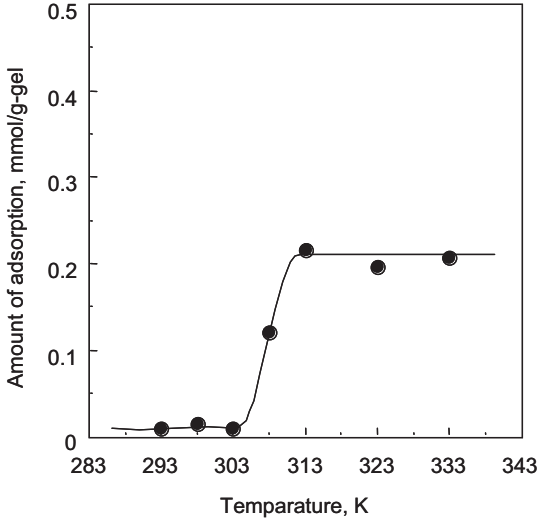


Fig. 3. Adsorbed amount of chloroform onto PVA polymer gel; gel number is 50; initial concentration is 200 ppm; volume of solution is 100 cm^3; and exposure time with agitation is 1 h.

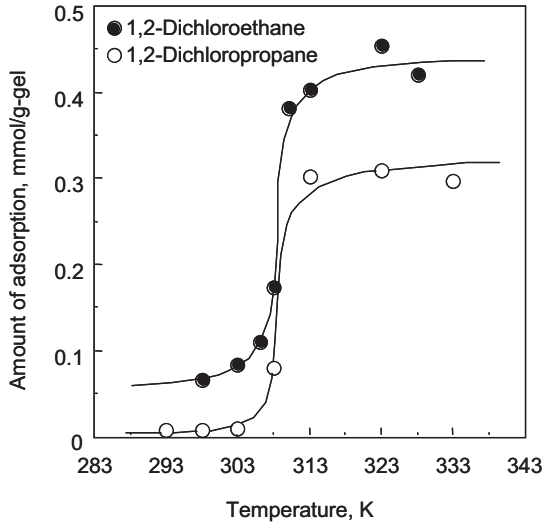


Fig. 4. Adsorbed amount of organic compounds onto PVA polymer gel; gel number is 50; initial concentration is 200 ppm; volume of solution is 100 cm^3; and exposure time with agitation is 1 h.

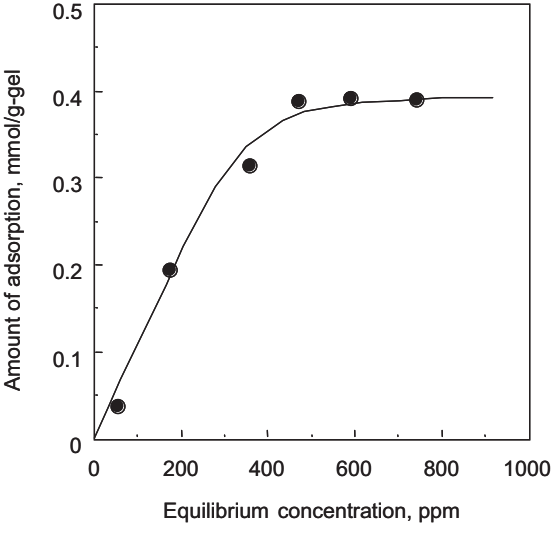


Fig. 5. Adsorption isotherm of chloroform onto PVA polymer gel in water at 323 K; gel number is 50; volume of solution is 100 cm^3; and exposure time with agitation is 1 h.

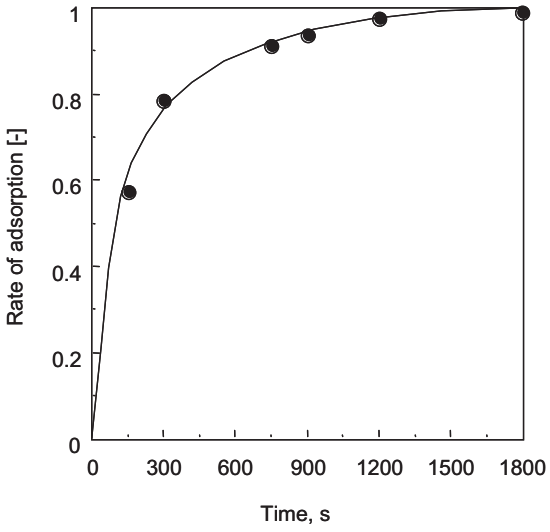


Fig. 6. Rate of adsorption for chloroform onto PVA polymer gel in water at 323 K; gel number is 50; initial concentration is 200 ppm; and volume of solution is 100 cm^3.

chloroform in water onto PVA polymer gel at 323 K. The rate of adsorption for chloroform onto PVA polymer gel in water is shown in Fig. 6. It takes 20 min to reach a saturated adsorption state. Figure 7 shows the effect of temperature swing on adsorption behavior. When the temperature is stepped between 298 and 333 K, the adsorption amount of chloroform changed recessively according to temperature swing.

Figure 8 shows the mechanism of adsorption behavior of organic compound onto PVA polymer gel by temperature swing. The expansion and contraction behaviors are mainly caused by the hydration and dehydration. PVA polymer gel in a contracted state at a higher temperature than 310 K can adsorb organic compounds from water. It is thought that the driving force of this adsorption is the hydrophobic interaction between the gel surface of the contracted state and the organic compound.

5. CONCLUSION

It was found that PVA polymer gel, synthesized in this study, is a temperature-sensitive polymer gels. The volume of gel in water was induced at around 310 K. At higher than 310 K, this temperature sensitive polymer

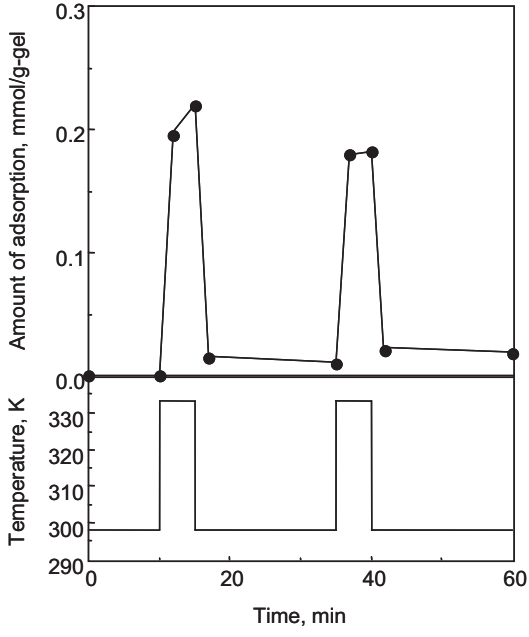


Fig. 7. Effect of temperature swing for adsorption of chloroform onto PVA polymer gel; gel number is 50; initial concentration is 200 ppm; volume of solution is 100 cm^3; and exposure time with agitation is 1 h.

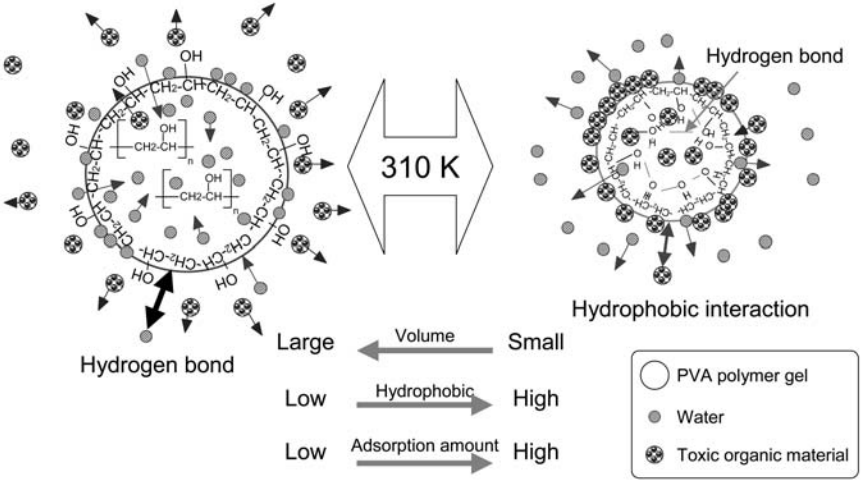


Fig. 8. Mechanism of adsorption-desorption process of organic materials on PVA polymer gel.

gel shrunk because of discharging water, whereas at lower temperature, the gel swelled by absorbing water. The adsorption behavior of organic compound in water was tested at various temperatures using the PVA polymer gel. The amount of adsorbed organic compounds increased remarkably at higher temperatures than at about 310 K. It was also observed that the PVA polymer gel could be effective for the adsorption removal of an extremely small amount of toxic organic compound in drinking water, and they could be repeatedly usable as an adsorbent. The mechanism of adsorption of organic compound on the PVA polymer gel could be explained by hydration and dehydration of the gel. The polymer gel is a high-function material that has potential application as a carrier for organic substance adsorption and in chemical substance transportation systems. From the results obtained in this study, PVA polymer gel is expected to have applications in drug delivery systems and removal of toxic organic compounds in water using the reversible volumetric change.

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