

Investigation of Temperature-Swing Adsorption of Aromatic Compounds in Water Using Polyampholyte Gels with Hydrophilic Nonionic Groups

Shintaro Morisada,¹ Hiroko Suzuki,¹ Yoshitsugu Hirokawa,² Yoshio Nakano¹

¹Department of Environmental Chemistry and Engineering, Tokyo Institute of Technology, Nagatsuta, Midori-Ku, Yokohama, Kanagawa, Japan

²Department of Materials Science, The University of Shiga Prefecture, Hassaka, Hikone, Shiga, Japan

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ABSTRACT: The adsorption and desorption behaviors of bisphenol-A in water have been studied using the temperature-responsive polyampholyte gels composed of sodium styrene sulfate (SSS), vinylbenzyl trimethylammonium chloride (VBTA), and *N,N'*-dimethylacrylamide (DMAA). The resultant behaviors of the SSS-VBTA-DMAA gels of three different monomer compositions are compared with those of the SSS-VBTA gel that can adsorb bisphenol-A at room temperature and desorb the pre-adsorbed bisphenol-A at higher temperature as in our previous report (Morisada et al., *Adsorption* 2008, 14, 621), to elucidate the effect of DMAA on the adsorption property of the polyampholyte gel. The adsorption isotherms, which were described by Henry's law, indicated that the adsorption amounts of bisphenol-A onto the SSS-VBTA-DMAA gels at 298 K are much larger than those at 353 K. At 298 K, the Henry's adsorption constant for the SSS-VBTA-DMAA gel with the

lowest mole fraction of DMAA was larger than that for the SSS-VBTA gel, whereas a further increase in the DMAA mole fraction resulted in a decrease in the adsorption constant. Moreover, the temperature-swing adsorption experiments demonstrated that the SSS-VBTA-DMAA gel can repeatedly adsorb bisphenol-A at 298 K and desorb some of the pre-adsorbed bisphenol-A at 353 K, where the desorption amount of bisphenol-A is larger than that from the SSS-VBTA gel. The results obtained here show that the addition of DMAA to the SSS-VBTA gel slightly improves the performance of the gel as a temperature-responsive adsorbent. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2968–2973, 2011

Key words: hydrogels; adsorption; stimuli-sensitive polymers; polyampholyte; aromatic compound; hydrophobic interaction

INTRODUCTION

Some hydrophobic aromatic compounds are referred to as possible endocrine-disrupting chemicals, which may affect the balance of normal hormonal functions in animals and humans.¹ The removal of the aromatic compounds in water is, thus, indispensable to environmental protection. In their removal processes, if the temperature-swing adsorption is employed using temperature-responsive polymer gels as adsorbent, simplification of the process and reduction of waste can be achieved: here, the temperature-responsive polymer gel is one of the stimuli-responsive polymer

gels that show the property changes in response to the changes in their external conditions.

Poly(*N*-isopropylacrylamide) gel is the most famous among the temperature-responsive polymer gels and have attracted much attention.^{2–12} Previously, we found that the poly(*N*-isopropylacrylamide) gel exhibits the temperature-swing adsorption behavior for the hydrophobic organic compounds in aqueous solutions.^{13,14} Some research groups also demonstrated the temperature-swing adsorption of hydrophobic compounds in aqueous solutions using poly(vinyl methylether) gel,^{15,16} photo-crosslinked gels,^{17,18} and poly(vinyl alcohol) gel.^{19,20} However, when these temperature-responsive polymer gels are applied to the removal of hydrophobic compounds from very dilute solutions such as environmental water, a vast amount of energy is required to heat a large amount of aqueous solution because they can adsorb the hydrophobic compounds at more or less higher temperature than room temperature. This indicates that the temperature-responsive polymer gel with the opposite temperature dependence of adsorption behavior is much more preferable for the adsorption removal of the hydrophobic compounds in a large amount of water.

Correspondence to: S. Morisada (smorisada@chemenv.titech.ac.jp).

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In the previous study,¹⁴ we succeeded in developing the temperature-responsive polyampholyte gel that can adsorb hydrophobic aromatic compounds at room temperature and desorb some of them at higher temperature, where the gel was composed of sodium styrene sulfate (SSS) and vinylbenzyl trimethylammonium chloride (VBTA). The mechanism of this temperature-swing adsorption behavior of the SSS-VBTA gel is considered as follows. The SSS-VBTA gel has both the hydrophobic aromatic rings and the hydrophilic ionic groups. In general, the hydration property of ions in water changes from structure-breaking (negative hydration) to structure-making (positive hydration) with increasing temperature.^{21–23} Accordingly, the hydrophilic property of the SSS-VBTA gel is considered to become dominant with increasing temperature because the hydration structure around its ionic groups becomes stronger. For this reason, the SSS-VBTA gel can adsorb the hydrophobic compounds through the hydrophobic interaction at room temperature and release the pre-adsorbed compounds at higher temperature. Also, it was found that in addition to the hydrophobic interaction, the interaction between the aromatic rings of the SSS-VBTA gel and the hydrophobic aromatic compounds may play an important role in their adsorption.

As mentioned above, we demonstrated that the SSS-VBTA gel can adsorb and desorb the hydrophobic aromatic compounds at room temperature and higher temperature, respectively. Unfortunately, however, the desorption amount was only about half of the adsorption amount: in other words, a considerable amount of the hydrophobic compounds was remained to be adsorbed on the gel even at higher temperature. For the temperature-swing adsorption, the desorption amount is essential, which practically corresponds to the absolute difference between the adsorption amounts at lower and higher temperatures. Thus, there is room for improvement in the adsorption behavior of the SSS-VBTA gel as a temperature-responsive adsorbent. The adsorption behavior of the SSS-VBTA gel is attributed to the balance between the hydrophilicity of the ionic groups and the hydrophobicity of the aromatic groups. This indicates that the addition of another monomer into the SSS-VBTA gel may change the adsorption property of the gel because of the change of its hydrophilic–hydrophobic balance. For the additional monomer, we have considered *N,N*-dimethylacrylamide (DMAA) to be suitable because DMAA is hydrophilic with no aromatic group and thus expected to change the hydrophilic–hydrophobic balance of the gel without interacting with aromatic compounds directly.

In this study, we investigate the adsorption behavior of the polyampholyte gels composed of SSS, VBTA, and DMAA using bisphenol-A as a model adsorbate. The adsorption isotherms of bisphenol-A for the

TABLE I
Monomer Concentrations Used for the Preparations of the SSS-VBTA and the SSS-VBTA-DMAA Gels

Gel	Concentration (M)			Mole fraction of DMAA, x_{DMAA}
	SSS	VBTA	DMAA	
SSS-VBTA gel	0.7	0.7	0	0
SSS-VBTA-DMAA gel	0.6	0.6	0.2	0.14
	0.5	0.5	0.4	0.29
	0.3	0.3	0.8	0.57

SSS-VBTA-DMAA gels of three different monomer compositions are obtained at room and higher temperatures to examine the possibility that the desorption amount can be increased. Subsequently, the temperature-swing adsorption experiments are carried out using the most promising terpolymer gel, judging from the results of the adsorption isotherms. To compare with the results of the SSS-VBTA-DMAA gels, the corresponding experiments are also conducted using the SSS-VBTA gel.

EXPERIMENTAL

Materials

SSS and VBTA were purchased from Aldrich (St. Louis, MO), and DMAA was kindly provided by Kohjin Co., Ltd. (Tokyo, Japan). *N,N*-Methylenebisacrylamide (BIS) and ammonium persulfate (APS) were used as a crosslinker and an initiator, respectively: these reagents were obtained from Wako Pure Chemical Industries Ltd. (Osaka, Japan). Bisphenol-A was purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan) and used as an adsorbate. Deionized and distilled water was used in all procedures, and all reagents were used as received in this study.

Preparation of polymer gels

All polymer gels were prepared by free-radical polymerization under nitrogen atmosphere. SSS, VBTA, and DMAA were dissolved in a 3 M NaCl aqueous solution: the monomer concentrations of the polymerization solutions are summarized in Table I. Note that the total monomer concentration was fixed at 1.4 M in all solutions, and the concentrations of SSS and VBTA were the same to keep the total charge of the gel neutral. BIS (0.02 M) was also dissolved in the aqueous solution. After addition of APS (0.002 M), the solution was transferred to a test tube containing glass capillaries of 20 μL . The polymerization was carried out at 353 K for 24 h. After gelation was completed, the cylindrical gels were taken out of the capillaries and

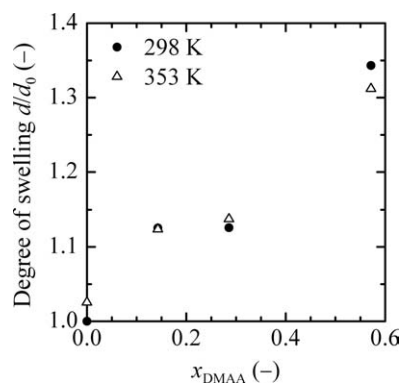


Figure 1 Swelling degrees of the SSS-VBTA gel ($x_{\text{DMAA}} = 0$) and the SSS-VBTA-DMAA gels ($x_{\text{DMAA}} = 0.14, 0.29,$ and 0.57) in water, d/d_0 , at 298 K (filled circles) and 353 K (open triangles) as a function of mole fraction of DMAA, x_{DMAA} . d_0 is the diameter of the SSS-VBTA gel at 298 K. See also Table I.

washed thoroughly with distilled water to remove the residual chemicals.

Swelling measurements

The cylindrical gel obtained above was immersed in 10 mL water at 298 or 353 K. The equilibrium diameter of the cylindrical gel in water at given temperature, d , was measured using an optical microscope (IX71, Olympus). The degree of swelling was represented by d/d_0 : here, d of the SSS-VBTA gel at 298 K was used as d_0 to clarify the effect of the monomer composition on the swelling of the gel.

Adsorption experiments

All adsorption experiments in this study were carried out in a batch system. To obtain the adsorption isotherms, the single cylindrical gel was soaked in 5 mL aqueous solution containing bisphenol-A at the initial concentrations ranging from 20 to 100 μM . The sample was vigorously shaken in a water bath at 298 or 353 K for more than 4 days. The concentration of bisphenol-A in the aqueous solution was determined by UV absorbance measured with a UV-vis spectrophotometer (V-550, Jasco), and then the amount of bisphenol-A adsorbed onto the gel was calculated from the mass balance. The wavelength used in the UV measurements was 276 nm.

In the temperature-swing adsorption experiments, the two cylindrical gels were immersed in 10 mL bisphenol-A aqueous solution at the initial concentration of 100 μM . The temperature-swing operation between 298 and 353 K was conducted as follows: (i) the sample was initially shaken in a water bath at 298 K; (ii) after 48 h, the sample was transferred to and shaken in another water bath at 353 K; (iii) after another 48 h, the sample was brought back to and shaken in the water bath at 298 K; and (iv) the procedures (ii) and (iii) were repeated.

RESULTS AND DISCUSSION

Degree of swelling

Figure 1 shows the swelling degrees d/d_0 of the SSS-VBTA and the SSS-VBTA-DMAA gels in water at 298 and 353 K as a function of the mole fraction of DMAA, x_{DMAA} : the values of d/d_0 at $x_{\text{DMAA}} = 0$ represent the results of the SSS-VBTA gel. For each value of x_{DMAA} , the swelling degrees d/d_0 at 298 and 353 K are only slightly different from each other, indicating that the volume of each gel is independent of temperature within the range of 298–353 K. Although the SSS-VBTA gel should be favorably hydrated because of the hydrophilicity of the constituent monomers, the electrostatic attraction between the negatively charged SSS and the positively charged VBTA prevents the significant swelling of the gel. As for the SSS-VBTA-DMAA gel, d/d_0 is larger than that of the SSS-VBTA gel and increases with increasing x_{DMAA} . This is because DMAA is also hydrated favorably, and the attractive interactions between SSS and VBTA become less significant with decreasing their mole fractions in the gels.

Adsorption isotherms

The adsorption isotherms of bisphenol-A for the SSS-VBTA and the SSS-VBTA-DMAA gels are shown in Figure 2, where C_e is the equilibrium concentration of bisphenol-A in the aqueous solution and q_e is the equilibrium amount of bisphenol-A adsorbed onto the gel. For the SSS-VBTA gel, the values of q_e

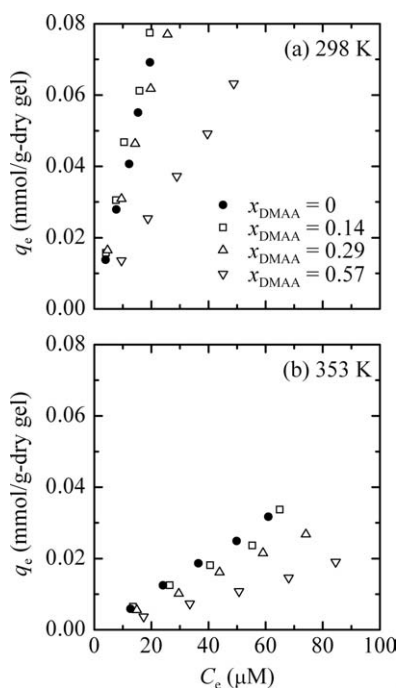


Figure 2 Adsorption isotherms of bisphenol-A for the SSS-VBTA gel ($x_{\text{DMAA}} = 0$, filled circles) and the SSS-VBTA-DMAA gels ($x_{\text{DMAA}} = 0.14, 0.29,$ and 0.57 , open symbols) at different temperatures: (a) 298 K; (b) 353 K. See also Table I.

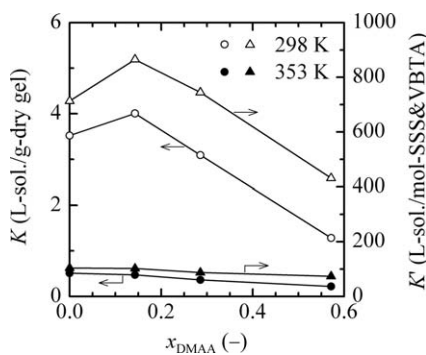


Figure 3 Adsorption constants K and K' of bisphenol-A for the SSS-VBTA gel ($x_{\text{DMAA}} = 0$) and the SSS-VBTA-DMAA gels ($x_{\text{DMAA}} = 0.14, 0.29, \text{ and } 0.57$) at 298 K (open symbols) and 353 K (filled symbols) as a function of mole fraction of DMAA, x_{DMAA} . See also Table I.

at 298 K are larger than those at 353 K. At low temperature, the SSS-VBTA gel, which has both the hydrophobic benzene rings and the hydrophilic ionic groups, can adsorb bisphenol-A through the hydrophobic interaction with the benzene rings. In general, the hydration property of an ion in aqueous solution changes from structure-breaking (negative hydration) to structure-making (positive hydration) with increasing temperature.^{21–23} This indicates that the hydrophilic property of the SSS-VBTA gel may become dominant with increasing temperature because the hydration structure around its ionic groups becomes stronger. Additionally, the solubility of bisphenol-A in water increases with increasing temperature. These may be the reasons why the adsorption amounts of bisphenol-A onto the SSS-VBTA gel decrease with increasing temperature.

For the SSS-VBTA-DMAA gels, the values of q_e at 298 K are also larger than those at 353 K, as seen in Figure 2. At 298 K, the values of q_e for the SSS-VBTA-DMAA gel of $x_{\text{DMAA}} = 0.57$ are smaller than those for the SSS-VBTA gel, whereas the adsorption isotherms for the terpolymer gels of smaller x_{DMAA} are close to that for the SSS-VBTA gel. At 353 K, on the other hand, the values of q_e decrease with increasing x_{DMAA} .

Adsorption constants

As seen in the results of the adsorption isotherms shown in Figure 2, the relations between q_e and C_e in the range of the concentrations investigated in this study can be described by Henry's law:

$$q_e = KC_e \quad (1)$$

where K is the Henry's adsorption constant. To clarify the effect of the monomer composition on the adsorbabilities of bisphenol-A, we evaluated the values of K by fitting Eq. (1) to each adsorption isotherm. Figure 3

shows the resultant values of K as a function of x_{DMAA} . At 298 K, the value of K for the SSS-VBTA-DMAA gel of $x_{\text{DMAA}} = 0.14$ is larger than that for the SSS-VBTA gel ($x_{\text{DMAA}} = 0$), and a further increase in x_{DMAA} leads to a decrease in K . At 353 K, on the other hand, the values of K are much smaller than those at 298 K and only slightly decrease with increasing x_{DMAA} . As mentioned in the previous section, the hydrophobic interaction between bisphenol-A and the benzene rings in the gels plays an important role in the bisphenol-A adsorption by the SSS-VBTA and the SSS-VBTA-DMAA gels. The results of the swelling degrees presented in Figure 1 show that the size of the polymer mesh of the gel increases with x_{DMAA} . For this reason, the accessibility of bisphenol-A to the benzene rings (i.e., SSS and VBTA) becomes easier with increasing x_{DMAA} , thereby leading to an increase in the value of K . Meanwhile, an increase in x_{DMAA} causes decreases both in the total number of SSS and VBTA and in the hydrophobicity of the gel: these decreases lead to a decrease in K . To consider only the effect of the hydrophobicity on the adsorbability, we computed the adsorption constants per total mole of SSS and VBTA, K' , from the relation between q_e and the equilibrium concentration per total mole of SSS and VBTA, C_e' . The obtained values of K' are shown in Figure 3. At both 298 and 353 K, the dependence of K' on x_{DMAA} is quite similar to that of K , indicating that the hydrophobicity decrease is the dominant negative factor in the adsorbability of bisphenol-A onto the gels.

Temperature-swing adsorption

In the temperature-swing adsorption process, the desorption amount is essential, which corresponds to the absolute difference between the adsorption amounts at lower and higher temperatures. Figure 4

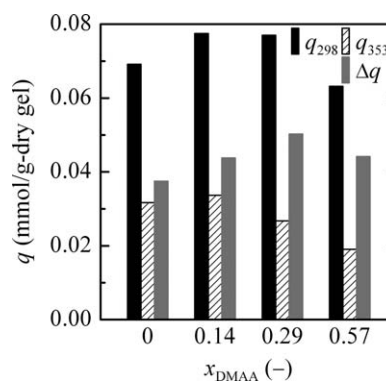


Figure 4 Amounts of bisphenol-A adsorbed onto the SSS-VBTA gel ($x_{\text{DMAA}} = 0$) and the SSS-VBTA-DMAA gels ($x_{\text{DMAA}} = 0.14, 0.29, \text{ and } 0.57$) at initial bisphenol-A concentration of 100 μM at 298 and 353 K, q_{298} and q_{353} , and the absolute differences between them, $\Delta q = |q_{298} - q_{353}|$. See also Table I.

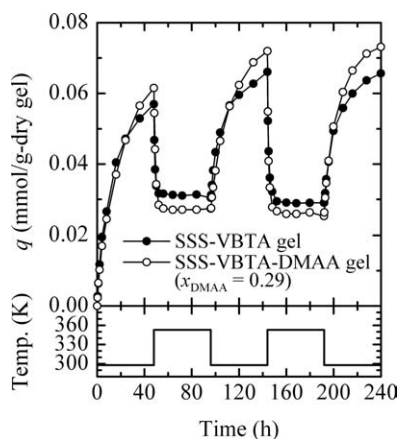


Figure 5 Time and temperature dependences of amount of bisphenol-A adsorbed onto the SSS-VBTA gel (filled circles) and the SSS-VBTA-DMAA gel of $x_{\text{DMAA}} = 0.29$ (open circles).

shows the equilibrium adsorption amounts of bisphenol-A at the initial bisphenol-A concentration of $100 \mu\text{M}$ at 298 and 353 K, q_{298} and q_{353} , as well as the absolute difference between them, $\Delta q = |q_{298} - q_{353}|$. Note that the values of q_{298} and q_{353} correspond to the results of the isotherms shown in Figure 2. As seen in Figure 4, both q_{298} and q_{353} for the SSS-VBTA-DMAA gel of $x_{\text{DMAA}} = 0.14$ are larger than those for the SSS-VBTA gel ($x_{\text{DMAA}} = 0$), whereas a further increase in x_{DMAA} results in a decrease in these adsorption amounts. As a result of such changes in q_{298} and q_{353} , Δq for the SSS-VBTA-DMAA gel of $x_{\text{DMAA}} = 0.29$ is largest among the gels used in this study, suggesting that this terpolymer gel is the most promising adsorbent for the temperature-swing adsorption of bisphenol-A.

The temperature-swing adsorption experiments were then conducted using the SSS-VBTA gel and the SSS-VBTA-DMAA gel of $x_{\text{DMAA}} = 0.29$, as shown in Figure 5: for convenience, the temperature of the water bath is used as a substitute for the sample temperature. As seen in Figure 5, both polymer gels adsorbed bisphenol-A at 298 K and desorbed about half of pre-adsorbed bisphenol-A rapidly after the temperature increases from 298 to 353 K. It is worth noting that these adsorption and desorption behaviors can be repeated by the temperature-swing operation. With increasing temperature, the hydrophilicity of the SSS-VBTA and the SSS-VBTA-DMAA gels may increase, and the solubility of bisphenol-A also increases. For these reasons, some of bisphenol-A adsorbed at 298 K can be desorbed at 353 K. As expected from the results shown in Figure 4, the desorption amount of bisphenol-A from the SSS-VBTA-DMAA gel of $x_{\text{DMAA}} = 0.29$ was larger than that from the SSS-VBTA gel. This demonstrates that the addition of DMAA to the SSS-VBTA gel can improve the temperature-swing adsorption behavior in some degree.

CONCLUSIONS

Previously, we reported that the polyampholyte gel composed of SSS and VBTA can adsorb bisphenol-A at room temperature and desorb the pre-adsorbed bisphenol-A at higher temperature: however, the desorption amount of bisphenol-A from the gel is rather small.¹⁴ This indicates that there is room for improvement in the temperature-swing adsorption behavior of the SSS-VBTA gel. In this study, we investigated the effects of the addition of DMAA into the SSS-VBTA gel on the adsorption property of the gel, in hope that the desorption amount of bisphenol-A would be increased. As a result, we have drawn the following conclusions.

1. The adsorption amounts of bisphenol-A on to the SSS-VBTA-DMAA gel at 298 K are larger than those at 353 K, which is the same trend as observed for the SSS-VBTA gel.
2. At 298 K, the Henry's adsorption constant for the SSS-VBTA-DMAA gel of $x_{\text{DMAA}} = 0.14$ is larger than that for the SSS-VBTA gel ($x_{\text{DMAA}} = 0$), whereas a further increase in x_{DMAA} results in a decrease in the adsorption constant. At 353 K, on the other hand, the adsorption constant only slightly decreases with increasing x_{DMAA} .
3. The SSS-VBTA-DMAA gel can repeatedly adsorb bisphenol-A at 298 K and desorb some of pre-adsorbed bisphenol-A at 353 K by the temperature-swing operation, where the desorption amount of bisphenol-A from the terpolymer gel is slightly larger than that from the SSS-VBTA gel.

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