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Temperature-swing adsorption of aromatic compounds in water using polyampholyte gel

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Abstract The adsorption property of the polyampholyte gel composed of sodium styrene sulfate (SSS) and vinylbenzyl trimethylammonium chloride (VBTA) has been investigated with several hydrophobic aromatic compounds as adsorbate. Using the *N*-isopropylacrylamide (NIPA) gel, the corresponding experiments were also performed for comparison. At room temperature, the NIPA gel hardly adsorbed the aromatic compounds, while it adsorbed them at higher temperatures. As for the SSS-VBTA gel, the adsorption amounts of the polyaromatic compounds decreased with increasing temperature, while the adsorption amounts of the monoaromatic compounds were almost independent of temperature and smaller than those of the polyaromatic compounds. These results indicate that the aromatic rings in the SSS-VBTA gel may play an important role in the adsorption of the aromatic compounds. Also, it has been demonstrated that the SSS-VBTA gel can repeatedly adsorb bisphenol-A at room temperature and desorb it at higher temperature by the temperature-swing operation: this behavior is diametrically opposite to that of the NIPA gel. This shows that the SSS-VBTA gel is much more suitable for the adsorption removal of the hydrophobic aromatic compounds from very dilute aqueous solutions, because a vast amount of energy is required for heating a large amount of water when using the NIPA gel.

Keywords Polyampholyte gel · Temperature-swing adsorption · Aromatic compound · Hydrophobic interaction

1 Introduction

The removal of hydrophobic aromatic compounds in water is indispensable to environmental protection because of their high toxicity. Especially, some of them are referred to as possible endocrine disrupting chemicals (EDCs) that may affect the balance of normal hormonal functions in animals and humans (Keith 1997). To remove the EDCs from water, a number of treatment processes, such as adsorption, filtration, chemical and biological degradation, and coagulation, have been investigated (Auriol et al. 2006).

In such removal processes, if a temperature-sensitive polymer gel is utilized as adsorbent for the temperature-swing adsorption, simplification of the process and reduction of waste can be achieved: here, the temperature-sensitive polymer gel is one of the stimuli-sensitive polymer gels that show property changes in response to some changes in their external conditions. Poly(*N*-isopropylacrylamide) (NIPA) gel reported by Hirokawa and Tanaka (1984) is well known as the temperature-sensitive gel and have attracted much attention (Nakano 2005). The NIPA gel undergoes a discontinuous volume change across the phase transition temperature $T_p \approx 306$ K: that is, it swells below T_p and collapses above T_p because the constituent polymer hydrates and dehydrates below and above T_p, respectively. Using the NIPA gel, our group investigated that the adsorption behavior of hydrophobic organic compounds in aqueous solutions and found that the NIPA gel repeatedly adsorbs

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the hydrophobic compounds above T_p and desorbs them below T_p, because the NIPA gel changes its property from hydrophilic to hydrophobic across T_p (Seida and Nakano 1996). Such temperature-swing adsorption of hydrophobic compounds was also demonstrated using poly(vinyl methyl ether) gel (Yamagiwa et al. 1995) and poly(vinyl alcohol) (Yamamoto et al. 2003). However, if these polymer gels are applied to remove 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 compounds at more or less higher temperature than room temperature. This indicates that the temperature-sensitive polymer gels that exhibits the opposite temperature dependence of the adsorption behavior is much more favorable for the adsorption removal of the hydrophobic compounds contained in a large amount of water.

To develop the temperature-sensitive polymer gel that can adsorb hydrophobic compounds at room temperature and desorb them at somewhat higher temperature, we considered the polyampholyte gel composed of sodium styrene sulfate (SSS) and vinylbenzyl trimethylammonium chloride (VBTA). 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 (Kaminsky 1957; Krestov and Abrosimov 1964; Out and Los 1980). Thus, we expected that with increasing temperature, the hydrophilic property of the SSS-VBTA gel would become dominant because the hydration structure around its ionic groups becomes stronger. In the previous study, we investigated the temperature dependence of the adsorption behavior of the SSS-VBTA gel using hydrophobic aromatic compound, bisphenol-A, as adsorbate and found that this gel can adsorb and desorb bisphenol-A at room temperature and higher temperature, respectively (Nakano et al. 2005). Although this results imply that the SSS-VBTA gel may change its property from hydrophobic to hydrophilic with increasing temperature as expected, the adsorption mechanism of the SSS-VBTA gel for aromatic compounds remains to be investigated because we employed only bisphenol-A as adsorbate in the previous study.

In the present study, we employ several aromatic compounds as adsorbate and compare their temperature dependence of the adsorption behavior for the SSS-VBTA gel to elucidate the adsorption mechanism of this system. To compare with the results of the SSS-VBTA gel, the corresponding experiments are also conducted using the NIPA gel.

2 Materials and methods

2.1 Chemicals

Sodium styrene sulfate (SSS) and vinylbenzyl trimethylammonium chloride (VBTA) were purchased from Aldrich, while *N*-isopropylacrylamide (NIPA) was kindly provided by Kohjin Co., Ltd. The chemical structures of the monomers are displayed in Fig. 1. *N*, *N′*-Methylenebisacrylamide (BIS) was used as a cross-linker, and ammonium persulfate (APS) and 2,2′-azobisisobutyronitrile (AIBN) were used as an initiator: these reagents were obtained from Wako Pure Chemical Industries Ltd. Dimethyl sulfoxide (DMSO) (Wako Pure Chemical Industries Ltd.) was used as a solvent for the synthesis of the NIPA gel as described in Sect. 2.2. Bisphenol-A, 4,4′-biphenol (Tokyo Kasei Kogyo Co., Ltd.), 2-naphthol, *p*-*t*-butylphenol, and phenol (Wako Pure Chemical Industries Ltd.) illustrated in Fig. 2 were employed as adsorbates. In the present study, all reagents were used as received.

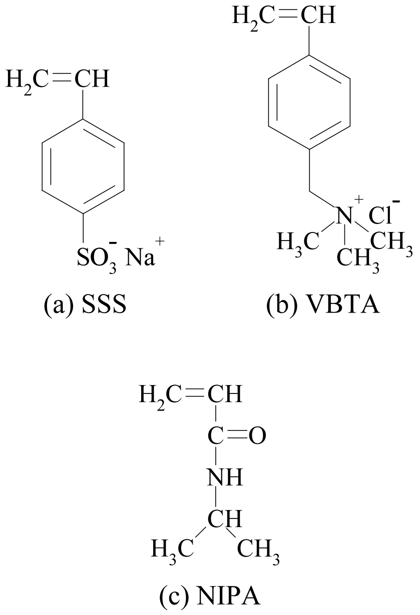

Fig. 1 Chemical structures of main monomers constituting the polymer gels: (**a**) sodium styrene sulfate (SSS); (**b**) vinylbenzyl trimethylammonium chloride (VBTA); (**c**) *N*-isopropylacrylamide (NIPA)

2.2 Preparation of polymer gels

Both the SSS-VBTA and the NIPA gels were prepared by free radical polymerization under nitrogen atmosphere. SSS (0.7 M), VBTA (0.7 M), and BIS (0.02 M) were dissolved in 3 M NaCl 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 hours. The NIPA gel was synthesized in the same manner but in DMSO with AIBN (0.002 M) as an initiator, where the concentration of NIPA was 2.6 M. Note that the mass concentrations of the monomer(s) for the polymerization of both the gels were equal to each other. After gelation was completed, the cylindrical gels were taken out of the capillaries and washed thoroughly with distilled water to remove the residual chemicals.

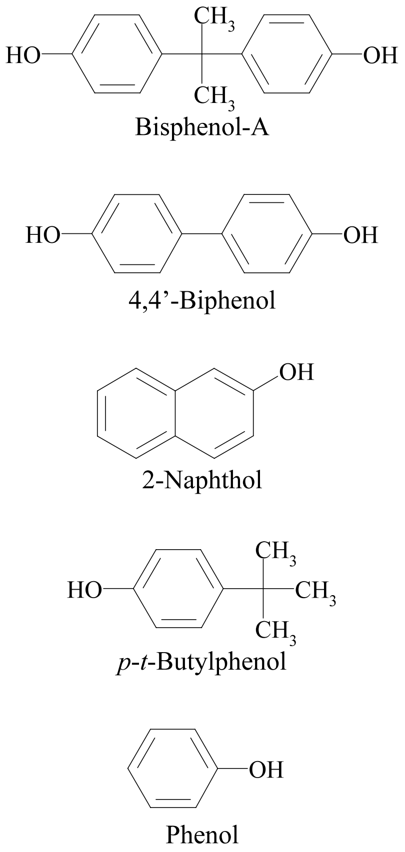

Fig. 2 Chemical structures of aromatic compounds employed as adsorbate

2.3 Adsorption experiments

The cylindrical gels of 5–12 mg in dry weight was soaked in 5–10 mL aqueous solution containing one of the five aromatic compounds with the initial concentrations ranging from 20 to 100 µM. The sample was vigorously shaken in a water bath at constant temperature. The concentration of the aromatic compound in the aqueous solution was determined by UV absorbance using a UV-Vis spectrophotometer (V-550, JASCO), and then the amount of the compound adsorbed onto the gel was calculated from the mass balance. The wave lengths used for the UV measurements are 276, 262, 274, 274, and 270 nm for bisphenol-A, 4,4′-biphenol, 2-naphthol, p-t-butylphenol, and phenol, respectively.

3 Results and discussion

3.1 Adsorption isotherms

The adsorption isotherms of the hydrophobic aromatic compounds for the NIPA and the SSS-VBTA gels are respectively shown in Figs. 3 and 4, where C_e is the equilibrium concentration of the aromatic compound in the aqueous solution and q_e is the equilibrium amount of the compound adsorbed onto the gel. As seen in Fig. 3, the NIPA gel hardly adsorbed the aromatic compounds at 298 K while it adsorbed them at 313, 333, and 353 K. This is because the NIPA gel changes its property from hydrophilic to hydrophobic across the phase transition temperature T_p around 306 K (Hirokawa and Tanaka 1984), and the adsorption of the aromatic compounds onto the NIPA gel at higher temperature than T_p is mainly caused by the solvent-induced hydrophobic interaction (Seida and Nakano 1996).

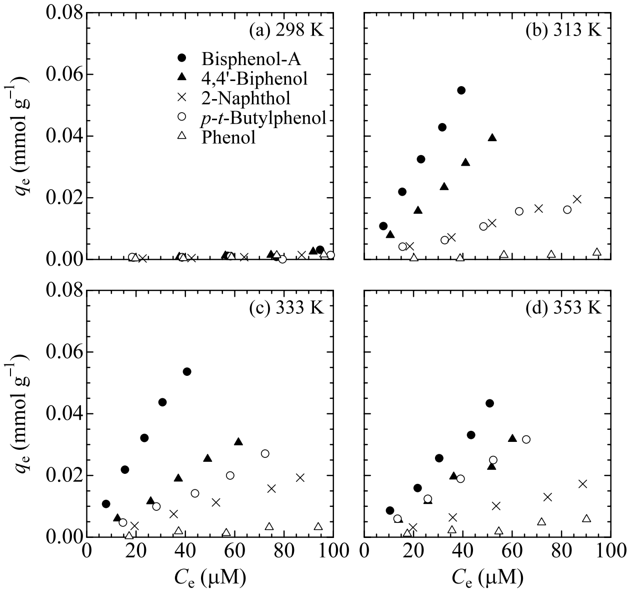

Fig. 3 Adsorption isotherms of aromatic compounds for the NIPA gel at different temperatures: (**a**) 298 K; (**b**) 313 K; (**c**) 333 K; (**d**) 353 K

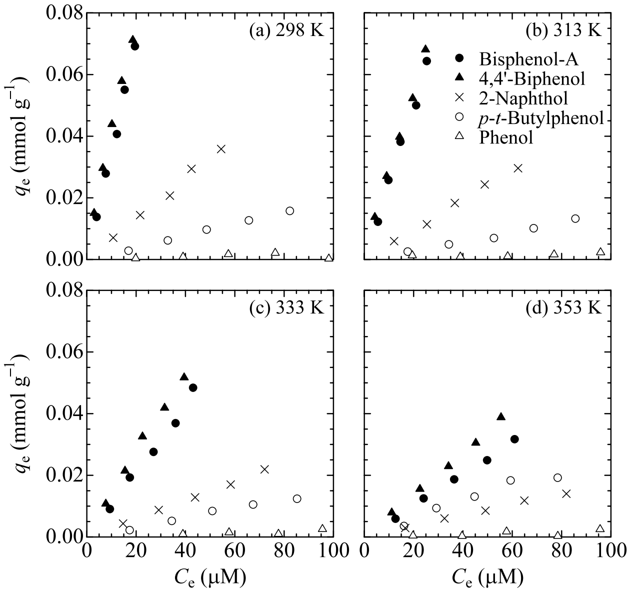

Fig. 4 Same as Fig. 3 but for the SSS-VBTA gel

For the SSS-VBTA gel, the adsorption amounts of the polyaromatic compounds (bisphenol-A, 4,4′-biphenol, and

2-naphthol) decrease with increasing temperature, while the adsorption amounts of the monoaromatic compounds (*p*-*t*-butylphenol and phenol) are almost unchanged at 298–353 K and much smaller than those of the polyaromatic compounds, as shown in Fig. 4. The SSS-VBTA gel has both the hydrophobic benzene rings and the hydrophilic ionic groups (see Fig. 1a, b). At room temperature, the SSS-VBTA gel may adsorb the hydrophobic aromatic compounds by the hydrophobic interaction due to its 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 (Kaminsky 1957; Krestov and Abrosimov 1964; Out and Los 1980). Therefore, 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 the aromatic compounds in water increases with increasing temperature. These may be the reason why the adsorption amounts of the polyaromatic compounds onto the SSS-VBTA gel decrease with increasing temperature.

3.2 Adsorption constants

As seen in the results of the adsorption isotherms shown in Figs. 3 and 4, the adsorption amounts of the aromatic compounds can be described by the following equation in the concentration region investigated in the present study:

$$q_e = KC_e \tag{1}$$

where K is the adsorption constant. To clarify the temperature dependence of the adsorption amounts of the five aromatic compounds onto the NIPA and the SSS-VBTA gels, we evaluated the adsorption constant K by fitting (1) to each adsorption isotherm. Figure 5 shows the resultant adsorption constants K as a function of temperature T. For the NIPA gel, the adsorption constants K at 298 K are close to zero, while the values of K at higher temperatures are larger than those at 298 K. This is because the NIPA gel exhibits the hydrophilic and hydrophobic properties below and above the phase transition temperature $T_p \approx 306$ K, respectively. For the SSS-VBTA gel, on the other hand, the values of K of the polyaromatic compounds (bisphenol-A, 4,4′-biphenol, and 2-naphthol) decrease with increasing temperature, while those of the monoaromatic compounds (*p*-*t*-butylphenol and phenol) are almost constant at 298–353 K, as seen in Fig. 5b.

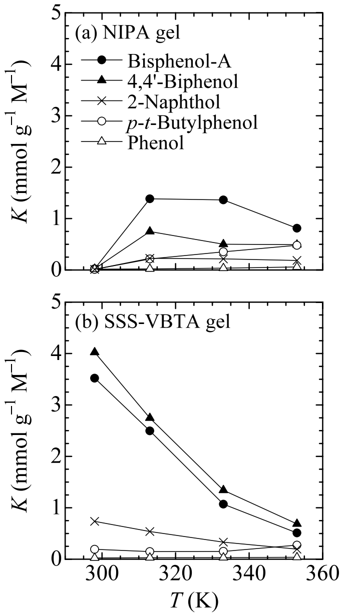

Fig. 5 Adsorption constants K of aromatic compounds as a function of temperature T: (**a**) the NIPA gel; (**b**) the SSS-VBTA gel

Table 1 *n*-Octanol/water partition coefficients P_{ow} and molecular masses M of aromatic compounds

Compound	log P_{ow}[a]	M (g mol^{-1})
Bisphenol-A	3.36[b]	228.3
4,4′-Biphenol	2.66[c]	186.2
2-Naphthol	2.80[d]	144.2
p-*t*-Butylphenol	3.02[e]	150.2
Phenol	1.45[f]	94.11

[a] Each value is an average over the values in the following literatures

[b] Korenman and Gorokhov (1973), Staples et al. (1998)

[c] Bradbury et al. (1996)

[d] Hansch and Anderson (1967), Korenman et al. (1974), Eadsforth (1986), Miyake et al. (1987), El Tayar et al. (1991), Ishihamaa et al. (1995), Pagliara et al. (1995), Donovan and Pescatore (2002), Poole et al. (2003)

[e] Machleidt et al. (1972), Geyer et al. (1984), Ritter et al. (1994), Makovskaya et al. (1995), Ritter et al. (1995)

[f] Fujita et al. (1964), Rogers and Cammarata (1969), Korenman (1972), Machleidt et al. (1972), Korenman and Gorokhov (1973), Eadsforth (1986), Schultz and Cajina-Quezada (1987), Berthod et al. (1988), Minick et al. (1988), Fujiwara et al. (1991), Kubá (1991); Ishihamaa et al. (1995)

From the results mentioned above, the hydrophobic interaction seems to play a major role in the adsorption of the aromatic compounds for both the NIPA and the SSS-VBTA gels. To compare the hydrophobicity of the five aromatic compounds in the present study, we employed the *n*-octanol/water partition coefficients P_{ow} as a measure of hydrophobicity of the compounds: P_{ow} is defined as the ratio of the concentration of a chemical in the *n*-octanol phase to its concentration in aqueous phase in the two-phase system of *n*-octanol and water (Eadsforth 1986). The values of log P_{ow} taken from the literatures are summarized in Table 1. Judging from the values of log P_{ow}, the order of hydrophobicity can be considered as bisphenol-A > *p*-*t*-

butylphenol > 2-naphthol > 4,4′-biphenol > phenol, which is different from the order of the values of K for both the gels as seen in Fig. 5. Thus, we thought that the van der Waals interaction plays another crucial factor. Because the magnitude of the van der Waals interaction is dependent on the molecular mass M, the values of M of the aromatic compounds are also listed in Table 1. The order of the values of K for the NIPA gel in Fig. 5a coincides with that of M. This indicates that the van der Waals interaction, as well as the hydrophobic interaction, is influential in the adsorption of the aromatic compounds for the NIPA gel.

For the SSS-VBTA gel, the order of the values of K disagrees with that of both log P_{ow} and M, as seen in Fig. 5b and Table 1. The values of K of bisphenol-A and 4,4′-biphenol are much larger than those of 2-naphthol, *p*-*t*-butylphenol, and phenol, as in Fig. 5b. It is worth noting that the adsorption constant K of *p*-*t*-butylphenol is smaller than those of 4,4′-biphenol and 2-naphthol, although *p*-*t*-butylphenol is considered to be more hydrophobic than the latter two, judging from the values of log P_{ow}. This implies that in addition to the hydrophobic interaction, the interaction between the aromatic rings of the SSS-VBTA gel and the aromatic compounds may play some role in their adsorption.

3.3 Temperature-swing adsorption

We have investigated the temperature dependence of the equilibrium behavior of adsorption of the aromatic compound onto the NIPA and the SSS-VBTA gels in Sects. 3.1 and 3.2. Next, we consider the adsorption/desorption of the aromatic compound on/from the gels by the temperature-swing operation at 298 and 353 K. Figure 6 shows the time t and temperature T dependence of the adsorption amount q of bisphenol-A. Here, the initial concentration of bisphenol-A in the aqueous solution is 100 µM, and the temperature of the system was changed every 48 hours. As shown in Fig. 6, the NIPA gel adsorbed bisphenol-A at 353 K, and desorbed most of it rapidly after the stepwise temperature change from 353 to 298 K. When the temperature-swing operation was repeated, the NIPA gel exhibited such adsorption/desorption behavior again. The SSS-VBTA gel, on the other hand, adsorbed bisphenol-A at 298 K and desorbed it at 353 K: it must be noted that the adsorption amount onto the SSS-VBTA gel at 298 K shown in Fig. 6 does not reach the equilibrium value as in Fig. 4. The adsorption/desorption behavior of the SSS-VBTA gel is diametrically opposite to that of the NIPA gel, as expected from the results of the adsorption isotherms in Figs. 3 and 4. As mentioned above, the NIPA gel hydrates below the phase transition temperature $T_{\mathrm{p}} \approx 306$ K and dehydrates above T_{p}, while the hydration of the SSS-VBTA gel becomes relatively stronger with increasing temperature. Such difference in the temperature dependence of the hydration results in the opposite behavior of their temperature-swing adsorption.

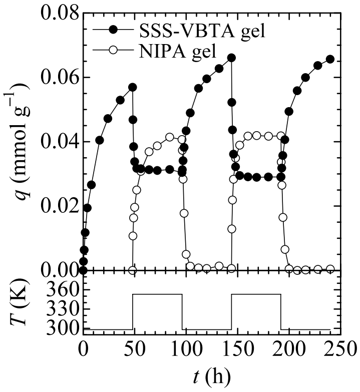

Fig. 6 Time and temperature dependences of amount of bisphenol-A adsorbed onto the SSS-VBTA gel (*solid circles*) and the NIPA gel (*open circles*)

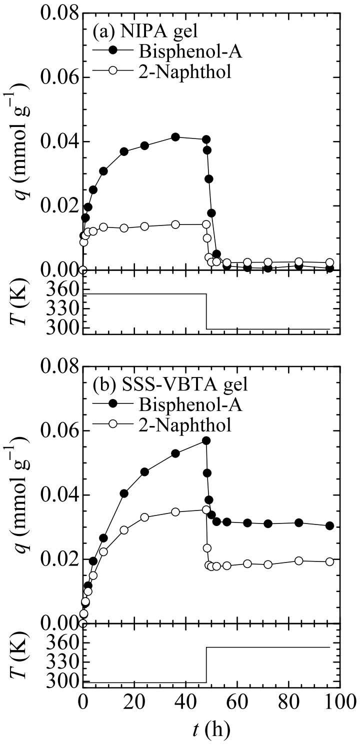

Fig. 7 Time and temperature dependences of amount of bisphenol-A (*solid circles*) and 2-naphthol (*open circles*) adsorbed onto the polymer gels: (**a**) the NIPA gel; (**b**) the SSS-VBTA gel

Although it is difficult to compare the kinetic processes of the adsorption for both the gels because of the difference in the system temperature and the equilibrium adsorption amount, the initial adsorption rate of bisphenol-A onto the SSS-VBTA gel at 298 K seems to be slower than that onto the NIPA gel at 353 K as seen in Fig. 6. To compare their adsorption kinetics, we also performed the temperature-swing adsorption experiments using 2-naphthol as adsorbate; considering the results of the adsorption constants in Fig. 5, it was expected that both the gels can adsorb and desorb 2-naphthol by the temperature-swing operation. The obtained results are shown in Fig. 7, where the results of bisphenol-A are also exhibited for comparison. As expected, the NIPA gel adsorbed 2-naphthol at 353 K and rapidly desorbed it at 298 K, while the adsorption/desorption behavior of the SSS-VBTA gel was opposite to that of the NIPA gel. Compared with the initial adsorption rate of 2-naphthol for the NIPA gel at 353 K, that for the SSS-VBTA gel at 298 K is slower as is case with bisphenol-A.

Generally, the models of the adsorption kinetics are important in water treatment process design. In the present study, the pseudo-second order model was used to evaluate the experimental data in the range of $0 < t \leq 48$ h in Fig. 7, because in many cases, this model expression provides the well correlation of the experimental data (Ho and McKay 1999; Sağ and Aktay 2002). The kinetic equation for the pseudo-second order model is described as:

$$\frac{dq}{dt} = k_2(q_e - q)^2 \tag{2}$$

where k_2 is the rate constant. Integrating (2) for the boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q$ gives:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

We then fitted (3) to the plots of t/q against time t and estimated the rate constant k_2 and the equilibrium adsorption amount q_e, as shown in Fig. 8. The resultant values and the correlation coefficients R^2 are summarized in Table 2. The extremely high values of the correlation coefficients demonstrate that the pseudo-second order model adequately describes all the adsorption data obtained in the present study. The kinetic process of adsorption is considered to depend on the system temperature and the concentration of adsorbate as well as the type of adsorbate. Thus, to analyze the adsorption kinetics of the SSS-VBTA and the NIPA gels in more detail, the adsorption experiments of several adsorbate at different temperatures should be conducted, which will be our future study.

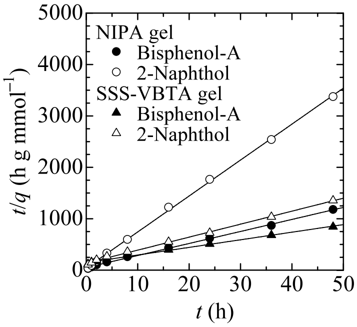

Fig. 8 Pseudo-second order kinetic plots for bisphenol-A (*solid symbols*) and 2-naphthol (*open symbols*) adsorbed onto the NIPA gel (*circles*) and the SSS-VBTA gel (*triangles*)

When the temperature-sensitive polymer gel is utilized as adsorbent, the absolute difference between the adsorption amounts at 298 and 353 K, namely, the *effective adsorption amount* is essential. From the results in Figs. 6 and 7, one may think that both the NIPA and the SSS-VBTA gels have an equivalent ability as adsorbent, because their effective adsorption amounts are almost similar to each other. However, if the NIPA gel is applied to remove 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 above the phase transition temperature. This indicates that the SSS-VBTA gel is much more suitable for adsorption removal of the hydrophobic compounds contained in a large amount of water from the energy-saving point of view.

4 Conclusions

We have investigated the adsorption property of the polyampholyte gel composed of sodium styrene sulfate (SSS) and vinylbenzyl trimethylammonium chloride (VBTA) using several hydrophobic aromatic compounds as adsorbate. To compare with the results of the SSS-VBTA gel, the corresponding experiments using the N-isopropylacrylamide (NIPA) gel were also conducted. As a result, we found that the NIPA gel hardly adsorbs the hydrophobic aromatic compounds at 298 K while it adsorbs them at 313–353 K, because the NIPA gel changes its property from hydrophilic to hydrophobic across the phase transition temperature T_p around 306 K. In contrast with the results of the NIPA gel, the adsorption amounts of the polyaromatic compounds for the SSS-VBTA gel decreased with increasing temperature.

Table 2 Pseudo-second order rate constants k_2, equilibrium adsorption amounts q_e, and correlation coefficients R^2 for the adsorption of bisphenol-A and 2-naphthol onto the NIPA and SSS-VBTA gels

Gel	Adsorbate	k_2 (g mmol^{-1} h^{-1})	q_e (mmol g^{-1})	R^2
NIPA gel	Bisphenol-A	10.8	0.0427	0.998
	2-Naphthol	113	0.0143	0.999
SSS-VBTA gel	Bisphenol-A	1.49	0.0676	0.995
	2-Naphthol	4.67	0.0396	0.998

As for the monoaromatic compounds, however, the adsorption amounts for the SSS-VBTA gel were almost independent of temperature and much smaller than those of the polyaromatic compounds. These results indicate that the aromatic rings in the SSS-VBTA gel may play an important role in the adsorption of the aromatic compounds.

Also, we have demonstrated that the SSS-VBTA gel can repeatedly adsorb bisphenol-A at 298 K and desorb it at 353 K by the temperature-swing operation; this adsorption/desorption behavior of the SSS-VBTA gel is diametrically opposite to that of the NIPA gel. This shows that the SSS-VBTA gel is much more suitable for the adsorption removal of hydrophobic aromatic compounds from very dilute aqueous solutions, because a vast amount of energy is required for heating a large amount of water to adsorb the hydrophobic compounds using the NIPA gel. In the near future, we will implement the practical water treatment using the temperature-swing adsorption with the SSS-VBTA gel as demonstrated in the present study.

Nomenclature

C_e	Equilibrium concentration of the aromatic compound in aqueous solution (μM)
K	Adsorption constant (mmol g^{-1} M^{-1})
k_2	Pseudo-second order rate constant (g mmol^{-1} h^{-1})
M	Molecular mass (g mol^{-1})
P_ow	n-Octanol/water partition coefficient
q	Amount of the aromatic compound adsorbed onto the polymer gel (mmol g^{-1})
q_e	Equilibrium amount of the aromatic compound adsorbed onto the polymer gel (mmol g^{-1})
t	Time (h)
T	Temperature (K)
T_p	Phase transition temperature of the NIPA gel (K)

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