

## ORIGINAL ARTICLE

# Molecularly imprinted polyacrylonitrile adsorbents for the capture of Cs<sup>+</sup> ions

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Polymeric materials can be directly converted into molecular recognition materials by alternative molecular imprinting. To produce adsorbents that specifically adsorb cesium ions, a polymeric adsorbent was converted from polyacrylonitrile, adopting cesium chloride as a print molecule. The adsorption ability of the molecularly imprinted adsorbent was studied by surface plasmon resonance spectroscopy and atomic absorption analysis. The results revealed that Cs<sup>+</sup>-recognition sites were formed in the presence of CsCl during the adsorbent preparation process. The affinity constant between Cs<sup>+</sup> and Cs<sup>+</sup>-recognition sites ranged from  $4.2 \times 10^3$  to  $7.1 \times 10^3 \text{ mol}^{-1} \text{ dm}^3$ . The adsorbents obtained in the present study are expected to be useful for the specific adsorption of Cs<sup>+</sup> from nuclear waste.

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## INTRODUCTION

After the Great East Japan Earthquake hit northeast Japan on 11th March 2011,<sup>1</sup> the reactor units of boiling water reactors were overheated because of the loss of cooling systems. This led to explosions and a release of radioactivity, initially into the air, followed by fatal leakage of contaminated water into the sea. This surrounding water is still contaminated with the released <sup>137</sup>Cs and <sup>90</sup>Sr, which have half-lives of 30 and 28.8 years, respectively. Not only membranologists but also molecular imprinters must contribute to solve the ensuing problems.

Thus far, Prussian blue<sup>2–5</sup> and zeolites<sup>6–11</sup> have been intensively studied as cesium adsorbents. In addition to these materials, molecularly imprinted materials can be potentially used as cesium adsorbents. Molecular imprinting is one of the most facile ways to endow polymeric materials with specific recognition sites toward target substrates such as organic materials,<sup>12–19</sup> metal ions<sup>13,18,20</sup> and anionic species.<sup>21,22</sup> Additionally, alternative molecular imprinting is a much more facile way to introduce molecular recognition sites into polymeric materials.<sup>23–25</sup> Alternative molecular imprinting can be traced back to the pioneering study reported in 1962 by Michaels *et al.*<sup>26</sup> In this method, a polymeric material was used as a functional polymer instead of functional and crosslinkable monomers for conventional molecular imprinting, as first proposed by Wulff and Sarhan.<sup>27</sup>

In the present study, the authors aimed to obtain molecularly imprinted adsorbents for the capture of Cs<sup>+</sup> from aqueous solutions. In studies on molecular imprinting, it is indispensable to confirm the formation of molecular recognition sites in the obtained molecularly imprinted adsorbents (materials). In the present study on Cs<sup>+</sup>-recognizing adsorbents, dissociative functional moieties were expected to disturb experiments, although dissociative functional

groups with anionic charges were expected to enhance the capture of Cs<sup>+</sup>. Thus, nonionic neutral polyacrylonitrile (PAN), which is expected to form durable materials, was adopted as a candidate polymer to form molecularly imprinted adsorbents, and Cs<sup>+</sup> (CsCl) was adopted as a print molecule.

The Cs<sup>+</sup>-capture performance of the molecularly imprinted PAN adsorbents is described in this article.

## EXPERIMENTAL PROCEDURE

### Materials

Acrylonitrile,<sup>28</sup> 2,2'-azobis(2-methylpropionitrile),<sup>29</sup> toluene<sup>28</sup> and *N,N*-dimethylformamide (DMF)<sup>28</sup> were purified by the usual methods. Methanol, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), CsCl, NaClO<sub>4</sub> and NaCl were used without purification. Water purified with an ultrapure water system (Simpli Lab. Millipore S.A., Molsheim, France) was used.

### Preparation of PAN

A total of 40.17 g (0.757 mol) of acrylonitrile, 660.3 mg ( $4.02 \times 10^{-3}$  mol) of 2,2'-azobis(2-methylpropionitrile) and 200 cm<sup>3</sup> of toluene were placed in an ampoule. The mixture was degassed by three freeze-pump-thaw cycles and sealed off under reduced pressure, which was below  $1.3 \times 10^{-2}$  Pa ( $10^{-4}$  mm Hg). The sealed ampoule was shaken in a water bath at a constant temperature of 45 °C for 96 h. The obtained precipitate, PAN, was first washed with toluene, then with methanol and finally dried *in vacuo*. An amount of 39.44 g of PAN was obtained.

### Construction of Cs<sup>+</sup>-recognition adsorbents

The molecularly imprinted films possessing molecular recognition sites for Cs<sup>+</sup> were prepared for surface plasmon resonance (SPR) spectroscopy as follows: a gold-deposited glass plate was immersed in a  $1.0 \times 10^{-5} \text{ mol dm}^{-3}$  solution of 1-octanethiol in ethanol for 30 min at ambient temperature before molecular imprinting. The film was prepared by spin casting a  $1.0 \text{ g dm}^{-3}$  HFIP solution

of PAN onto the pre-treated, gold-deposited glass plate. The rotation speed for spin casting was 3000 r.p.m. A prescribed amount of the print molecule (CsCl) was dissolved in the spin-casting solution for the preparation of molecularly imprinted films. The molecularly imprinted adsorbents with molecular imprinting ratios of 0.25, 0.50, 0.75 and 1.00 were named Cs-025, Cs-050, Cs-075 and Cs-100, respectively. The molecular imprinting ratio was defined as the ratio of the mole number of CsCl print molecules to that of the constitutional repeating unit of PAN. The molecularly imprinted film for Na<sup>+</sup> was prepared using DMF as the solvent and NaClO<sub>4</sub> as the print molecule. The control film was prepared from HFIP solution without a print molecule.

The molecularly imprinted adsorbents for the study of atomic absorption were prepared as follows: 10 cm<sup>3</sup> of 20 g dm<sup>-3</sup> HFIP solution of PAN containing CsCl as a print molecule was poured into a flat laboratory dish of 9.0 cm diameter and dried at ambient temperature for 24 h, and then additionally at 50 °C for 24 h. To make the adsorbent for Na<sup>+</sup> recognition, 10 cm<sup>3</sup> of DMF solution (20 g dm<sup>-3</sup>) was poured into a flat laboratory dish of 9.0 cm diameter and dried at 50 °C for 288 h. The control adsorbent was prepared from a DMF solution without a print molecule.

The print molecule, such as CsCl and NaClO<sub>4</sub>, was removed from the molecularly imprinted adsorbents by H<sub>2</sub>O until the print salt was almost undetectable in H<sub>2</sub>O in atomic absorption analysis. The thicknesses of the CsCl-imprinted adsorbent, NaClO<sub>4</sub>-imprinted adsorbent and the control are summarized in Table 1.

### Evaluation of molecular recognition ability of molecularly imprinted adsorbents

The molecular recognition ability of the prepared films toward Cs<sup>+</sup> or Na<sup>+</sup> was evaluated by SPR spectroscopy. Incident light with 670 nm was chosen. The change in the incident angle ( $\Delta\theta$ ) as a result of the addition of substrate was recorded on the SPR instrument (SPR670S; Nippon Laser and Electronic Laboratory, Nagoya, Japan). During the measurement, H<sub>2</sub>O was passed over the molecularly imprinted material surface at 5.0 mm<sup>3</sup> min<sup>-1</sup>. The flow was periodically replaced with the aqueous solution containing CsCl or NaCl. The experiments were carried out at 27 °C.

The amounts of CsCl or NaCl incorporated into the adsorbents were quantitatively determined by conventional adsorption experiments. The adsorbent was immersed in a 1.0 × 10<sup>-2</sup> mol dm<sup>-3</sup> aqueous CsCl or NaCl solution and equilibrated at 27 °C. After equilibration with the aqueous solution, the adsorbent was removed from the immersing solution. The free solution adhering on the surface was blotted, and the adsorbent was then transferred to H<sub>2</sub>O to desorb Cs<sup>+</sup> or Na<sup>+</sup> from it. An aliquot of the aqueous solution from desorption was used for quantitative estimation by atomic absorption (AA-6500 Shimadzu Atomic Absorption Spectrophotometer; Shimadzu, Kyoto, Japan).

## RESULTS AND DISCUSSION

### Adsorption of Cs<sup>+</sup>

In the present study, adsorption phenomena of molecularly imprinted adsorbents were studied using SPR spectroscopy because SPR spectroscopy provides a rapid and facile evaluation method<sup>30–35</sup> compared with the adsorption experiments that are usually used for the evaluation of molecularly imprinted materials.<sup>36</sup> The relationship between the reflected intensity and the angle of incidence gives the minimum reflected intensity, corresponding to the excitation of surface plasmons at the gold-solution interface. The value of the incident angle giving the minimum reflected intensity ( $\theta$ ) shifts with

**Table 1** Thickness of various adsorbents

Adsorbent	Control	Cs-025	Cs-050	Cs-075	Cs-100
Thickness (μm)	41	76	212	205	333
Adsorbent		Na-025			
Thickness (μm)		71			

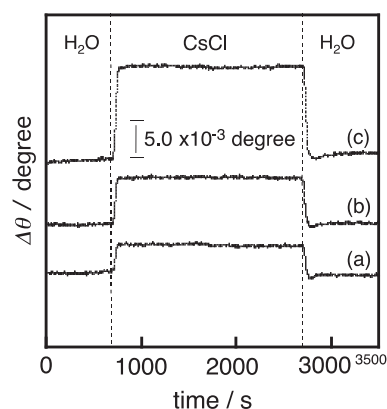
the change in the reflective index of the interfacial region close to the gold surface.<sup>37,38</sup> The shift in  $\theta$  ( $\Delta\theta$ ) is proportional to the amount of adsorbed substrate at the surface. Using  $\Delta\theta$ , an apparent adsorption isotherm of a given target molecule can be drawn. In the present study, Cs<sup>+</sup> was adopted as the print molecule because the present study was carried out with the aim of obtaining adsorbents of Cs<sup>+</sup> for the capture and disposal of nuclear waste.

As an example, Figure 1 shows the change, with time, of the angle ( $\Delta\theta$ ) of the PAN control adsorbent in response to the addition of substrate Cs<sup>+</sup>.

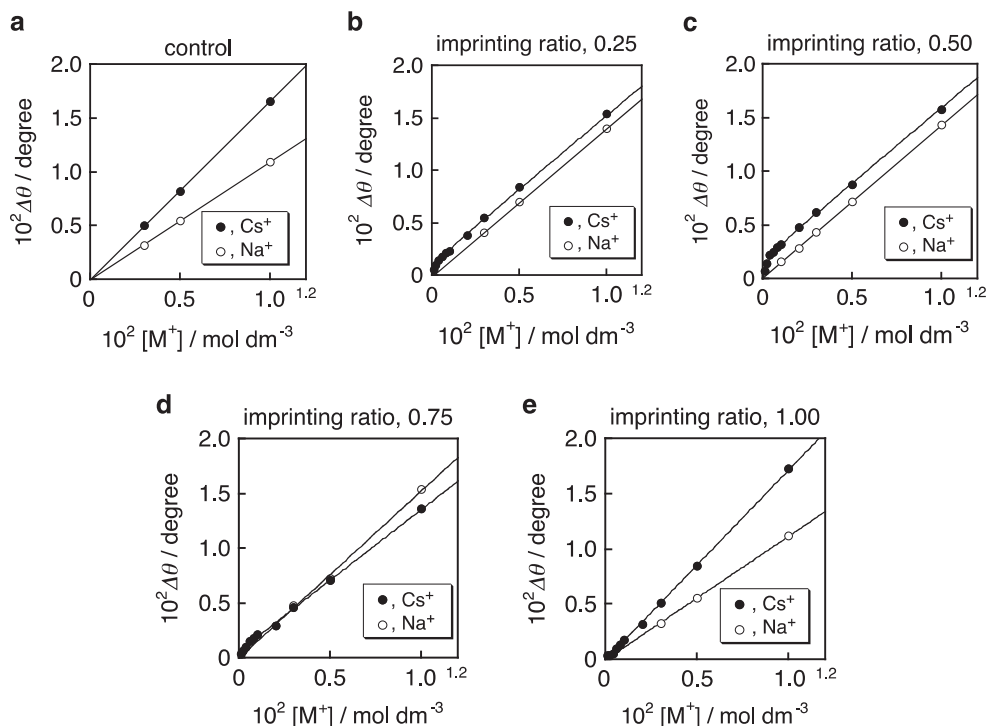
The relationship between the observed shift in the incident angle ( $\Delta\theta$ ) and the substrate (metal ion) concentration leads to an apparent adsorption isotherm. Figure 2 summarizes the apparent adsorption isotherms of Cs<sup>+</sup> and Na<sup>+</sup> for the control PAN and PAN adsorbents molecularly imprinted with Cs<sup>+</sup>. Figure 2a reveals that specific recognition sites toward Cs<sup>+</sup> or Na<sup>+</sup> were nearly absent in the control PAN adsorbent. Contrary to the control PAN adsorbent, the adsorbents molecularly imprinted with Cs<sup>+</sup>, such as Cs-025, Cs-050 and Cs-075 (Figures 2b–d), gave dual adsorption isotherms toward Cs<sup>+</sup>, whereas Na<sup>+</sup> was incorporated into these adsorbents nonspecifically. Against our expectations, the apparent adsorption isotherm of Cs-100, which had a molecular imprinting ratio of 1.0 (Figure 2e), hardly showed a dual adsorption isotherm toward Cs<sup>+</sup>. Na<sup>+</sup> was again adsorbed nonspecifically on Cs-100. The increase in the molecular imprinting ratio might result in an increase in the amount of the print molecule. Those molecules that did not effectively work as a print molecule only resulted in the formation of pores. This shows that the print molecule did not have a substantial effect.

In adsorption studies on enantiomers<sup>31,35</sup> or on analogues, such as adenosine and guanosine,<sup>30,32–34</sup> the amount of each substrate adsorbed can be estimated from  $\Delta\theta$ . Although the absolute value cannot be determined from  $\Delta\theta$  in such studies, relative values, such as the adsorption selectivity, can be determined.

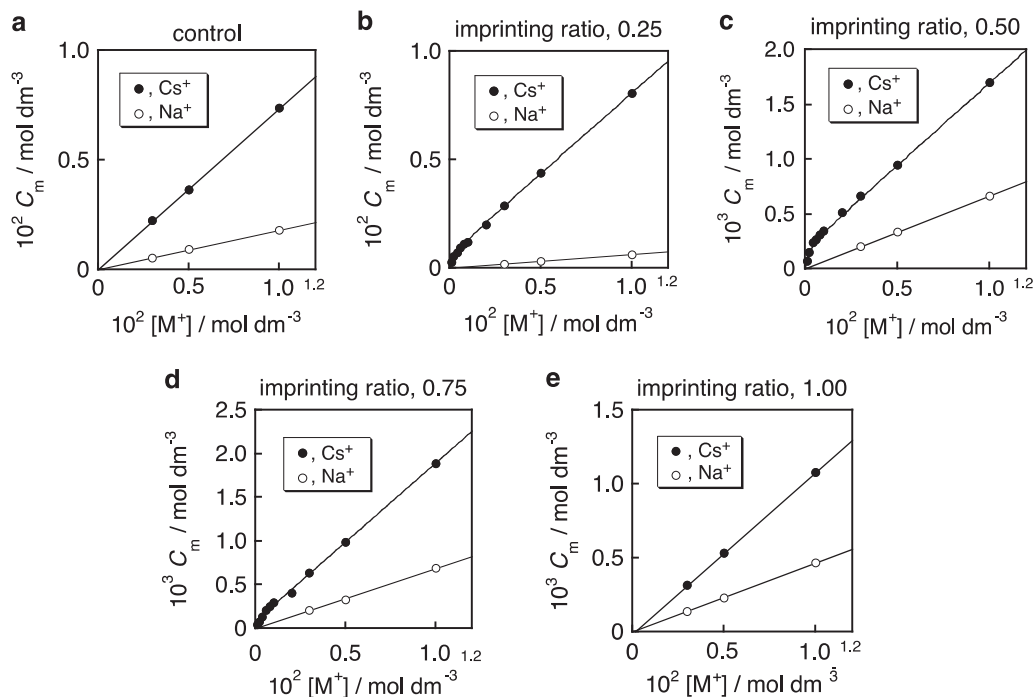
In the present study,  $\Delta\theta$  for Cs<sup>+</sup> and Na<sup>+</sup> cannot be compared because of the very different natures of these two types of alkali metal ions.<sup>39</sup> However, it is interesting and indispensable to quantitatively determine the adsorption selectivities of the adsorbents in the present study. To this end, adsorption experiments were carried out. Using the concentration of adsorbed Cs<sup>+</sup> or Na<sup>+</sup> determined by the adsorption study at 1.0 × 10<sup>-2</sup> mol dm<sup>-3</sup> and the results of SPR spectroscopy at



**Figure 1** Typical time courses of the angle change ( $\Delta\theta$ ) of surface plasmon resonance (SPR) in response to the addition of Cs<sup>+</sup> (CsCl) from an aqueous solution to the polyacrylonitrile (PAN) control adsorbent. The sensor part was first stabilized in aqueous solution and then flowed through Cs<sup>+</sup>, and finally washed by an aqueous solution: (a) [CsCl] = 3.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>; (b) [CsCl] = 5.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>; (c) [CsCl] = 1.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>.



**Figure 2** Adsorption isotherms of Cs<sup>+</sup> and Na<sup>+</sup> of the control polyacrylonitrile (PAN) adsorbent (a), and PAN adsorbents molecularly imprinted with Cs<sup>+</sup>, namely, Cs-025 (b), Cs-050 (c), Cs-075 (d) and Cs-100 (e). Adsorption isotherms are given in angle change ( $\Delta\theta$ ).



**Figure 3** Adsorption isotherms of Cs<sup>+</sup> and Na<sup>+</sup> of the control polyacrylonitrile (PAN) adsorbent (a), and PAN adsorbents molecularly imprinted with Cs<sup>+</sup>, namely, Cs-025 (b), Cs-050 (c), Cs-075 (d) and Cs-100 (e). Adsorption isotherms are given in concentration ( $\text{mol dm}^{-3}$ ).

the same concentration, the apparent adsorption isotherm determined by SPR spectroscopy was converted to the absolute values ( $\text{mol dm}^{-3}$ ). Such converted apparent adsorption isotherms are shown in Figure 3.

The dual adsorption isotherms of Cs<sup>+</sup> for Cs-025, Cs-050 and Cs-075 display nonspecific and specific adsorption in the

Cs<sup>+</sup>-recognition sites, which were formed in the presence of the print molecule Cs<sup>+</sup> during the adsorbent preparation process.<sup>30–34</sup> The concentration of Cs<sup>+</sup> in the adsorbent can be represented by the following equation:

$$[\text{Cs}^+]_{\text{PAN}} = k_{A,\text{Cs}}[\text{Cs}^+] + K_S[\text{Site}]_0[\text{Cs}^+]/(1 + K_S[\text{Cs}^+]) \quad (1)$$

where  $[Cs^+]_{PAN}$  (mol dm<sup>-3</sup>) denotes the concentration of Cs<sup>+</sup> in the adsorbent,  $k_{A,Cs}$  is the adsorption constant for nonspecific adsorption,  $[Cs^+]$  (mol dm<sup>-3</sup>) is the concentration of Cs<sup>+</sup> in an aqueous solution equilibrated with the PAN adsorbent molecularly imprinted with Cs<sup>+</sup>,  $K_S$  (mol<sup>-1</sup> dm<sup>3</sup>) denotes the affinity constant between Cs<sup>+</sup> and Cs<sup>+</sup>-recognition sites and  $[Site]_0$  (mol dm<sup>-3</sup>) is the total concentration of Cs<sup>+</sup> recognition sites in the adsorbent.

The nonspecific adsorption isotherm for the control PAN adsorbent is represented by Equation (2). The adsorption isotherm for Cs-100 can be approximately represented by Equation (2):

$$[M^+]_{PAN} = k_{A,i}[M^+] \quad (2)$$

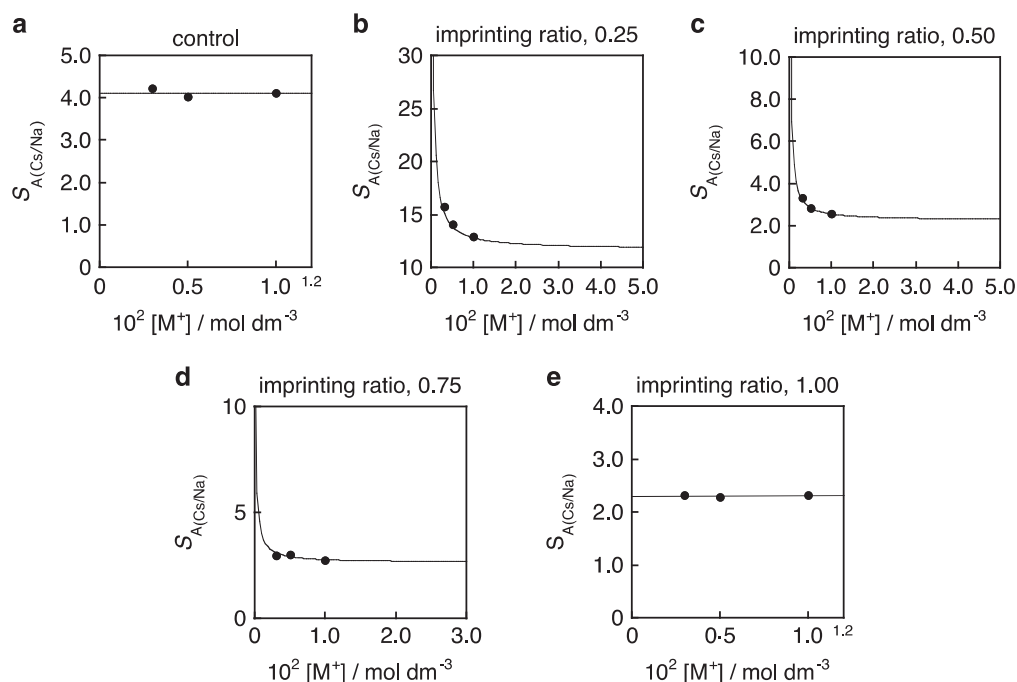
where  $[M^+]_{PAN}$  (mol dm<sup>-3</sup>) denotes the concentration of metal ions nonspecifically adsorbed on the adsorbent (M<sup>+</sup>, Cs<sup>+</sup> or Na<sup>+</sup>),  $k_{A,i}$  is the adsorption constant (i, Cs or Na) and  $[M^+]$  (mol dm<sup>-3</sup>) denotes the concentration of Cs<sup>+</sup> or Na<sup>+</sup> in aqueous solution equilibrated with the adsorbent.

The parameters in Equations (1) and (2), which were determined from the best fits to each adsorption isotherm in Figure 3, are summarized in Table 2. The adsorption constants for both cesium

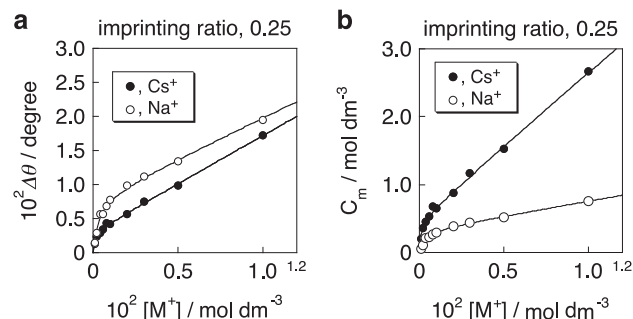
**Table 2 Parameters for adsorption isotherms**

Adsorbent	Control	Cs-025	Cs-050	Cs-075	Cs-100
Imprinting ratio <sup>a</sup>	0	0.25	0.50	0.75	1.00
$k_{A,Cs}$	0.74	0.74	0.15	0.18	0.11
$K_S$ (mol <sup>-1</sup> dm <sup>3</sup> )	—	$4.2 \times 10^3$	$7.1 \times 10^3$	$6.9 \times 10^3$	—
$[Site]_0$ (mol dm <sup>-3</sup> )	—	$7.1 \times 10^{-4}$	$2.0 \times 10^{-4}$	$1.0 \times 10^{-4}$	—
$k_{A,Na}$	0.18	0.063	0.066	0.068	0.047

Abbreviations:  $k_{A,Cs}$ , adsorption constant for nonspecific adsorption of Cs<sup>+</sup>;  $K_S$ , affinity constant between Cs<sup>+</sup> and Cs<sup>+</sup>-recognition sites;  $[Site]_0$ , total concentration of Cs<sup>+</sup> recognition sites in the adsorbent. PAN, polyacrylonitrile;  $k_{A,Na}$ , adsorption constant for nonspecific adsorption of Na<sup>+</sup>.  
<sup>a</sup>(Mole number of Cs<sup>+</sup>)/(mole number of constitutional repeating unit of PAN).


**Figure 4** Adsorption selectivity of the control polyacrylonitrile (PAN) adsorbent (a), and PAN adsorbents molecularly imprinted with Cs<sup>+</sup>, namely, Cs-025 (b), Cs-050 (c), Cs-075 (d) and Cs-100 (e).

and sodium ions were decreased by the presence of Cs<sup>+</sup> during the adsorbent preparation process, except in the Cs-025 adsorbent. The adsorption constant of Cs<sup>+</sup> for Cs-025 was the same as that for the control adsorbent.


**Figure 5** Adsorption isotherms of Cs<sup>+</sup> and Na<sup>+</sup> for polyacrylonitrile (PAN) adsorbents molecularly imprinted with Na<sup>+</sup>, namely, Na-025. Adsorption isotherms are given in angle change ( $\Delta\theta$ ) (a) and in concentration (mol dm<sup>-3</sup>) (b).

**Table 3 Parameters for adsorption isotherms for Na<sup>+</sup>-imprinted adsorbent<sup>a</sup>**

	Cs <sup>+</sup>	Na <sup>+</sup>
$k_{A,Cs}$	$2.2 \times 10^2$	—
$K_S$ (mol <sup>-1</sup> dm <sup>3</sup> )	$8.3 \times 10^3$	$3.2 \times 10^3$
$[Site]_0$ (mol dm <sup>-3</sup> )	$4.8 \times 10^{-1}$	$3.3 \times 10^{-1}$
$k_{A,Na}$	—	$4.4 \times 10$

Abbreviations:  $k_{A,Cs}$ , adsorption constant for nonspecific adsorption of Cs<sup>+</sup>;  $K_S$ , affinity constant between Na<sup>+</sup> (Cs<sup>+</sup>) and Na<sup>+</sup> (Cs<sup>+</sup>) recognition sites;  $[Site]_0$ , total concentration of Na<sup>+</sup> (Cs<sup>+</sup>) recognition sites in the adsorbent;  $k_{A,Na}$ , adsorption constant for nonspecific adsorption of Na<sup>+</sup>.  
<sup>a</sup>The molecular imprinting ratio was fixed to be 0.25.

The affinity constant,  $K_S$ , was expected to increase with the decrease in the molecular imprinting ratio, as observed in the recognition of adenosine by modified polysulfone with an oligopeptide derivative of glutamyl residues.<sup>30</sup> In the present study, however, the maximum affinity constant was observed at the molecular imprinting ratio of 0.50 (Cs-050). This might be explained as follows: the print molecule Cs<sup>+</sup> (CsCl) attached to molecular recognition sites located in the central area of the adsorbent was difficult to wash out during the extraction process. This is because some Cs<sup>+</sup>-recognition sites that were thought to show a high-affinity constant were isolated by long distances in the Cs-025 adsorbent.

Among the three types of adsorbent, the Cs-025 adsorbent exhibited the maximum concentration of Cs<sup>+</sup>-recognition sites, which were formed in the presence of the print molecule Cs<sup>+</sup> (or CsCl) during the adsorbent preparation process. Generally, the amount of Cs<sup>+</sup>-recognition sites is thought to increase with the increase in the amount of the print molecule, Cs<sup>+</sup>, during the adsorbent construction process. However, the increase in the amount of print molecules resulted in the increase in the amount of porogens. This might be because of the decrease in the concentration of Cs<sup>+</sup>-recognition site with the increase in the molecular imprinting ratio.

The adsorption selectivity toward Cs<sup>+</sup> against Na<sup>+</sup> can be determined from the experimental data represented by Equation (3):

$$S_{A(\text{Cs}/\text{Na})} = ((\text{Cs}^+)_{\text{PAN}}/(\text{Na}^+)_{\text{PAN}})/([\text{Cs}^+]/[\text{Na}^+]) \quad (3)$$

where  $(\text{Cs}^+)_{\text{PAN}}$  and  $(\text{Na}^+)_{\text{PAN}}$  are the amounts of Cs<sup>+</sup> and Na<sup>+</sup>, respectively, incorporated into the adsorbent, and  $[\text{Cs}^+]$  and  $[\text{Na}^+]$  denote the concentrations of Cs<sup>+</sup> and Na<sup>+</sup>, respectively, in the solution equilibrated with the adsorbent. In addition to this, the adsorption selectivity  $S_{A(\text{Cs}/\text{Na})}$  can be theoretically calculated by substituting Equations (1) and (2) into Equation (3):

$$S_{A(\text{Cs}/\text{Na})} = (k_{A,\text{Cs}}/k_{A,\text{Na}})([\text{Cs}^+]/[\text{Na}^+]) \times \{1 + K_S[\text{Site}]_0/(1 + K_S[\text{Cs}^+])(k_{A,\text{Cs}}[\text{Cs}^+])\} \quad (4)$$

The adsorption selectivity at ambient concentrations can be calculated using Equation (4).

The adsorption selectivities for the five types of adsorbent in the case that the adsorbent is in contact with an equimolar mixture are shown in Figure 4. Those determined from experimental results are shown by closed circles while each line is the adsorption selectivity calculated from Equation (4) adopting parameters summarized in Table 2. The adsorption selectivity for the control adsorbent is not dependent on the substrate concentration because both Cs<sup>+</sup> and Na<sup>+</sup> were nonspecifically adsorbed on it. In the case of the Cs-100 adsorbent, the adsorption selectivity is apparently independent of the substrate concentration. The Cs<sup>+</sup>-imprinted adsorbents, such as Cs-025, Cs-050 and Cs-075, show a dependence on substrate concentration, as anticipated from the dual adsorption isotherm showing that Cs<sup>+</sup> was incorporated onto the adsorbent. As a result, the adsorption selectivity increases with the decrease in concentration.

#### Mechanism for construction of Cs<sup>+</sup>-recognition sites

It is interesting and indispensable to elucidate the mechanism for the formation of Cs<sup>+</sup>-recognition sites on the Cs<sup>+</sup>-imprinted adsorbent. To this end, Na<sup>+</sup> was used as a print molecule instead of Cs<sup>+</sup> to prepare a Na<sup>+</sup>-imprinted adsorbent. In the present study, NaClO<sub>4</sub> was adopted as a source for print molecules of Na<sup>+</sup> because NaCl is nearly insoluble in both HFIP and DMF. Figure 5a shows the apparent adsorption isotherms of Cs<sup>+</sup> and Na<sup>+</sup>, which were determined by following a similar procedure as that described in the previous section.

Contrary to expectations, both Cs<sup>+</sup> and Na<sup>+</sup> were incorporated onto the Na<sup>+</sup>-imprinted adsorbent, following a dual-adsorption mechanism. In a sense, the observed phenomena are natural. The parameters for the dual-adsorption isotherm were determined from the best fit to each adsorption isotherm shown in Figure 5b and are summarized in Table 3.

Both Cs<sup>+</sup> and Na<sup>+</sup> were adsorbed, following a dual adsorption mechanism even when the adsorbent was constructed in the presence of Na<sup>+</sup> (NaClO<sub>4</sub>) as a print molecule. The actual species of the print molecule are solvated metal ions rather than naked metal ions. Accordingly, molecular recognition sites constructed in the presence of Cs<sup>+</sup> might be smaller than those in the presence of Na<sup>+</sup>. Although the dimensions of each print molecule in the molecular imprinting process have not been clarified at the moment, the dimensions of Na<sup>+</sup> might be larger than those of Cs<sup>+</sup>, by analogy with the hydrated radii of these metal ions<sup>40</sup> and the dimensions and solvation numbers for Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup> in organic solvents.<sup>41</sup> The hydrated radii of Na<sup>+</sup> and Cs<sup>+</sup> were reported to be  $3.58 \times 10^{-10}$  and  $3.29 \times 10^{-10}$  m, respectively.<sup>40</sup> This supports the results obtained in the present study; Na<sup>+</sup> was nonspecifically adsorbed on the Cs<sup>+</sup>-imprinted adsorbent, as shown in Figures 2 and 3. As a result, the hydrated Cs<sup>+</sup> can be incorporated into the Na<sup>+</sup>-recognition sites because hydrated Cs<sup>+</sup> is smaller than hydrated Na<sup>+</sup>. Furthermore, it is anticipated that solvated Cs<sup>+</sup> should be smaller than solvated Na<sup>+</sup> in both HFIP and DMF, which should be addressed in a future study.

The affinity constant for Cs<sup>+</sup> was determined to be higher compared with that for Na<sup>+</sup>. From this, it is concluded that the dimensions of Na<sup>+</sup>-recognition sites provide a better fit for Cs<sup>+</sup> than Na<sup>+</sup>. In addition, it is reasonable to expect that the radius of Na<sup>+</sup> solvated by DMF might be similar to the hydrated radius of Cs<sup>+</sup>, which should be clarified with supporting data in a future study. This may also explain why the total concentration of recognition sites for Cs<sup>+</sup> was determined to be higher compared with those for Na<sup>+</sup>.

#### CONCLUSIONS

Polymeric materials can be directly converted into molecular recognition materials by applying alternative molecular imprinting. This approach can be used to obtain adsorbents for the specific adsorption of cesium ions. To this end, a polymeric adsorbent was converted from PAN, adopting cesium chloride as a print molecule. The adsorption ability of the molecularly imprinted adsorbent was studied by SPR spectroscopy and atomic absorption analysis. The results revealed that Cs<sup>+</sup>-recognition sites were constructed in the presence of CsCl during the adsorbent preparation process. The affinity constant between Cs<sup>+</sup> and Cs<sup>+</sup>-recognition sites ranged from  $4.2 \times 10^3$  to  $7.1 \times 10^3 \text{ mol}^{-1} \text{ dm}^3$ . The adsorbents obtained in the present study are expected to be useful for specific adsorption to capture the nuclear waste, Cs<sup>+</sup>.

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