Polymer Journal, Vol. 37, No. 12, pp. 939–945 (2005)

Adsorbent for Di-*n*-butyl Phthalate using Chitosan Beads with Upper- or Lower-Rim Substituted Water-soluble Calixarenes

Akihiro YANAGI,[1,†] Hideyuki OTSUKA,[2] and Atsushi TAKAHARA[2]

[1]*Oita Industrial Research Institute, 1-4361-10 Takae-nishi, Oita 870-1117, Japan*
[2]*Institute for Materials Chemistry and Engineering, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan*

(Received May 10, 2005; Accepted August 19, 2005; Published December 15, 2005)

ABSTRACT: The complexation of di-*n*-butyl phthalate (**DBP**) by two different series of water-soluble calixarenes {*p*-sulfonatocalix[*n*]arenes [**SCA*n*** ($n = 4$, 6, and 8)] and calix[*n*]arene-*O*-propane-3-sulfonate [**CA*n*PS** ($n = 4$, 6, and 8)]} and the **DBP** adsorption ability of chitosan beads modified with **SCA*n*** and **CA*n*PS** were investigated. The six- and eight-membered calixarenes (**SCA6**, **SCA8**, **CA6PS**, and **CA8PS**) could include **DBP** in their hydrophobic cavities in the homogeneous aqueous phase. The amount of **DBP** adsorbed by chitosan beads modified with **SCA6** was approximately five times as large as that for unmodified chitosan beads. On the other hand, the chitosan beads modified with **SCA8** show the nearly the same amount of adsorbed **DBP** as compared to unmodified chitosan beads. In the case of the chitosan beads modified with **CA*n*PS**, no correlation was observed with the **DBP** inclusion capability of **CA*n*PS**.
[DOI 10.1295/polymj.37.939]

KEY WORDS Calixarene / Chitosan / Di-*n*-butyl Phthalate / Inclusion / Adsorption / Polyion Complex /

Endocrine-disrupting chemicals (EDCs) and persistent organic pollutants have received considerable attention in recent years. Nonylphenol, 4-octylphenol, and bisphenol A have been reported to exhibit estrogenic activity,[1–3] and various other chemicals are suspected to be EDCs. Alkyl phthalates are representative examples[4,5] and are still under investigation. These chemicals have been detected in rivers and sediments because of their widespread use as plasticizers. Activated carbon has generally been used as an adsorbent for organic pollutants in water. However, the breakthrough time of activated carbon is not long because the selectivity for adsorbates is insufficient, and thus, frequent reactivation of the used activated carbon becomes essential. In addition, a large amount of thermal energy is required for the reactivation process. These problems can be solved if an adsorbent with recognition ability is prepared. To this end, several studies have reported adsorbents with molecular recognition sites, *e.g.*, the adsorbent with cyclodextrin that can adsorb bisphenol A and alkyl phthalates.[6–8] If a receptor has a hydrophobic cavity formed by aromatic rings, strong interaction is expected between the receptor and the noxious hydrophobic chemicals. The authors proposed an adsorbent modified with calixarene,[9] which is a cyclic oligomer that consists of aromatic rings crosslinked by methylene groups, as a binding site.

From a practical viewpoint, the convenient fabrication of receptors and adsorbents is important. It is known that Calix[*n*]arenes ($n = 4$, 6, and 8) can be easily synthesized from *p*-alkylphenol and formaldehyde with good yields[10–12] and can be easily modified by the introduction of functional groups into the *p*-position of the phenol (upper-rim) and phenolic hydroxyl group (lower-rim).[13–15] Therefore, it is appropriate that these analogues are nominated as the basic skeleton of a alkyl phthalates receptor. As for the fabrication of the adsorbent, polyion complexation is one kind of convenient modification methods for polymers. Immobilization of anionic calixarenes can be achieved by a polyion complex formation with cationized polymers. In addition, the upper-rim and lower-rim of calixarenes can be easily substituted as previously described. Thus, we synthesized two series of anionic sulfonated calixarenes, *i.e.*, *p*-sulfonatocalix[*n*]arenes [**SCA*n***] ($n = 4$, 6, and 8)] and calix[*n*]arene-*O*-propane-3-sulfonate [**CA*n*PS** ($n = 4$, 6, and 8)]. We also synthesized 2,6-dimethyl sulfonatophenol (**DMSP**) and 3-(2,6-dimethylphenoxy)propane-1-sulfonate (**DMPPS**) as references (Figure 1). With regard to the backbone of this adsorbent, hydrophilic polymers should be chosen so that the hydrophobic cavities of calixarenes can function effectively as molecular receptors driven by hydrophobic interaction with size-selectivity. Therefore, an environmentally benign hydrophilic cationic polymer derived from the discarded shells of crabs and shrimp–chitosan was employed.

†To whom correspondence should be addressed (Tel: +81-97-596-7100, Fax: +81-97-596-7005, E-mail: a-yanagi@oita-ri.go.jp).

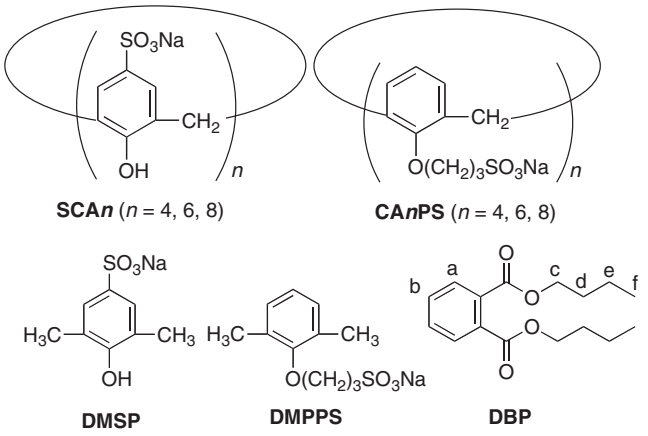

Figure 1. Chemical structures of sulfonated calixarenes, model acyclic compounds, and **DBP**.

In this paper, we chose di-*n*-butyl phthalate (**DBP**) as a target molecule because of the slightly higher water solubility of **DBP** among alkyl phthalates. We describe the **DBP** inclusion properties of the sulfonated calixarenes and the **DBP** adsorption ability of the chitosan beads modified with sulfonated calixarenes in an aqueous system. As for the fabrication of adsorbent with assembled receptors, it was supposed that the field with the assembled receptors on the adsorbent was different from the field formed by free receptors in the solution. Thus, we also describe the influence for the **DBP** adsorption from the field formed by the assembled receptors on the adsorbent.

EXPERIMENTAL

General Procedures

All chemicals were of commercial reagent quality and were used without further purification. **SCA*n***[16] and **CA*n*PS**[17] were synthesized by the reported method. **DMSP** and **DMPPS** were synthesized by the same methods as those for the corresponding compounds, as described later.

^{1}H NMR spectroscopic measurements were carried out at 298 ± 2 K with a Bruker DPX-400 (400 MHz), a JEOL JNM-EX400 (400 MHz), or a Bruker ARX-300 (300 MHz). IR spectra were obtained with a JASCO FT/IR-700S infrared spectrometer using the KBr pellet method. X-Ray photoelectron spectroscopic (XPS) measurements were made with a Phi Quantum 2000 (Physical Electronics) using focused (100 μm spot) monochromatic Al $K\alpha$ radiation at 15 kV and 1.3 mA with a pass energy of 29.35 eV. The UV spectra were measured on a Hitachi U-2000. Scanning electron microscopy (SEM) observations were made on a JEOL JSM-7400F operated at 5 kV for the freeze-dried adsorbents with osmium coating.

Syntheses of the Corresponding Monomeric Compounds

DMSP. 2,6-Dimethylphenol (7.1 g, 56.3 mmol) was mixed with 60 cm^3 of concentrated H_2SO_4, and the solution was heated at 353 K for 2 h. An aliquot was drawn from the solution and poured into water in order to monitor the progress of the reaction. The reaction was completed when no water-insoluble material was detected. After cooling, the reaction mixture was carefully poured into 150 g of ice water, and then the insoluble material was filtered off. The filtrate was washed with chloroform and treated with activated carbon. A white precipitate was then obtained from the filtrate by a salting-out method with NaCl. The precipitate was dissolved in 60 cm^3 of water and neutralized by $BaCO_3$. Precipitated $BaSO_4$ was removed by filtration and Na_2CO_3 was then added to the filtrate in order to exchange the counter cation. When the pH reached 8–9, the addition of Na_2CO_3 was stopped. The solution was filtrated and the obtained filtrate was concentrated to dryness. The residue was recrystallized from methanol and chloroform. Yield 64%. Paper chromatography (PC) yielded a single spot on chromatography paper (water/2-propanol = 1/2 v/v); m.p. > 573 K; IR (KBr, cm^{-1}) 3496 (–OH), 1182, 1056 (–SO_2); ^{1}H NMR (D_2O, 300 MHz, ppm): δ 7.22 (s, 2H, ArH), 2.04 (s, 6H, CH_3).

Anal. Calcd for $C_8H_9O_4SNa\cdot0.2CHCl_3$: C, 39.70%; H, 3.74%.

Found: C, 39.80%; H, 3.85%.

DMPPS. 2,6-Dimethylphenol (2.5 g, 20 mmol) was mixed with 70 cm^3 of THF, and the solution was refluxed for 1 h under a nitrogen atmosphere. After cooling, sodium hydride (1.6 g, 40 mmol; 60% dispersion in oil) was added and the mixture was stirred for 1 h. Propane-1,3-sultone (3.6 cm^3, 40 mmol) was then added dropwise and the mixture was stirred at room temperature for 22 h. Excess NaH was decomposed with methanol, after which the mixture was diluted with water, and the insoluble material was filtered off. The filtrate was concentrated to approximately 50 cm^3 and sodium acetate was added to salt out the sodium salt. The precipitate was washed with hot chloroform in order to remove residual propane-1,3-sultone. Yield 81%. PC yielded a single spot on chromatography paper (water/2-propanol = 1/2 v/v); m.p. > 573 K; IR (KBr, cm^{-1}) 1192, 1051 (–SO_2); ^{1}H NMR (D_2O, 300 MHz, ppm): δ 7.03 (d, 2H, ArH), 6.94 (t, 1H, ArH), 3.87 (t, 2H, C–O–CH_2), 3.05 (t, 2H, S–CH_2), 2.15 (m, 8H, $OCH_2C\underline{H}_2$, CH_3).

Anal. Calcd for $C_{11}H_{15}O_4SNa\cdot0.2CHCl_3$: C, 46.36%; H, 5.28%.

Found: C, 46.22%; H, 5.32%.

Immobilization of the Molecular Receptors onto Chitosan Beads

In order to fabricate the adsorbent with the molecular receptors, the receptors bearing sulfonate groups were immobilized onto chitosan beads by polyion complexation.[18] In the present study, we chose Chitopearl Basic AL-01 (**AL-01**), which is manufactured by Fuji Spinning Co., Ltd. (Tokyo, Japan). **AL-01** comprises unsubstituted chitosan beads with a particle diameter of 74–210 μm.

The anionic molecular receptors were complexed onto the cationic **AL-01** as follows: Four grams of **AL-01** in 40 cm^3 of water was added in 160 cm^3 of 2.5 wt % acetic acid aqueous solution (66.3 mmol). The aqueous solution of the molecular receptor was added dropwise in the **AL-01** dispersion. The detailed conditions of the volume of water and the amount of the molecular receptors are shown in Table I. After stirring sufficiently, the precipitate was obtained by filtration and then washed with water until the pH of the filtrate reached approximately 7. The obtained precipitate was used as adsorbent in further experiments. The ratios of the molecular receptor to the chitosan unit in the adsorbents were estimated from the ratios of sulfur in the molecular receptor to the nitrogen of chitosan in **AL-01** by XPS.

*Inclusion of **DBP** in the Molecular Receptors*

The complexation behavior of **SCA*n***, **DMSP**, **CA*n*PS**, or **DMPPS** as a molecular receptor with **DBP** was examined by a ^{1}H NMR measurement as follows (400 MHz, T = 298 ± 2 K).[19] A stock methanol-d_4 solution of **DBP** was added to 2.5–124 mM of **SCA*n***, **DMSP**, **CA*n*PS**, or **DMPPS** solution in D_2O. At this time, the concentration of **DBP** was maintained constant in the range 1.2–1.3 mM and the host–guest solution contained 0.8% of methanol-d_4 from stock solutions. When **SCA6** or **SCA8** was used as a receptor, the association constants (K_a) were calculated using a nonlinear curve fitting of the aromatic signals of **DBP**.[20]

Table I. The conditions of polyion complexation

Adsorbent	Receptor	Mixed quantity of receptor (as phenol unit[a]) (mmol)		Water for dissolving receptor (cm^3)
DMSP-C	**DMSP**	12.4	(12.4)	40
SCA4-C	**SCA4**	3.10	(12.4)	40
SCA6-C	**SCA6**	2.07	(12.4)	40
SCA8-C	**SCA8**	1.55	(12.4)	550
DMPPS-C-H	**DMPPS**	12.4	(12.4)	40
CA4PS-C-H	**CA4PS**	3.10	(12.4)	40
CA6PS-C-H	**CA6PS**	2.07	(12.4)	200
CA8PS-C-H	**CA8PS**	1.55	(12.4)	800
DMPPS-C-L	**DMPPS**	0.248	(0.248)	40
CA4PS-C-L	**CA4PS**	0.062	(0.248)	40
CA6PS-C-L	**CA6PS**	0.041	(0.248)	40
CA8PS-C-L	**CA8PS**	0.031	(0.248)	40

[a]Calculated from the number of phenol unit in receptor.

***DBP** Adsorption Tests*

Adsorption tests for **DBP** on **AL-01** modified with the molecular receptors were carried out in 300 cm^3 Erlenmeyer flasks. One gram of the modified chitosan beads and 100 cm^3 of 67 mM phosphate buffer (pH 7.0) containing 10 mM of **DBP** were placed in the flask and shaken for 24 h at 298 K. The adsorbed **DBP** was extracted in *n*-hexane and detected by a UV spectrophotometer.

RESULTS AND DISCUSSION

***DBP** Inclusion Properties of the Sulfonated Calixarenes*

Figure 2 shows the ^{1}H NMR spectra of **DBP** and **DBP** with **SCA6** in D_2O. The signals attributed to

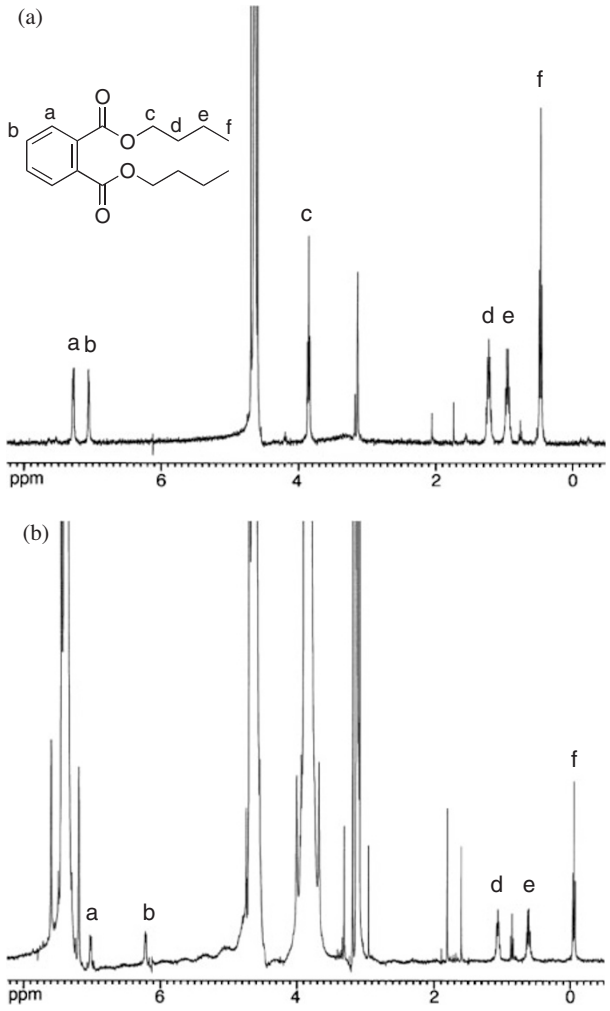

Figure 2. ^{1}H NMR spectra of (a) **DBP** and (b) **DBP** with **SCA6** in D_2O (with 0.8% of CD_3OD): [**DBP**], 1.24 mM; [**SCA6**], 61.5 mM.

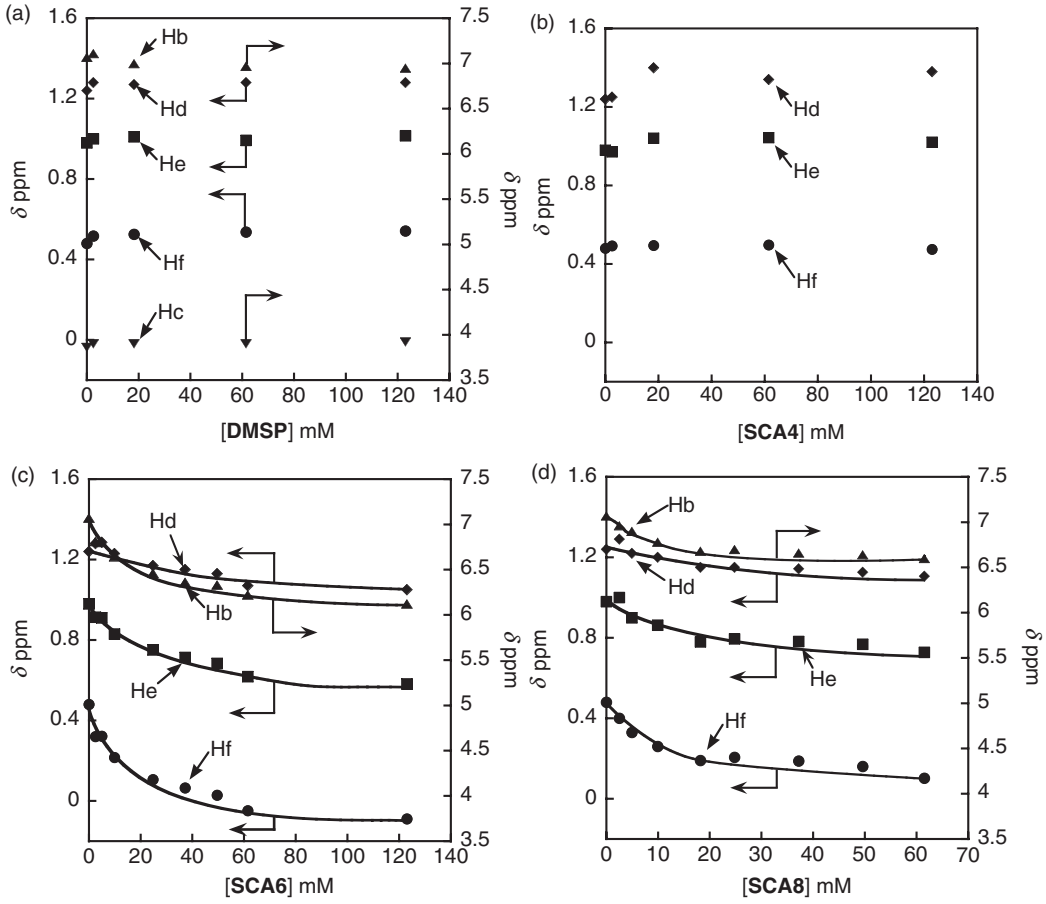

Figure 3. ^{1}H NMR chemical shift (in ppm) of **DBP** in D_2O (with 0.8% of CD_3OD) in the presence of (a) **DMSP**; (b) **SCA4**; (c) **SCA6**; (d) **SCA8**.

the aromatic protons and the alkyl protons of **DBP** were shifted to a higher magnetic field in the presence of **SCA6**. These results were caused by the magnetic shielding effect of the aromatic rings of the host showing that **SCA6** could include **DBP** in its cavity. The chemical shifts of the protons of **DBP** are plotted against several concentrations of **SCA6** in Figure 3c. The signals due to **DBP** shifted to a higher magnetic field as the concentration of **SCA6** was increased, and the plots of the signals were converged to each value. The K_a of **SCA6** calculated from the Hb proton of **DBP** was 215 M^{-1}. The same tendency was observed in the case wherein **SCA8** was used as a molecular receptor (Figure 3d). Therefore, **SCA8** can bind **DBP** in the aqueous phase ($K_a = 372\,M^{-1}$). The binding ability of **SCA8** to **DBP** was stronger than that of **SCA6** due to the flexible skeleton. In addition, when **DMSP** or **SCA4** was used as a molecular receptor, the chemical shift of the protons of **DBP** did not shift to a higher magnetic field (Figures 3a and 3b). These results indicated that neither **DMSP** nor **SCA4** included **DBP**.

Figure 4 shows the ^{1}H NMR chemical shifts of **DBP** when **CA*n*PS** or **DMPPS** was used as a molecular receptor in the same manner as **SCA*n*** or **DMSP**. This trend of the results was similar to that of the results of **SCA*n*** and **DMSP**. **CA6PS** and **CA8PS** could include **DBP** in their cavities because the signals attributed to the alkyl protons of **DBP** were shifted to a higher magnetic field in the presence of **CA6PS** or **CA8PS** (Figures 4c and 4d). When **CA*n*PS** was used as a molecular receptor, the aromatic protons of **DBP** were not determined due to the overlap of the aromatic protons of **CA*n*PS**. Therefore, the K_a of **CA6PS** and **CA8PS** could not be estimated for comparison with **SCA6** and **SCA8**. In the cases of **CA4PS** and **DMPPS**, there were no **DBP** inclusion phenomena similar to **SCA4** and **DMSP**.

Ratios of Molecular Receptors to Chitosan Unit in the Adsorbents

Table II shows the ratios of the molecular receptors to the chitosan unit in adsorbents evaluated from XPS. The S_{2p}/N_{1s} ratio had approximately the same value in each series, *i.e.*, **SCA*n*-C**, **CA*n*PS-C-H**, and **CA*n*PS-C-L** ($n = 4$, 6, and 8). If the conformational structures and hole size of sulfonated calixarenes are not considered, then the hydrophobicities of the prepared chitosan beads were almost the same in the case of each corresponding compound, *i.e.*, **DMSP-C**, **DMPPS-C-H**, or **DMPPS-C-L**.

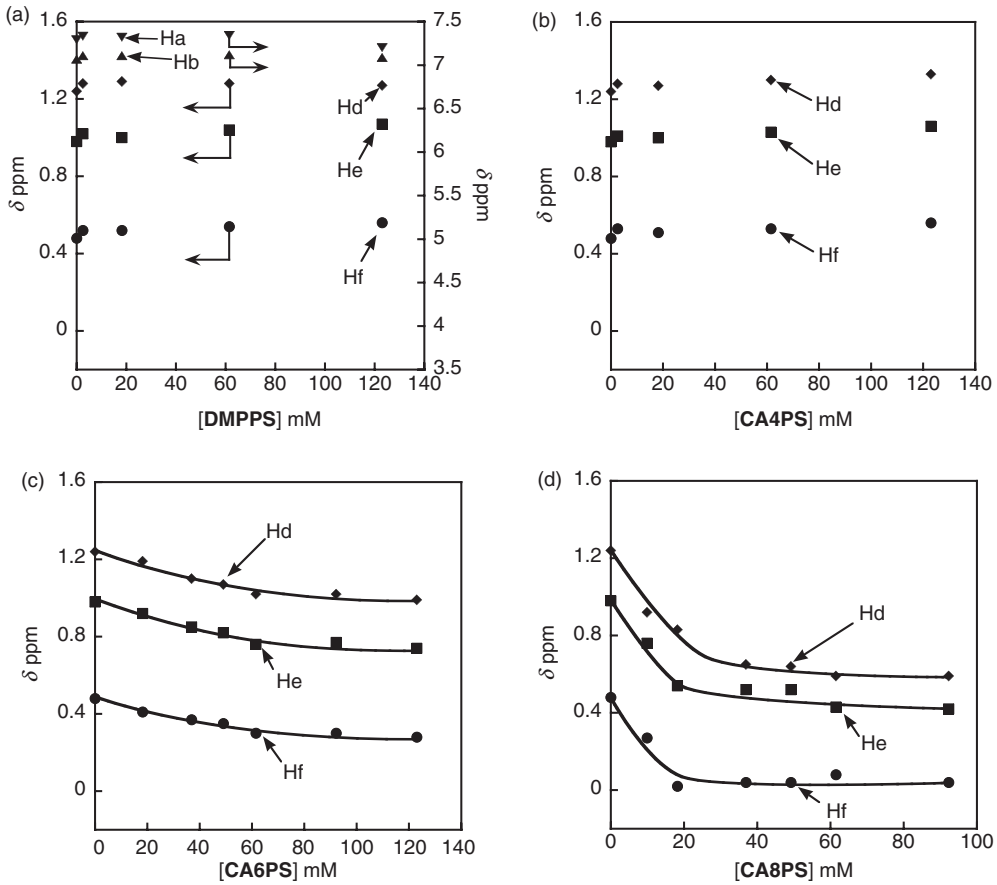

Figure 4. ^{1}H NMR chemical shift (in ppm) of **DBP** in D_2O (with 0.8% of CD_3OD) in the presence of (a) **DMPPS**; (b) **CA4PS**; (c) **CA6PS**; (d) **CA8PS**.

Table II. Ratios of molecular receptors to chitosan in adsorbent determined by XPS

Adsorbent	Receptor	Mixed quantity of receptor as phenol unit[a] (mmol)	S_{2p} (in receptor)/ N_{1s} (in chitosan)	Chitosan unit:receptor
DMSP-C	**DMSP**	12.4	0.47 ($\sigma^b = 0.02$)	100:47
SCA4-C	**SCA4**	12.4	0.65 ($\sigma^b = 0.03$)	100:16.3
SCA6-C	**SCA6**	12.4	0.59 ($\sigma^b = 0.04$)	100:9.8
SCA8-C	**SCA8**	12.4	0.63 ($\sigma^b = 0.04$)	100:7.9
DMPPS-C-H	**DMPPS**	12.4	0.55 ($\sigma^b = 0.05$)	100:55
CA4PS-C-H	**CA4PS**	12.4	0.79 ($\sigma^b = 0.04$)	100:19.8
CA6PS-C-H	**CA6PS**	12.4	0.77 ($\sigma^b = 0.05$)	100:12.8
CA8PS-C-H	**CA8PS**	12.4	0.86 ($\sigma^b = 0.05$)	100:10.8
DMPPS-C-L	**DMPPS**	0.248	0.18 ($\sigma^b = 0.02$)	100:18
CA4PS-C-L	**CA4PS**	0.248	0.23 ($\sigma^b = 0.03$)	100:5.8
CA6PS-C-L	**CA6PS**	0.248	0.26 ($\sigma^b = 0.07$)	100:4.3
CA8PS-C-L	**CA8PS**	0.248	0.31 ($\sigma^b = 0.07$)	100:3.9

[a]Calculated from the number of phenol unit in receptor. [b]σ is a standard deviation calculated from 20 data.

*Adsorption Properties of **AL-01** Modified with the Molecular Receptors*

Table III shows the **DBP** adsorption properties of the modified chitosan beads. **SCA6-C** had approximately five times the adsorption ability of unmodified chitosan beads. **DMSP-C**, **SCA4-C**, and **SCA8-C** did not show such a large improvement in adsorption. As described above, **SCA8** showed a stronger binding ability to **DBP** than **SCA6** in homogeneous aqueous solution, but **SCA8-C** showed poor adsorption ability.

Table III. Adsorption of **DBP** by chitosan beads modified with molecular receptors

Adsorbent	Receptor	Chitosan unit: immobilized phenol unit	Adsorbed **DBP** ($mg\,g^{-1}$)
AL-01	none	none	11
DMSP-C	**DMSP**	100:47	26
SCA4-C	**SCA4**	100:65	25
SCA6-C	**SCA6**	100:59	57
SCA8-C	**SCA8**	100:63	14
DMPPS-C-H	**DMPPS**	100:55	>80
CA4PS-C-H	**CA4PS**	100:79	>80
CA6PS-C-H	**CA6PS**	100:77	>80
CA8PS-C-H	**CA8PS**	100:86	>80
DMPPS-C-L	**DMPPS**	100:18	>80
CA4PS-C-L	**CA4PS**	100:23	>80
CA6PS-C-L	**CA6PS**	100:26	51
CA8PS-C-L	**CA8PS**	100:31	33

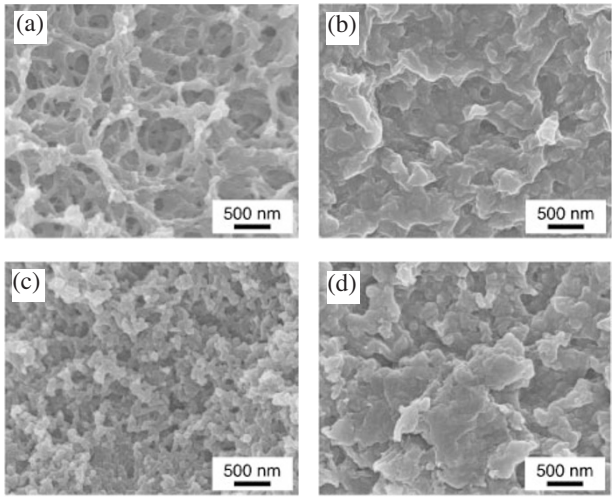

Figure 5. SEM images of (a) **AL-01**; (b) **AL-01** treated with acetic acid (2.5 wt %); (c) **CA8PS-C-H**; (d) **CA8PS-C-L**.

This is probably due to the difference in the ring size and flexibility between **SCA6** and **SCA8**. The ring size and flexibility of molecular receptors might play an important role in the complexation between **DBP** and a free molecular receptor. A large ring on the host would lead to an easy insertion of a guest and the flexible structure would change the conformation for suitable hydrophobic interaction between the host and guest. On the other hand, larger ring size and greater flexibility, which implies a large number of units, might cause the deformation (or loss) of the hydrophobic cavity by immobilization onto chitosan beads. Since **SCA8** has eight sulfonate groups that can link to the amino groups in chitosan, anchoring by several methods as well as a large number of anchorings would limit the conformational changes of **SCA8**.

When **CA*n*PS-C-H**, **DMPPS-C-H**, **CA*n*PS-C-L**, and **DMPPS-C-L** were examined in adsorption test, the trend was entirely different from **SCA*n*-C**. The ratios of the immobilized phenol unit derived from molecular receptors to the chitosan unit in **CA*n*PS-C-H** and **DMPPS-C-H** were approximately the same as the ratios in **SCA*n*-C** and **DMSP-C**, as shown in Table II. However, the amount of adsorbed **DBP** by **CA*n*PS-C-H** or **DMPPS-C-H** was significantly larger than that of **SCA*n*-C** or **DMSP-C**. For example, the **DBP** adsorption ability of **DMPPS-C-H** was three times as high as that of **DMSP-C**. The hydrophobicity of **DMPPS** is supposed to be high as compared to **DMSP** because **DMPPS** has an *O*-propane-1-sulfonate group instead of a phenolic hydroxyl group. Therefore, the adsorption of **DBP** by **DMPPS-C-H** would be caused by the hydrophobic domains formed by the homogeneously immobilized **DMPPS**. Correspondingly, the adsorption of **DBP** by **CA6PS-C-H** and **CA8PS-C-H** is considered to have occurred in the hydrophobic domains, which was formed by **CA6PS** and **CA8PS**, instead of the inclusion as previously described. This hypothesis was also supported by **CA6PS-C-L** and **CA8PS-C-L**, which decreased the ratios of the molecular receptor to the chitosan unit compared to **CA6PS-C-H** and **CA8PS-C-H**. The decrease in the immobilization ratio and the increase in the number of the ring member imply the sparse hydrophobic domains on the chitosan beads. Therefore, it appears that **CA8PS-C-L** showed poor adsorption ability as compared to **CA4PS-C-L**.

*The Morphologies of **AL-01** Modified with the Molecular Receptors*

In order to evaluate the influence of the immobilization ratio of the calixarene derivatives to chitosan unit, SEM observation were carried out. Figure 5 shows the SEM images of (a) **AL-01**, (b) **AL-01** treated with acetic acid (2.5 wt %), (c) **CA8PS-C-H**, and (d) **CA8PS-C-L** coated by osmium after freeze-dried. **CA8PS-C-H** was observed as a porous body similar to **AL-01**. However, **CA8PS-C-L** was observed to dissolve the surface partially similar to **AL-01** treated with acetic acid. **CA8PS** has eight sulfonate groups that can function as a crosslinker to amino groups in chitosan. The high immobilization ratio suggested the high crosslinking density. Therefore, the difference of the surface morphologies between **CA8PS-C-H** and **CA8PS-C-L** was caused by the immobilization ratios of **CA8PS**. In other words, the morphology of **CA8PS-C-L** reflected the sparse immobilization of **CA8PS** (hydrophobic domains) compared with **CA8PS-C-H**.

CONCLUSIONS

SCA6-C was shown to adsorb **DBP** in contrast to **SCA8-C** although **SCA8** has a stronger binding ability to **DBP** than **SCA6** has in the homogeneous aqueous solution. These results suggest that the conservation of the steric complementarity between a molecular receptor and a target molecule is of considerable importance to the fabrication of adsorbents with the immobilization of molecular receptors. In the case of **AL-01** modified with **CA*n*PS**, no correlation was observed with the **DBP** inclusion abilities of **CA*n*PS**. It was probably caused by the hydrophobic domains, which is formed by **CA*n*PS** or **DMPPS**, instead of the inclusion. These results suggest the following: (1) the molecular receptor should be designed by considering the difference in the fields formed using a free receptor or assembled receptors and (2) the field should be fabricated such that the intermolecular interaction between molecular receptors and target molecules can perform effectively as molecular receptors.

Acknowledgment. This work was partially supported by "Nanotechnology Support Project" of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

REFERENCES

1. R. White, S. Jobling, S. A. Hoare, J. P. Sumpter, and M. G. Parker, *Endocrinology*, **135**, 175 (1994).
2. K. W. Gaido, L. S. Leonard, S. Lovell, J. C. Gould, D. Babaï, C. J. Portier, and D. P. McDonnell, *Toxicol. Appl. Pharmacol.*, **143**, 205 (1997).
3. S. C. Laws, S. A. Carey, J. M. Ferrell, G. J. Bodman, and R. L. Cooper, *Toxicol. Sci.*, **54**, 154 (2000).
4. S. Jobling, T. Reynolds, R. White, M. G. Parker, and J. P. Sumpter, *Environ. Health Perspect.*, **103**, 582 (1995).
5. C. A. Harris, P. Henttu, M. G. Parker, and J. P. Sumpter, *Environ. Health Perspect.*, **105**, 802 (1997).
6. M. Nishiki, T. Tojima, N. Nishi, and N. Sakairi, *Carbohydr. Lett.*, **4**, 61 (2000).
7. S. Murai, S. Imajo, Y. Maki, K. Takahashi, and K. Hattori, *J. Colloid Interface Sci.*, **183**, 118 (1996).
8. S. Murai, S. Imajo, Y. Takasu, K. Takahashi, and K. Hattori, *Environ. Sci. Technol.*, **32**, 782 (1998).
9. A. Yanagi, H. Otsuka, and A. Takahara, *Chem. Lett.*, **34**, 218 (2005).
10. C. D. Gutsche and M. Iqbal, *Org. Synth.*, **68**, 234 (1990).
11. C. D. Gutsche, B. Dhawan, M. Leonis, and D. Steward, *Org. Synth.*, **68**, 238 (1990).
12. J. H. Munch and C. D. Gutsche, *Org. Synth.*, **68**, 243 (1990).
13. K. Araki, A. Yanagi, and S. Shinkai, *Tetrahedron*, **49**, 6763 (1993).
14. V. Böhmer, *Angew. Chem. Int. Ed.*, **34**, 713 (1995).
15. A. Ikeda and S. Shinkai, *Chem. Rev.*, **97**, 1713 (1997).
16. S. Shinkai, H. Kawaguchi, and O. Manabe, *J. Polym. Sci., Part C: Polym. Lett.*, **26**, 391 (1988).
17. S. Shinkai, T. Arimura, K. Araki, H. Kawabata, H. Satoh, T. Tsubaki, O. Manabe, and J. Sunamoto, *J. Chem. Soc., Perkin Trans. 1*, **1989**, 2039.
18. A. Tsuge, K. Masumi, T. Moriguchi, and K. Sakata, *Aust. J. Chem.*, **51**, 1175 (1998).
19. M. Baur, M. Frank, J. Schatz, and F. Schildbach, *Tetrahedron*, **57**, 6985 (2001).
20. L. Fielding, *Tetrahedron*, **56**, 6151 (2000).