Adsorptive Removal of Bisphenol A by Calix[4]crown Derivatives: Significant Contribution of Hydrogen Bonding Interaction to the Control of Adsorption Behavior

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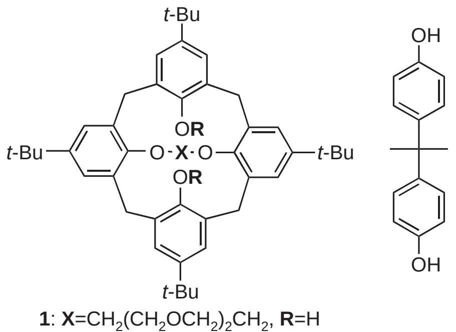
Adsorptive removal of bisphenol A by finely powdered calix[4]crown derivatives has been investigated. Adsorption ability was strongly dependent on the molecular structures of the calix[4]crowns examined. Batch adsorption experiments and X-ray crystallographic analysis revealed that the present adsorption behavior was controlled not only by hydrophobic interaction but also by hydrogen-bonding interaction on the solid surface.

Owing to stricter pollution regulations and lower energy demands, an efficient process to remove endocrine-disrupting chemicals (EDCs) from the environment is being demanded. For this purpose, a number of techniques have so far been investigated,[1] including adsorption, nanofiltration, chemical degradation, biodegradation, and coagulation. When we consider the real environment, however, collection of trace EDCs is crucial for the successful destruction of them. We envisaged adsorptive removal as one of the desirable candidates for establishing the efficient enrichment of trace EDCs because of the attractive prospects, i.e., (1) the simple operation, (2) wide coverage of contaminants, (3) no requirement of peculiar external energy, and (4) no generation of degradation products of unknown toxicity. Activated carbon,[1b,2a] sugar-based organo gel,[2b] calix[6]arene polymer,[2c,2d] and cyclodextrin polymer[2e,2f] were examined as adsorbents for the removal of EDCs.

As a novel scaffold of adsorbent, we have examined calix[4]crown, which has been the subject of considerable attention in host–guest chemistry,[3] and investigated the application of **1**, **2**, and **3** (Figure 1) as adsorbents to remove EDC from an aqueous medium through solid–liquid adsorption phenomenon. Bisphenol A (BPA, Figure 1) was employed here as a model EDC commonly detected in waste water. The purpose of the present study is twofold, i.e., (1) evaluation of the adsorption behavior of **1**, **2**, and **3** in removing BPA and (2) elucidation of the removal mechanism when the calix[4]crowns are applied as adsorbents. Very fortunately, a co-crystal involving both **1** and BPA in a 1:1 ratio was obtained, and its X-ray crystallographic analysis provided an insight into the adsorption mechanism. In this paper, we report the adsorption behaviors observed in the calix[4]crowns, together with the removal mechanism.



1: **X**=$CH_2(CH_2OCH_2)_2CH_2$, **R**=H
2: **X**=$CH_2(CH_2SCH_2)_2CH_2$, **R**=H
3: **X**=$CH_2(CH_2OCH_2)_2CH_2$, **R**=Bn

BPA

Figure 1. Chemical structures of adsorbents and a model EDC.

Calix[4]crowns **1**, **2**, and **3** with a cone conformation were prepared according to the described procedure.[4] Their adsorption abilities were evaluated by batch adsorption experiments in which finely powdered samples of **1**, **2**, and **3** with the uniform particle size of 63 μm were used as adsorbents. Seven milligrams of calix[4]crown were placed in 50-cm^3 stopped glass tubes, and each tube was charged with 10 cm^3 of aqueous solution of varying BPA concentration from 0 to 120 mg dm^{-3}. The tubes were shaken at 300 rpm for 1 h at 25 °C, and the residual concentration of BPA was determined by means of HPLC analysis. Adsorption isotherms are shown in Figure 2, in which adsorption capacities are plotted against equilibrium solute concentrations. The adsorption capacities increased with the increasing equilibrium concentrations, and the relationship between them was successfully analyzed by the Freundlich equation[5] expressed as,

$$W = K_F C^{1/n}, \tag{1}$$

where W is the adsorption capacity at the equilibrium solute concentration C, and K_F and $1/n$ are the Freundlich constants. The calculated constants are summarized in Table 1. A steep rise in the adsorption capacity was observed in **1**, indicating the high affinity of solute–surface contact. The observed difference in the adsorption behavior shown in Figure 2 was clearly reflected in the $1/n$ constants; **1** exhibited almost 3 and 6 times greater $1/n$ than **2** and **3**, respectively (Table 1). An increase in $1/n$ resulted in a decrease in the K_F constants, suggesting that the

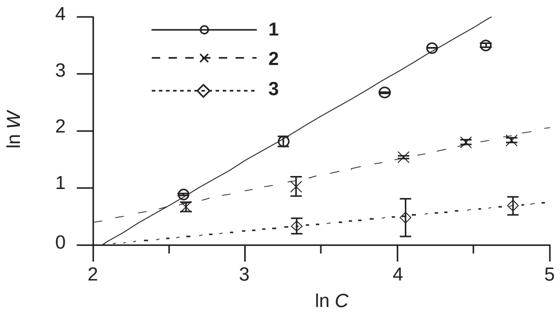


Figure 2. Adsorption isotherms of BPA onto finely powdered calix[4]crowns **1**, **2**, and **3** at 25 °C.

Table 1. Freundlich isotherm constants

Compound	$1/n$	$K_F/\text{mg g}^{-1}$
1	1.56 ± 0.10	0.04 ± 0.02
2	0.55 ± 0.03	0.49 ± 0.06
3	0.25 ± 0.02	0.60 ± 0.04

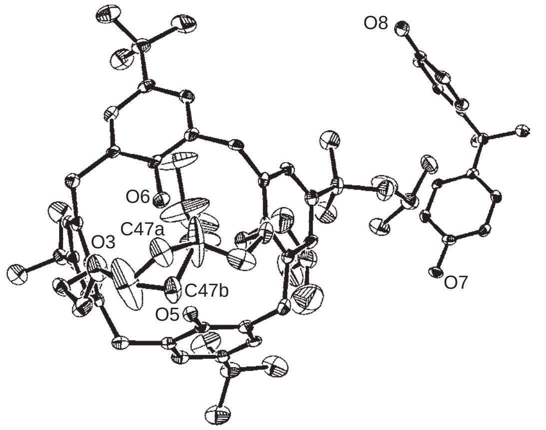


Figure 3. ORTEP drawing of **1**•BPA•3CHCl$_3$ showing 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

present adsorption behavior was controlled by the surface properties of the adsorbents as pointed out by Kawasaki and co-workers.[2a]

To gain an insight into the removal mechanism, our efforts were directed to prepare a co-crystal involving both an adsorbent and BPA. A colorless plate crystal[6] suitable for X-ray crystallographic analysis was obtained by slow evaporation of a chloroform/methanol/hexane solution (55:40:5, v/v) of **1** and BPA. As shown in Figure 3, calixarene moiety of **1** adopts a cone conformation, and one carbon atom within the oxyethylene chain is disordered at C(47a) and C(47b) with equal occupancy factors of 0.5. In the asymmetric unit, three chloroform molecules are present as solvates; one is encapsulated in the cavity of **1**, and the others are located in the packing. In the crystal (Figure 4), one BPA molecule forms three types of intermolecular hydrogen bonds with two adjacent calixcrowns **1** related by symmetry operations of (1) $1-x,\ 1-y,\ -z$ and (2) $1-x,\ 1/2+y,\ 1/2-z$. Bifurcated hydrogen bonds are formed between one phenolic hydroxy group O(8) of BPA and both of an oxygen atom O(3) of the crown bridge in **1** and a phenolic hydroxy group O(6) of the same calix[4]crown; O(8)···O(3) and O(8)···O(6) distances are 2.748(3) and 3.010(3) Å, respectively. The third hydrogen bond is formed between the other phenolic hydroxy group O(7) of BPA and a phenolic hydroxy group O(5) of another neighboring calixcrown **1** [O(7)···O(5) distance: 2.720(3) Å]. As a consequence, the alternating arrangement of **1** and BPA along the *c* axis gives rise to infinite supramolecular one-dimensional chains in an antiparallel direction.

Although success in the X-ray crystallographic analysis is limited to a co-crystal containing **1** and BPA, it is plausible to presume from the above experimental results that hydrogen-bonding interaction, in addition to hydrophobic one, plays an important role in the present adsorption behavior. In fact, calix[4]crown **1** well adsorbed BPA, whereas the dibenzylated derivative **3** could not do so because of the lack of hydroxy groups and the steric hindrance arising from the benzyl groups. Moreover, because of the lower hydrogen-bonding ability of sulfur atom than oxygen, a decline in the adsorption capacity was eventually observed in the thia-analogue **2**. As a result, it is very likely that difference in the molecular structures of the calix[4]crowns descends to the particle surface, on which hydrogen-bonding interaction via hydroxy groups and/or oxyethylene chain fulfills a decisive role in the contact with BPA.

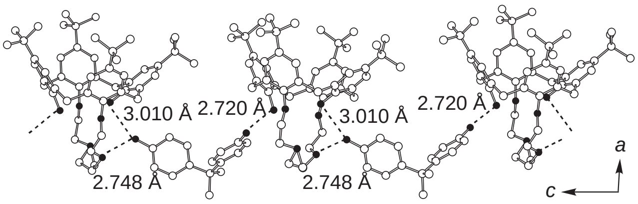


Figure 4. Schematic representation of an infinite supramolecular one-dimensional chain structure established by intermolecular hydrogen-bonding interactions between **1** and BPA. Carbon and oxygen atoms are represented by open and closed circles, respectively.

In conclusion, we demonstrated that finely powdered calix[4]crowns could remove BPA from an aqueous medium through solid–liquid adsorption phenomenon. It was found that the present adsorption behavior was controlled not only by hydrophobic interaction but also by hydrogen-bonding interaction on the solid surface. Further derivatization of calix[4]crown framework is under progress to develop an excellent adsorbent with a high adsorption capacity.

References and Notes

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6 Crystal data for **1**•BPA•3CHCl$_3$: C$_{68}$H$_{85}$Cl$_9$O$_8$, $M_r = 1349.47$, monoclinic, space group $P2_1/c$, $a = 17.4063(8)$ Å, $b = 13.0233(6)$ Å, $c = 30.268(1)$ Å, $\beta = 93.173(3)^\circ$, $V = 6850.9(5)$ Å^3, $Z = 4$, $D_\text{calcd} = 1.308$ g/cm^3, $R = 0.064$ for 23107 observed reflections with $I > 3\sigma(I)$ from 67683 unique reflections. CCDC deposition number: 268327.

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