SELECTIVE REMOVAL OF CHLORINATED AROMATICS FROM INSULATING OIL BY CYCLODEXTRIN ADSORBENTS

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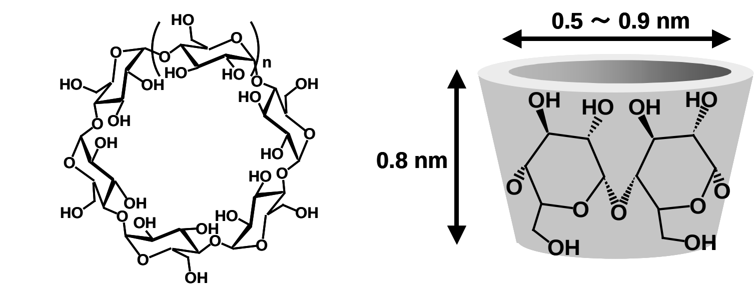
Abstract

The ability of various types of cyclodextrin (CD) derivatives to adsorb chlorinated aromatics in insulating oil was evaluated. 6-*O*-*tert*-Butyldimethylsilylated β-CD (Si-β-CD) exhibited the highest ability to adsorb chlorinated aromatics in insulating oil among the CD derivatives examined in this work. In particular, 1,2,4-trichlorobenzene (90 ppm) was almost completely removed from the insulating oil by using this CD adsorbent. On the other hand, 6-*O*-*tert*-butyldimethylsilylated α-CD (Si-α-CD), which has a smaller ring than that of Si-β-CD, showed no affinity towards the chlorinated aromatics. The adsorption ability of native β-CD towards the chlorinated aromatics was much lower than that of Si-β-CD. These results show that both the ring size and the chemical modification of CD play an important role in the adsorption of chlorinated aromatics in insulating oil.

Introduction

Enormous amounts of polychlorinated biphenyls (PCBs) and PCB-contaminated oils have been stored in Japan for more than three decades. For the treatment of these PCBs, various chemical destruction methods, such as dechlorination of PCBs with alkalines[1] and supercritical water oxidation of PCBs[2], have been developed. These methods, however, have a serious drawback in that they require high reaction temperatures and/or prolonged reaction times to destroy the PCBs. Thus, these methods are not considered ideal for the efficient treatment of large amounts of insulating oils contaminated by small amounts of PCBs (1-100 ppm). If a new PCB adsorbent is developed, which allows the selective removal of PCBs from insulating oils, and permits the easy recovery of adsorbed PCBs by washing with small amounts of organic solvents, one can significantly reduce the amount of PCB-contaminated insulating oils. The development of such an innovative adsorbent is strongly desired from the viewpoints of energy conservation and environmental protection.

Cyclodextrins (CDs) are a class of cyclic oligosaccharides consisting of several α-(1,4)-linked D-glucopyranose units. They have a hydrophobic cavity into which a guest molecule of an appropriate size and shape is incorporated mainly through hydrophobic interactions in aqueous solutions (Figure 1). The ability of CDs to form inclusion complexes with organic

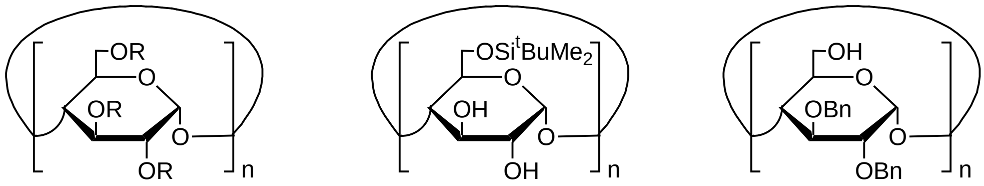


α-CD (n = 1), β-CD (n = 2), γ-CD (n = 3)

Figure 1. Structures of cyclodextrins (CDs).

molecules has found applications in many areas[3,4]. Since the nanoenvironment of the CD cavity is known to be comparable to that of 1,4-dioxane[5] and the size and shape of polychlorinated benzenes and PCBs are suitable to be incorporated into the CD cavity, the appropriate chemical modification of CDs can also lead to the inclusion (adsorption) of these polychlorinated aromatics in oils. We report herein that CD derivatives function as new effective adsorbents to remove chlorinated aromatics from insulating oil.

Materials and Methods



Me-α-CD: R = CH_3, n = 6
Me-β-CD: R = CH_3, n = 7
Ac-α-CD: R = Ac, n = 6
Ac-β-CD: R = Ac, n = 7

Si-α-CD: n = 6
Si-β-CD: n = 7
Si-γ-CD: n = 8

Bn-β-CD: n = 7
Bn-γ-CD: n = 8

Figure 2. Structures of cyclodextrin derivatives.

Permethylated cyclodextrins (Me-CDs), peracethylated cyclodextrins (Ac-CDs), 6-*O*-*tert*-butyldimethylsilylated cyclodextrins (Si-CDs), and 2,3-*O*-dibenzylated cyclodextrins (Bn-CDs) were chosen as adsorbents (Figure 2). These compounds were synthesized from the corresponding native CDs according to methods cited in the literature[6]. 1,2,4-Trichlorobenzene (1,2,4-TrCBz), 1,3,5-trichlorobenzene (1,3,5-TrCBz), 4-chlorobiphenyl (4-MCB), 4,4'-dichlorobiphenyl (4,4'-DiCB), and 3,4,4'-trichlorobiphenyl (3,4,4'-TrCB) were chosen as chlorinated aromatics.

Adsorption ability of CD derivatives towards these chlorinated aromatics in insulating oil was evaluated as follows: CD derivatives were added into the insulating oil including chlorinated aromatics (90 ppm), and the resulting mixtures were stirred for a certain period of time at ambient temperature. After removal of CD derivatives (solid) by filtration, concentrations of chlorinated aromatics remaining in the insulating oil were determined by GC-MS analyses.

Results and Discussion

Adsorption ability of various types of CD derivatives, including Me-CDs, Ac-CDs, Si-CDs, and Bn-CDs, towards chlorinated aromatics in insulating oil was examined. Figure 3 shows the percentage of chlorinated aromatics (1,2,4-TrCBz, 1,3,5-TrCBz, 4-MCB) removed from the insulating oil by the CD derivatives. Me-CDs and Ac-CDs showed no adsorption towards these chlorinated compounds. Si-β-CD exhibited the highest ability to adsorb these chlorinated compounds among the CD derivatives examined in this work. In particular, 1,2,4-TrCBz was almost completely removed from the insulating oil by using Si-β-CD. On the other hand, Si-α-CD, which possesses a smaller ring than that of Si-β-CD, showed no affinity towards these chlorinated compounds. The adsorption ability of native β-CD was much lower than that of Si-β-CD. These results show that both the ring size and the chemical modification of the CD play an important role

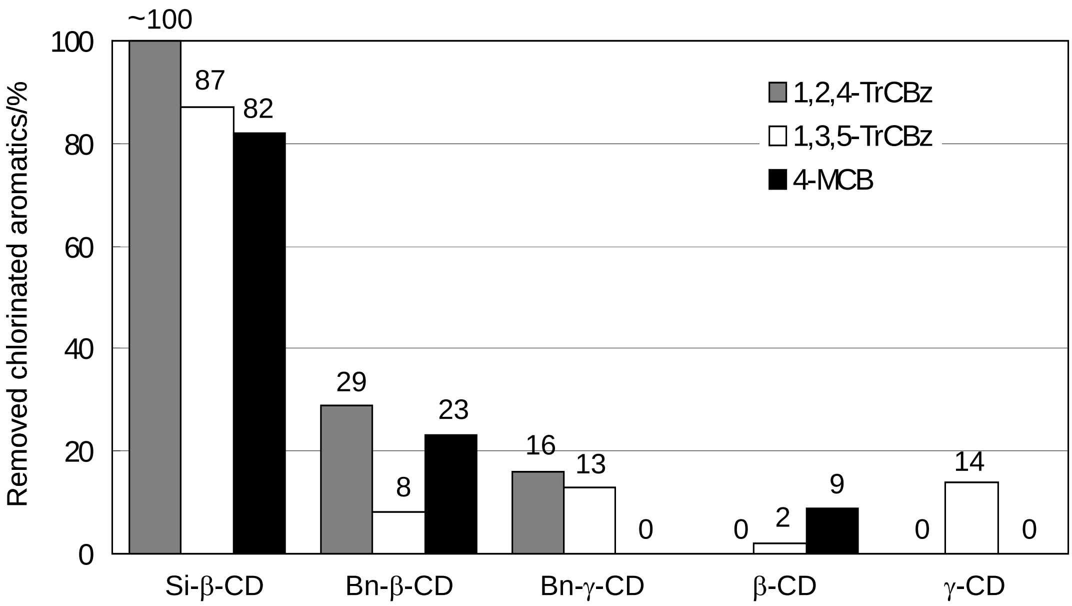


Figure 3. Percentage of chlorinated aromatics removed from insulating oil after stirring with various types of CD derivatives for 15 h at 25 °C. Initial concentrations of chlorinated aromatics in insulating oil were 90 ppm. The amounts of CD derivatives added were 20 mg.

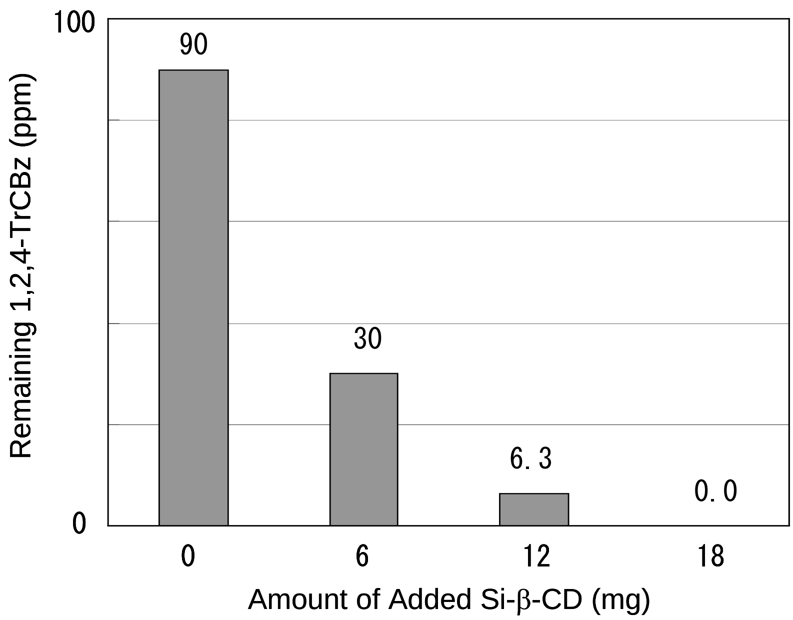


Figure 4. Relationship between the amount of 1,2,4-TrCBz remaining in insulating oil (242 mg) and the amount of added Si-β-CD. Initial concentration of 1,2,4-TrCBz was 90 ppm.

in the adsorption of chlorinated aromatics in the oil. The adsorption ability of Si-β-CD was higher than that of Bn-β-CD, indicating that the chemical modification of primary hydroxyl groups of CD is more effective in adsorbing chlorinated aromatics compared with the chemical modification of secondary hydroxyl groups. By using Si-β-CD adsorbent, PCBs such as 4,4'-DiCB were also removed from the insulating oil.

The adsorption of chlorinated aromatics in the insulating oil was monitored as a function of added Si-β-CD. Figure 4 shows the relationship between the amount of added Si-β-CD and the amount of 1,2,4-TrCBz remaining in the insulating oil. The amount of adsorbed 1,2,4-TrCBz increased with an increase in the amount of added Si-β-CD, and 1,2,4-TrCBz (90 ppm) was completely removed from the insulating oil (242 mg) upon the addition of 18 mg of Si-β-CD.

It was also found that more than 70% of adsorbed chlorinated aromatics were recovered from corresponding CD complexes by washing with non-polar organic solvents.

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