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NOTES

SELECTIVITY AND MOLECULAR SIEVING EFFECTS OF ORGANIC COMPOUNDS BY A β-CYCLODEXTRIN-PILLARED LAYERED DOUBLE HYDROXIDE

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INTRODUCTION

Much attention has been given to new families of microporous sorbents resulting from the pillaring of inorganic layered compounds, such as smectite and vermiculite, with polynuclear complex ions or bulky organic molecules (Pinnavaia 1983; Boyd et al. 1991; Cadena and Cazares 1996). Various anions have been intercalated into the interlayers of these layered compounds with molecular sieving effects noted when incorporating anions of appropriate sizes (Barrer 1978, 1989; Lee et al. 1989; Jaynes and Boyd 1990, 1991; Lagaly and Beneke 1991; Jaynes and Vance 1996). Recently, layered double hydroxides (LDHs), which are anionic clays, have also attracted considerable interest due to the unique intercalation properties of these materials (Meyn et al. 1990). With positively charged LDH structures, several anionic species have been intercalated into the gallery region of the LDHs, with the resulting intercalates used for several applications in various fields (Miyata and Kumura 1973; Cavani et al. 1991; Clearfield et al. 1991; Carrado et al. 1993; Chibwe and Pinnavaia 1993). As a result, considerable interest has been devoted in the last few years to the preparation and characterization of microporous LDH materials for potential uses in catalysis, sorption and separation technologies.

Cyclodextrins are cyclic oligosaccharides of D-glucopyranose that possess a unique structure of a nonpolar doughnut-shaped ring. The ring can trap a great variety of organic molecules the size of 1 or 2 benzene rings, or larger compounds containing a side chain of comparable size, to form inclusion complexes (Bender and Komiyama 1978; Szejtli 1982; Fenyvesi et al. 1996). Cyclodextrins are typical "host" components and are very useful as micro-encapsulating agents for stabilizing volatile or toxic organic compounds. Kijima and colleagues (1984, 1986) were among the first to report the use of cyclodextrin as a "guest" component by incorporating modified cyclodextrin into both Cu(II) montmorillonite and α-zirconium phosphate. Mondik et al. (1992) found that modified β-cyclodextrin could also be incorporated into a zeolitic structure.

In an effort to broaden the diversity of layered materials, we have investigated the pillaring reactions of LDHs with β-cyclodextrin. We developed novel intercalated compounds by incorporating carboxymethyl β-cyclodextrin into a magnesium aluminum (Mg/Al) LDH (Zhao and Vance 1997). The intercalation of cyclodextrin molecules as interlayer guest species in LDHs is important because this host-guest interaction can impart unique structural features and physicochemical properties to these materials. In addition, cyclodextrin-LDH complexes represent a new class of organic-mineral structures that may have sorption characteristics similar to those observed with organic-smectites for hydrophobic organic compounds. The present work was undertaken initially to explore the potentials of the new intercalate, β-cyclodextrin pillared LDH, as a sorbent for organic compounds.

MATERIALS AND METHODS

Magnesium-aluminum LDH ($[Mg_3Al(OH)_8]NO_3 \cdot 2H_2O$ was synthesized according to the procedures described previously (Meyn et al. 1990; Zhao and Vance 1997). Briefly, a solution of 64 g of $Mg(NO_3)_2 \cdot 6H_2O$ and 23.4 g of $Al(NO_3)_3 \cdot 9H_2O$ in 250 mL of distilled, deionized water was added dropwise to a solution of 25.0 g NaOH and 36.4 g of $NaNO_3$ in 290 mL of water

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over approximately 1 h. The mixture was held at 65 °C for 16 d. The precipitate was separated by centrifugation, dialyzed and dried at 40 °C. Carboxymethyl β-cyclodextrin (CMCD) (in sodium form) was obtained from Cerestar Company (Hammond, Indiana) and used without further purification. It has an empirical formula of $(C_{42}H_{70-n}O_{35})\cdot(CH_2COONa)_n$, an average molecular weight of 2255 and an average carboxymethyl substitution degree of 14. For brevity, it will be abbreviated as CMCD(14).

The complex of CMCD(14) and Mg/Al LDH was obtained by treating Mg/Al LDH twice at 65 °C with a 4.8 m*M* CMCD(14) solution. The products were washed extensively with water, centrifuged and dried at 40 °C. Organic carbon and X-ray diffraction (XRD) analyses were performed by using high-temperature combustion and a Scintag XDS 2000™ diffractometer with Cu*K*α radiation, respectively (Zhao and Vance 1997, 1998). The organic carbon content was 11.1% and the amount of CMCD(14) sorbed by Mg/Al LDH was calculated to be 190 mmol/kg LDH, which is close to the value obtained from our earlier sorption experiments (222 ± 13 mmol/kg LDH) (Zhao and Vance 1997).

Batch sorption isotherms were determined by weighing 100-mg samples into 25 mL Corex glass centrifuge tubes that contained 25–28 mL distilled water. Reagent grade organic compounds (Aldrich, 99+%) were added using a Hamilton microliter syringe either as the neat liquid or as a methanol-based stock solution. The concentration of organic compounds did not exceed their water solubility. After appropriate volumes of the chemicals were added, the centrifuge tubes were immediately closed with foil-lined screw caps and shaken for 24 h on a reciprocating shaker at ambient temperature (25 ± 1 °C). After centrifugation, a 10-mL aliquot of the supernatant liquid was extracted in a septum-capped, 20-mL vial with 10 mL of hexane (for trichloroethylene, tetrachloroethylene, 1,2,3-trichlorobenzene and 1,3,5-trichlorobenzene) or 10 mL of carbon disulfide (for benzene, toluene, *o*-, *m*-, *p*-xylenes, ethylbenzene and naphthalene). A portion of the hexane or carbon disulfide containing the extracted chemicals was analyzed using gas chromatography. Isotherms were constructed by plotting the amounts sorbed versus the concentrations remaining in solution. The average blank recoveries were high (>93%) and the data were not adjusted for these recoveries.

RESULTS AND DISCUSSION

The CMCD(14)-Mg/Al LDH intercalate prepared in this study exhibited the same XRD pattern as reported previously (Zhao and Vance 1997), having a *d*(003) value of 15.5 Å. In our previous study (Zhao and Vance 1997), CMCD(14) molecules were believed to adopt a loosely packed perpendicular monolayered arrangement within the Mg/Al LDH interlayers. We concluded that only half of the Mg/Al LDH interlayer space was occupied by CMCD(14) molecules, with the cyclodextrin rings stacked about 6.5 Å apart within the LDH interlayers (Zhao and Vance 1997). The complex could therefore have 2 types of micropores, the cyclodextrin cavity and the intermolecular space (Figure 1).

The sorption isotherms of trichloroethylene, tetrachloroethylene, benzene, toluene, *o*-, *m*-, *p*-xylenes, ethylbenzene, 1,2,3-trichlorobenzene, 1,3,5-trichlorobenzene and naphthalene from aqueous solution by CMCD(14)-Mg/Al LDH intercalate are presented in Figure 2. The original Mg/Al LDH sorption for the chemicals studied was found to be negligible (data not shown), due to its hydrophilicity arising from the hydroxyl groups and interlayer anion. Figure 2 indicates that all isotherms were characterized by high linearity. Therefore, the sorption coefficients (K_{iw}), corresponding to the ratio of the amount (mg/kg) of the sorbed chemical in the CMCD(3)-Mg/Al LDH intercalate to its equilibrium solution concentration (mg/L) in water, or from the slopes of the linear isotherms, were calculated and are listed in Table 1. The higher K_{iw} values correspond to a greater degree of sorption. To normalize the sorption on an organic-matter basis, organic-matter-corrected sorption coefficients (K_{om}) were calculated from the K_{iw} values, which are also listed in Table 1.

Because the entry of organic compounds into the CMCD(14)-Mg/Al LDH intercalate was believed to be a diffusion-controlled mechanism, the relationship between estimated molecular diffusion volume and the difference between log K_{om} and log K_{ow} was evaluated (Jaynes and Boyd 1991) (Figure 3). There was a general inverse relationship between log K_{om} and log K_{ow}, indicating that the sorption affinity of CMCD(14)-Mg/Al LDH for organic compounds tends to decrease with an increase of molecular diffusion volume. This suggests that molecular size/shape factors are involved in the sorption process of organic compounds by CMCD(14)-Mg/Al LDH. However, the above-mentioned relationship varied among the different organic guest compounds, despite the overall decreasing tendency in the difference between log K_{om} and log K_{ow} as a function of diffusion molecular volume (Figures 2 and 3 and Table 1). Figure 4 also shows that the sorption affinities varied among the chemicals studied. For example, with some guests, the organic-matter normalized sorption coefficients increased slightly with log K_{ow} value, while for others it decreased. The reason for this variation is explained later.

For the chlorinated compounds, the sorption affinity of CMCD(14)-Mg/Al LDH follows the decreasing order of tetrachloroethylene > 1,2,3-trichlorobenzene > trichloroethylene > 1,3,5-trichlorobenzene, while the aromatic hydrocarbons followed the order of *m*-xylene > toluene, benzene > ethylbenzene, *o*, *p*-xylene >

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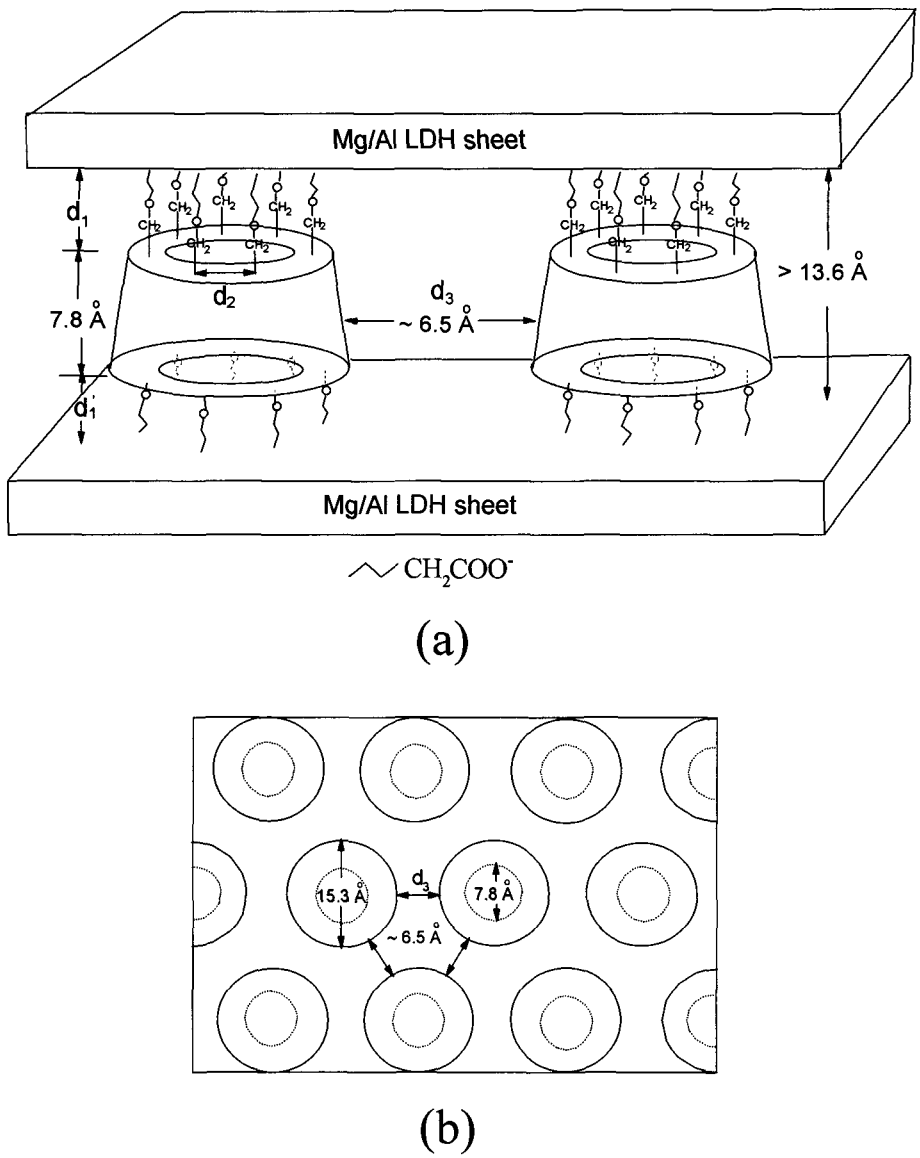


Figure 1. Schematic representation of the possible interlamellar geometry of CMCD(14) molecules within Mg/Al LDH interlayers in aqueous medium: a) side-view; b) top-view.

naphthalene (Figure 2 and Table 1). Compared to 1,2,3-trichlorobenzene, it is evident that 1,3,5-trichlorobenzene was excluded by the CMCD(14)-Mg/Al LDH, though they have the same molecular weight and volume. Although the molecular weight and diffusion volume of trichloroethylene are lower than that of trichlorobenzene, its uptake was greater than 1,3,5-trichlorobenzene and less than 1,2,3-trichlorobenzene.

A similar phenomenon was also found with the aromatic hydrocarbons. Naphthalene was sorbed the least by CMCD(14)-Mg/Al LDH, while sorption varied among xylenes and ethylbenzene, with the greatest sorption occurring with *m*-xylene, even though these guests have the same molecular weight and diffusion volume. These results indicate that sorption of organic compounds by CMCD(14)-Mg/Al LDH was related not only to the molecular size of the guest, but also to molecular shape/configuration, as well as hydrophobicities.

Numerous studies (Szejtli 1982 and references therein) have shown that low-polarity organic pollutants (including some of the organic compounds used in this study) can be encapsulated by the cavity of β-cyclodextrin or its derivatives in aqueous solution. The inclusion of hydrophobic organic compounds by the cyclodextrin cavity is presumably due to a partition

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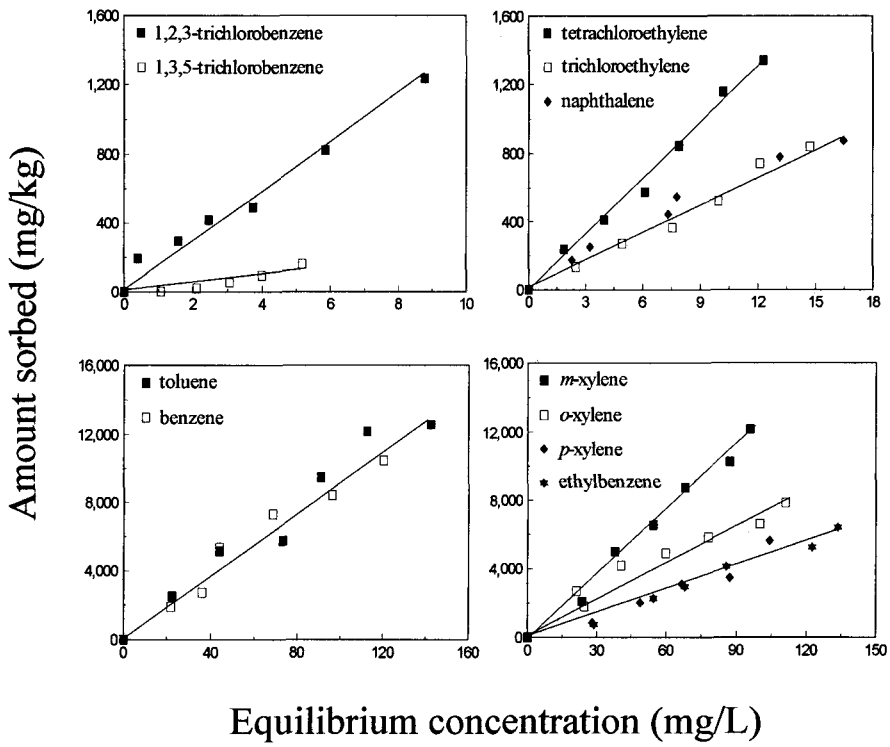


Figure 2. Isotherms for the sorption of hydrophobic organic compounds by a CMCD(14)-Mg/Al LDH intercalate.

Table 1. Selected physicochemical properties and the Log of sorption coefficient (K_{iw}) values for organic compounds sorbed on the CMCD(14)-Mg/Al LDH intercalate.

Organic compound	Aqueous solubility† (mg/L)	Critical dimensions of guest‡ Length (Å)	Breadth (Å)	Thickness (Å)	Molecular diffusion volume§ (Å³)	Log K_{ow}†	Log K_{iw}¶	Log K_{om}#
Benzene	1791	7.4 (5.6)	6.7 (4.8)	3.7	151	2.13	1.93	2.52
Trichloethylene	1155	6.7	6.5	~3.7	155	2.61	1.76	2.35
Toluene	535	8.6 (7.1)	6.7 (4.8)	4.0	184	2.73	1.96	2.55
o-Xylene	175	8.6	7.9	4.0	208	3.12	1.80	2.39
Ethylbenzene	161	10.6 (8.4)	6.7 (4.8)	4.0	208	3.15	1.68	2.27
p-Xylene	156	9.8	6.7	4.0	208	3.15	1.71	2.30
Tetrachloroethylene	150	6.7	6.5	~3.7	184	3.40	2.04	2.63
m-Xylene	146	8.6	7.9	4.0	208	3.20	2.11	2.70
Naphthalene	30	8.8 (7.3)	7.4 (5.6)	3.7	267	3.36	1.72	2.31
1,2,3-Trichlorobenzene	18	8.6	7.8	3.7	271	4.14	2.12	2.71
1,3,5-Trichlorobenzene	6	8.9	8.6	3.7	271	4.49	1.50	2.09

† The data of aqueous solubilities and log K_{ow} values were adapted from Zhao and Vance (1998) and references therein. Log K_{ow} = the Log of partition coefficient value between octanol and water.

‡ The dimensions of guest are in 3 directions at right angles. Data for benzene, toluene, *m*-xylene were adapted from Barrer (1978); the others were estimated from bond lengths and Van der Waals group and atom dimension given by Pauling (1960). Numbers in parentheses were from Jaynes and Boyd (1991).

§ Molecular diffusion volume was estimated by using Fuller's group contribution method (Lyman et al. 1981).

¶ Log K_{iw} = the Log of partition coefficient value between the CMCD(14)-Mg/Al LD intercalate and water; all isotherm data were evaluated by linear regression equation.

Log K_{om} = the Log of organic-matter-corrected sorption coefficient. $K_{om} = K_{iw}$ [100/(%OC × *f*)], where *f* equals the molecular weight of the CMCD(14) divided by the weight of C in the CMCD(14).

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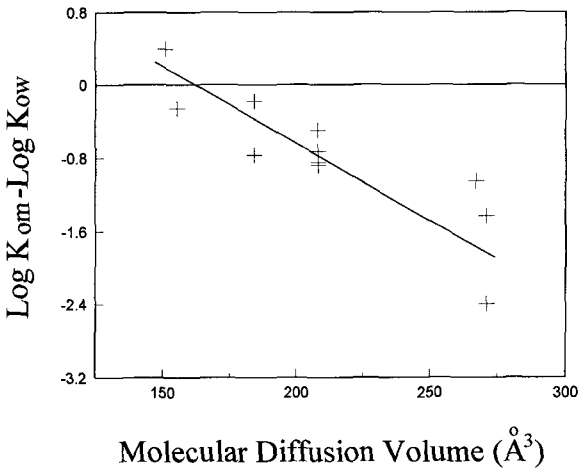


Figure 3. Relationship between molecular diffusion volume (Å^3) and the difference between log K_{om} and log K_{ow}.

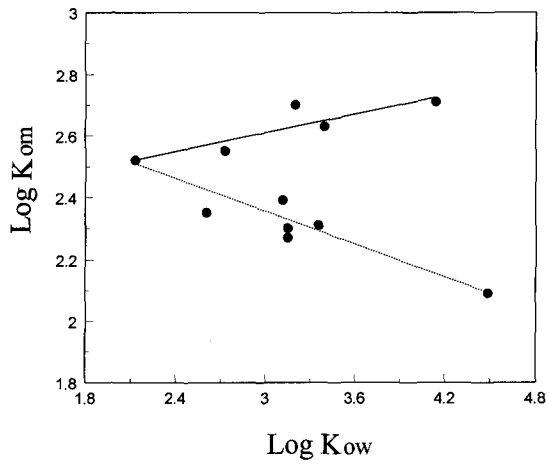


Figure 4. Relationship between log K_{om} and log K_{ow} for hydrophobic organic compounds sorbed by a CMCD(14)-Mg/Al LDH intercalate.

mechanism (Chiou et al. 1979; Wang and Brausseau 1993; Zhao and Vance 1998). A linear positive relationship was reported between the partitioning coefficients and the log K_{ow} values of relatively small organic compounds based on the study of the enhancement of aqueous solubilities of nonpolar organic chemicals by hydroxypropyl-β-cyclodextrin (HPCD) (Wang and Brausseau 1993). In our previous study (Zhao and Vance 1998), we also found that carboxymethyl β-cyclodextrin with a substitution degree of 3 [CMCD(3)] could be intercalated into Mg/Al LDH, forming either a parallel monolayer or a perpendicular bilayer arrangement between the Mg/Al LDH interlayers. The resulting CMCD(3)-Mg/Al LDH complex was also capable of retaining various nonionic, hydrophobic organic pollutants from aqueous solution. The sorption affinity of the CMCD(3)-Mg/Al LDH complex for most of the organic compounds studied was positively related to their hydrophobicities and a linear positive relationship was found between the log K_{iw} or log K_{om} (organic-matter-normalized log K_{iw}) and log K_{ow} values; however, the present study indicated both positive (points along the solid line) and negative (points along the dashed line) relationship (Figure 4). In addition, the sorption affinities of CMCD(14)-Mg/Al LDH for organic compounds were generally much lower than those obtained from HPCD and CMCD(3) (Wang and Brausseau 1993, 1995), as well as CMCD(3)-Mg/Al LDH (Zhao and Vance 1998), which were believed to be due to a contribution of the cyclodextrin cavity. This would suggest intercalation could influence the inclusion properties of CMCD(14) molecules.

A study by Lee et al. (1989) indicated that tetramethylammonium-smectite had a high degree of selectivity for aromatic compounds based on molecular size/shape, resulting in high uptake of benzene and progressively lower uptake of larger aromatic molecules from water, which followed the decreasing order of benzene > toluene > xylene ≈ ethylbenzene > dichlorobenzene > trichlorobenzene > lindane. Other studies (Jaynes and Boyd 1990, 1991; Jaynes and Vance 1996) have also indicated that molecular size/shape effects were involved in the uptake of organic compounds by organic cation-exchanged smectites. However, the selectivity and sieving characteristics observed in this study appear to be more complicated.

Factors influencing selectivity and sieving presumably stems from the geometry of the CMCD(14) molecules within Mg/Al LDH interlayer, as well as the molecular size/shape of guest. There are 2 possible sorption sites for organic molecules: one is the cyclodextrin cavity and the other is the inter-cyclodextrin micropore. With regards to the accessibility of the cyclodextrin cavity, it was found that upon wetting the basal spacing, $d(003)$, of the CMCD-Mg/Al LDH intercalate expanded from 15.5 to 18.4 Å, an increase of 2.9 Å. Assuming the CMCD(14)-Mg/Al LDH could be fully expanded in aqueous solution and the carboxymethyl group points straight to the Mg/Al LDH layer, the distance (d_1 or d'_1, $d'_1 < d_1$) between the Mg/Al LDH sheet and the cyclodextrin ring would be approximately 5 to 7 Å, while the distance (d_2) between carboxymethyl groups would be around 7.0 Å, or less if the contribution of Van der Waals radii of atoms was considered. Therefore, the cavity is lined with 14 carboxymethyl groups, with a limited area (approximately 5~7 Å by 7.0 Å) available for organic molecules to enter the cyclodextrin cavity. Judging from the dimensions of the organic compounds studied (Table 1), we can conclude that the cyclodextrin cavity would be inaccessible for most of the compounds stud-

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ied. This arrangement, to some extent, may impart a sieving effect to the intercalated complex for certain smaller organic compounds.

However, because cyclodextrins are very hydrophilic on their "rims", largely lipophilic on the remainder of their inner and outer surfaces (Lindoy 1989) and spaced approximately 6.5 Å apart (d_3), the resulting inter-cyclodextrin micropore seems more likely to be the sorption site for hydrophobic organic species than does the cyclodextrin cavity. The spatial dimension of inter-cyclodextrin micropore could impart a molecular sieving effect to the CMCD(14)-Mg/Al LDH complex for certain organic compounds, depending on their molecular shape/size.

The above results were obtained using a macroscopic method (batch sorption isotherms); therefore, it is difficult to characterize whether the organic molecules are retained in the inter-cyclodextrin micropores or in the cyclodextrin cavity. Definite explanation of the sorption sites and the relationship between molecular configuration and sorption behavior by CMCD(14)-Mg/Al LDH intercalate must await further work by using vapor phase sorption and/or spectroscopic studies.

CONCLUSIONS

A study was conducted to examine the sorptive properties of a novel organic-mineral complex [CMCD(14)-Mg/Al LDH] for hydrophobic organic molecules from aqueous medium. The CMCD(14)-Mg/Al LDH complex exhibits sieving effects for the organic guest species based on molecular size/shape factors. This selectivity appeared to result from the inter-cyclodextrin micropores, as well as the limited accessibility of the cyclodextrin cavity due to the orientation of carboxymethyl groups. Such selectivity and sieving effects may be useful in chromatographic applications. Further studies are in progress to examine possible sorption sites and mechanisms, sorption behaviors of organic compounds from the vapor phase, as well as potential use of the CMCD(14)-Mg/Al LDH complex in chromatographic applications.

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