

Molecular Inclusion Properties of Hydrophobic Organic Compounds by a Modified β -Cyclodextrin Intercalated within a Layered Double Hydroxide

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(Received: 11 June 1997; in final form: 14 October 1997)

Abstract. A study was conducted to evaluate the inclusion properties of various nonionic hydrophobic organic compounds by a novel intercalate derived from magnesium-aluminum layered double hydroxide (Mg/Al LDH) and carboxymethyl- β -cyclodextrin with a degree of substitution of 3 [CMCD(3)]. The isotherm sorption results at 25 °C showed that the CMCD(3)-Mg/Al LDH intercalate could retain all the organic compounds (trichloroethylene, tetrachloroethylene, benzene, toluene, *p*-, *o*-, *m*-xylene, ethylbenzene, 1,2,3-trichlorobenzene, naphthalene) studied and its sorption affinity for organic compounds was positively related to their hydrophobicities. The host-guest interaction was attributed to a partition process of the organic compounds into cyclodextrin cavities as well as intermolecular pores. A stereoselective interaction might also be involved due to the intercalation of CMCD(3) within Mg/Al LDH interlayers.

Key words: inclusion, sorption, partition, hydrophobic organic compounds, β -cyclodextrin, layered double hydroxide, intercalation compound.

1. Introduction

Recently, pillared layered materials have attracted widespread interest due in part to their potential utility as catalysts and molecular sieving adsorbents [1, 2]. Pillared microporous solids are generally derived from materials with ion exchange capabilities, such as 2:1 phyllosilicate clays, layered double hydroxides and zirconium phosphates [1]. Layered double hydroxides (LDHs), also known as anionic clays, are an important class of materials due to their potential technological importance as catalysts, strong ion exchangers, optical hosts, ceramic precursors and antacids [3, 4]. With positively charged LDH structures, various anionic species have been intercalated into the gallery region of LDH layers with the resulting intercalates used for several applications in various fields such as catalysis reactions and separation/adsorption technology [3–12].

Cyclodextrins are cyclic oligosaccharides of D-glucopyranose that possess a unique structure of a nonpolar doughnut-shaped ring which can accommodate different kinds of organic compounds in their cavities to form inclusion complex-

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es [13–17]. Cyclodextrins are typical *host* components and are useful as micro-encapsulating agents for stabilizing volatile or toxic organic compounds. Kijima and colleagues [18, 19] were one of the first to report cyclodextrin as a *guest* component by incorporating modified cyclodextrin into layered Cu(II) montmorillonite and into α -zirconium phosphate. Mondik et al. [20] found that modified β -cyclodextrin could also be incorporated into a zeolitic structure. In an effort to broaden the diversity of pillared materials, we have investigated the pillaring reactions of LDHs with β -cyclodextrin [21] and found that carboxymethyl- β -cyclodextrin (CMCD) could be intercalated within a magnesium-aluminum layered double hydroxide (Mg/Al LDH). The intercalation of cyclodextrin molecules as interlayer guest species in LDHs is important because this host-guest interaction imparts unique structural features and physicochemical properties. Cyclodextrin-LDH complexes represent a new class of organic-minerals that might have sorption characteristics equally important to those observed with organic-smectites for organic compounds.

The main purpose of this study was to examine the molecular inclusion behavior of the novel intercalate, CMCD(3)-Mg/Al LDH, for various nonionic, hydrophobic organic compounds from aqueous solution and to determine how CMCD(3)-Mg/Al LDH may be useful for various practical applications.

2. Experimental

2.1. REAGENTS

Reagent grade, hydrated metal nitrates and ten organic compounds (trichloroethylene, tetrachloroethylene, benzene, toluene, *p*-, *o*-, *m*-xylene, ethylbenzene, 1,2,3-trichlorobenzene, naphthalene) were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used as received. Carboxymethyl- β -cyclodextrin (CMCD) (in sodium salt form) was obtained from Cerestar Company (Hammond, IN) 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 1375, and an average degree of carboxymethyl substitution (*n*) of 3.

2.2. PREPARATION OF CMCD(3)-Mg/Al LDH COMPLEX

Mg/Al LDH ($[Mg_3Al(OH)_8]NO_3 \cdot 2H_2O$) was synthesized according to the procedure described previously [3, 21]. Studies indicated that pillaring was difficult to achieve at 25 °C, therefore, the CMCD(3)-Mg/Al LDH intercalate used in this study was obtained by treating Mg/Al LDH twice at 65 °C using a 6.95 mM (4,000 mg/L C) CMCD(3) solution. The resulting products (CMCD-Mg/Al LDH) were then washed with water extensively, centrifuged and dried at 40 °C. Organic carbon analysis was performed in triplicate on the final product using high temperature combustion.

2.3. SORPTION OF HYDROPHOBIC ORGANIC COMPOUNDS

Sorption isotherms were determined for aqueous solutions of organic compounds by using a batch equilibration technique, with experiments conducted at ambient temperature (22 ± 1 °C). To determine the sorptive capacity of CMCD(3)-Mg/Al LDH, 100 mg samples were weighed into 25 mL Corex glass centrifuge tubes with Teflon-lined screw-caps, and enough distilled water added leaving a minimum headspace to avoid the loss of solutes by evaporation. Organic compounds were added either directly as a neat liquid or in methanol stock solutions using a Hamilton microliter syringe. The concentration of organic compounds did not exceed their water solubilities. After appropriate volumes of the chemicals were added, the centrifuge tubes were immediately closed with foil-lined screw caps to minimize vaporization, and then shaken for 24 h on a reciprocating shaker. After shaking, the tubes were centrifuged for 30 min at 9,000 rpm to separate the liquid and solid phases. The supernatant liquid (5–10 mL) was then transferred into a glass vial containing 10–15 mL of hexane (for trichloroethylene, tetrachloroethylene and 1,2,3-trichlorobenzene) or carbon disulfide (for benzene, toluene, xylenes, ethylbenzene and naphthalene). The vials were closed and shaken vigorously for 1 h on a reciprocating shaker. An aliquot of the hexane or carbon disulfide layer was then removed for gas chromatography (GC) analysis. Isotherms were constructed by plotting the amounts sorbed versus the concentrations remaining in solution. The amount sorbed was calculated from the difference between the quantity of compound added and the quantity in the equilibrium solution.

To ensure the quality of the data, “blanks” were prepared and handled in parallel with the studies discussed above. The average solute recovery percentages were high (>93%) and the data were not adjusted for these recoveries.

2.4. INSTRUMENTATION

Organic compounds extracted by hexane or carbon disulfide were quantified using a Hewlett Packard 5980 series II gas chromatograph (GC) equipped with both electron capture and flame ionization detectors. A Hewlett Packard HP-5 capillary column with He as the carrier gas was used for all separations. Sample peak areas were quantified by reference to a linear regression analysis of peak areas determined on standards that were included in each run.

X-ray diffraction (XRD) analyses were conducted as described previously [21] using a Scintag XDS 2000 diffractometer with Cu-K α radiation. Thermal gravimetric analyses (TGA) were performed using a Dupont TGA 2950 analyzer. For the TGA analysis, samples were heated to 500 °C at a heating rate of 5 °C/min.

3. Results and Discussion

3.1. CHARACTERIZATION OF CMCD(3)-Mg/Al LDH COMPLEX

The CMCD(3)-Mg/Al LDH intercalate exhibited the same X-ray diffraction pattern as reported previously [21], having a d_{003} value of 20.63 Å. In our previous study, we proposed that the intercalated CMCD(3) molecules, (i) were attached to the Mg/Al LDH layers through their carboxymethyl groups, (ii) could adopt either a parallel monolayer or a perpendicular-bilayer arrangement (Figure 1) and (iii) were loosely packed within the Mg/Al LDH interlayer, accounting for only half of the Mg/Al LDH interlayer space [21]. Presumably, the parallel monolayer geometry would make the CMCD cavities more accessible to target molecules than would the perpendicular-bilayer arrangement. However, upon wetting, it was found that the basal spacing (d_{003}) of the CMCD-Mg/Al LDH intercalate expanded from 20.63 Å up to 26.80 Å, an increase of 6.17 Å. Considering the dimension of the β -cyclodextrin, which has an approximate torus thickness of 7.8 Å, an outer diameter of 15.3 Å and an inner diameter of 7.8 Å [14], in aqueous solution, the perpendicular-bilayer arrangement would also be accessible to certain guest species of appropriate size/shape, attributable to the further expandability of the CMCD(3)-Mg/Al LDH intercalate.

The CMCD(3)-Mg/Al LDH prepared in this study has an organic carbon content of 15.05%. The amount of CMCD(3) retained by Mg/Al LDH was calculated to be 416 mmol/kg LDH, very close to the value (415 ± 24 mmol/kg LDH) obtained from our previous research [21]. Figure 2 represents the thermal gravimetric analysis (TGA) curves obtained with the parent CMCD(3) and Mg/Al LDH and the resulting CMCD(3)-Mg/Al LDH complex. By derivation of the TGA data, it is possible to distinguish different temperature ranges corresponding to different reaction steps. The parent CMCD(3) compound exhibited two mass loss events. The first event (≈ 46 °C) was attributed to loss of cavity water molecules, and the second sharp event (≈ 264 °C, difference of 36 °C against pure β -cyclodextrin) was due to the melting of CMCD(3) molecules accompanied by decomposition. As observed previously [4, 22], pristine Mg/Al LDH exhibited three weight loss stages, the first (≈ 100 °C) and second (≈ 230 °C) were attributed to both surface adsorbed water and interlayer water molecules [4], the third (300–500 °C) was due to dehydroxylation and the elimination of anions resulting in the breakdown of the layered structure [22]. The intercalation of CMCD(3) increased the weight loss compared to pristine Mg/Al LDH. It was also observed that the second weight loss for pure Mg/Al LDH disappeared as a result of CMCD(3) intercalation. The CMCD(3)-Mg/Al LDH intercalate exhibited two stages of weight loss, the first (≈ 70 °C) due to both Mg/Al LDH interlayer water and CMCD(3) cavity water molecules, the second (≈ 280 °C) due to the decomposition of CMCD(3) molecules together with the breakdown of the Mg/Al LDH layer structure. As compared to the parent CMCD(3) and Mg/Al LDH materials, the second weight loss of CMCD(3)-Mg/Al LDH was more gradual and shifted slightly to higher temperatures, and the

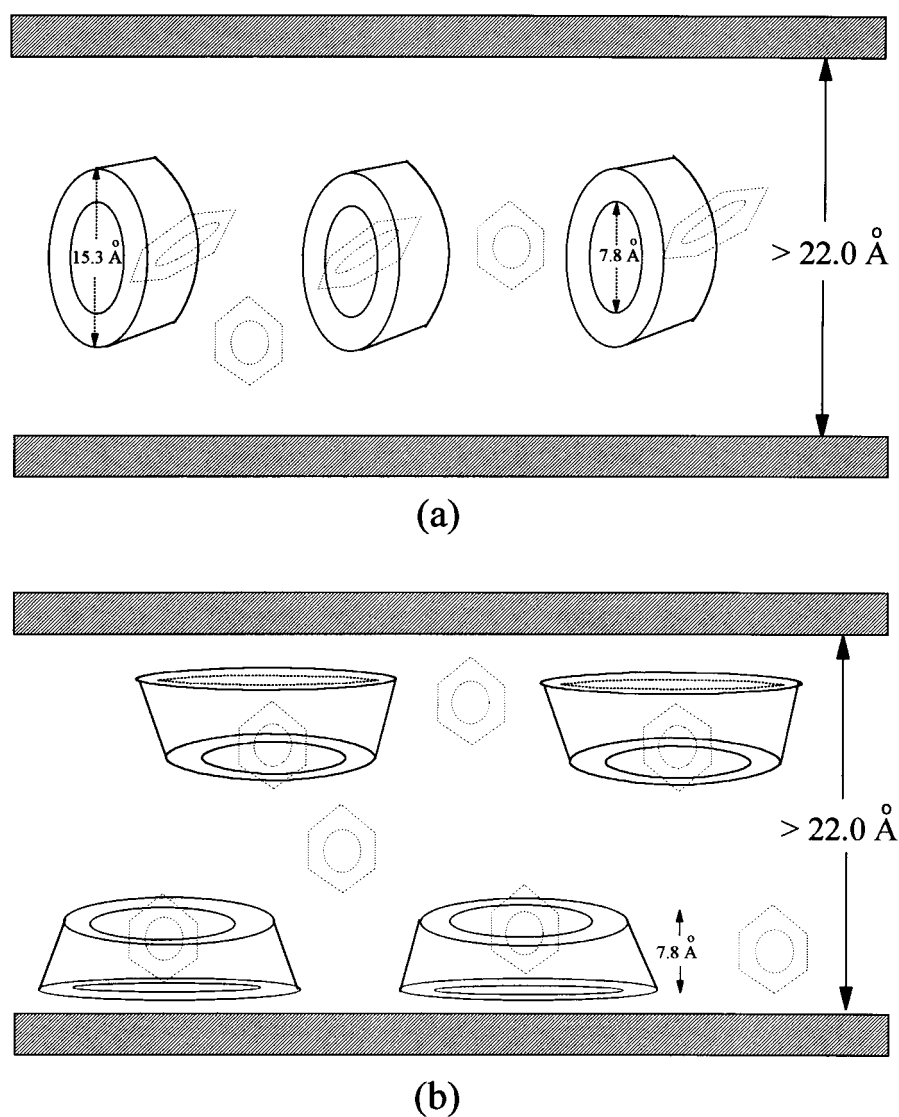


Figure 1. Schematic representation of guest inclusion towards the CMCD(3)-Mg/Al LDH intercalate in aqueous solution: (a) an expanded parallel-monolayer arrangement and (b) an expanded perpendicular-bilayer arrangement.

intercalated CMCD(3) molecules began to decompose around 289 °C, indicating there was enhanced thermal stability of intercalated CMCD(3) molecules within Mg/Al LDH interlayers.

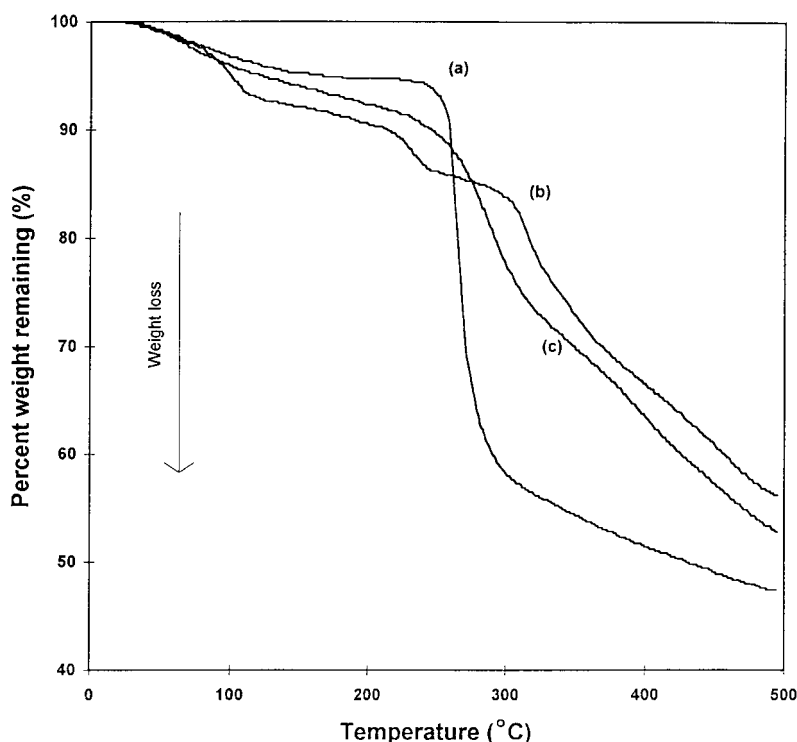


Figure 2. Thermal gravimetric analysis (TGA) curves for: (a) CMCD(3), (b) Mg/Al LDH and (c) the CMCD(3)-Mg/Al LDH intercalate.

3.2. INCLUSION COMPLEXATION OF ORGANIC COMPOUNDS

Cyclodextrins are typical “host” molecules that can trap a great variety of molecules having the size of one or two benzene rings, or even larger compounds possessing side chains of comparable size, to form inclusion complexes [14]. The size of the β -cyclodextrin cavity has been reported to be 346 \AA^3 [14], therefore, the prerequisite for solutes to enter the cavity is that their molecular volume must be smaller than the cavity volume. Wang and Brusseau [15] represented the molecular volumes of solutes using their diffusion volume, because the entry of solutes into the cyclodextrin cavity is considered a diffusion-controlled mechanism. Using the same method [15], the molecular diffusion volumes (\AA^3) of the 10 organic compounds used in the present study were calculated and are listed in Table I. Comparing the molecular volumes of the compounds studied to that of the cyclodextrin cavity, we expected that all the compounds studied could enter β -cyclodextrin if the intercalation reaction has little steric hindrance on the accessibility of their cavities. As far as we know, most of the organic compounds used in this study have been found to be able to form complexes in solution with β -cyclodextrin and its derivatives [14–16], while no published data are available for 1,2,3-trichlorobenzene.

Table I. Physical and chemical properties of organic compounds and the CMCD(3)-Mg/Al LDH intercalate.

Compound	Solubility (mg/L)	Molecular diffusion volume \AA^3	Log K_{ow} *	Log K_{iw} #	Log K_{om} §	Log K_{cc} §§
Benzene	1791	151	2.13	1.93	2.39	2.35
Trichloroethylene	1155 ^a	155	2.61 ^b	2.19	2.65	2.61
Toluene	535	184	2.73	2.18	2.64	2.60
<i>o</i> -Xylene	175	208	3.12	2.29	2.75	2.71
Ethylbenzene	161	208	3.15	2.35	2.81	2.77
<i>p</i> -Xylene	156	208	3.15	2.18	2.64	2.60
Tetrachloroethylene	150	184	3.40	2.43	2.89	2.85
<i>m</i> -Xylene	146	208	3.20	2.06	2.52	2.48
Naphthalene	30.0	267	3.36 ^c	2.56	3.02	2.98
1,2,3-Trichlorobenzene	18.0 ^d	271	4.14 ^d	2.84	3.30	3.26

* K_{ow} = partition coefficient between octanol and water.

K_{iw} = partition coefficient between the CMCD(3)-Mg/Al LDH intercalate and water.

§ K_{om} = organic-matter-normalized partition coefficients, $K_{om} = K_{iw} [100/(\%OC \times f)]$, where f equals the molecular weight of the CMCD(3) divided by the weight of C in the CMCD(3).

§§ K_{cc} = normalized to cavity carbon atom content of CMCD(3), $K_{cc} = K_{iw}/0.379$.

^a Verschueren [32].

^b Rutherford and Chiou [33].

^c Hansch and Leo [34].

^d Chiou [35] and Chiou et al. [36].

Remaining solubility and log K_{ow} values are from Howard [37].

Because cyclodextrins are very hydrophilic on their “rims”, largely lipophilic on the remainder of their inner and outer surfaces [23], and the intercalated cyclodextrin packed loosely within the Mg/Al LDH interlayer, we may expect that the inter-cyclodextrin micropores would be another potential sorption site. However, this kind of intermolecular space would presumably be less attractive for hydrophobic organic compounds as compared to the cyclodextrin cavity, because the former would be more hydrophilic than the latter due to its expandability in aqueous medium and the hydrophilicity of the Mg/Al LDH interlayers.

Sorption isotherms for all 10 organic compounds with CMCD(3)-Mg/Al LDH intercalates at 25 °C are shown in Figure 3. Figure 3 indicated all isotherms were characterized by high linearity, suggesting a partitioning process contributed to the sorption [24]. Besides, the sorption results also indicated that parent Mg/Al LDH had very little affinity for the organic compounds studied (data not shown here), presumably due to the hydrophilicity of the Mg/Al LDH.

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 I. The higher K_{iw} values correspond to a

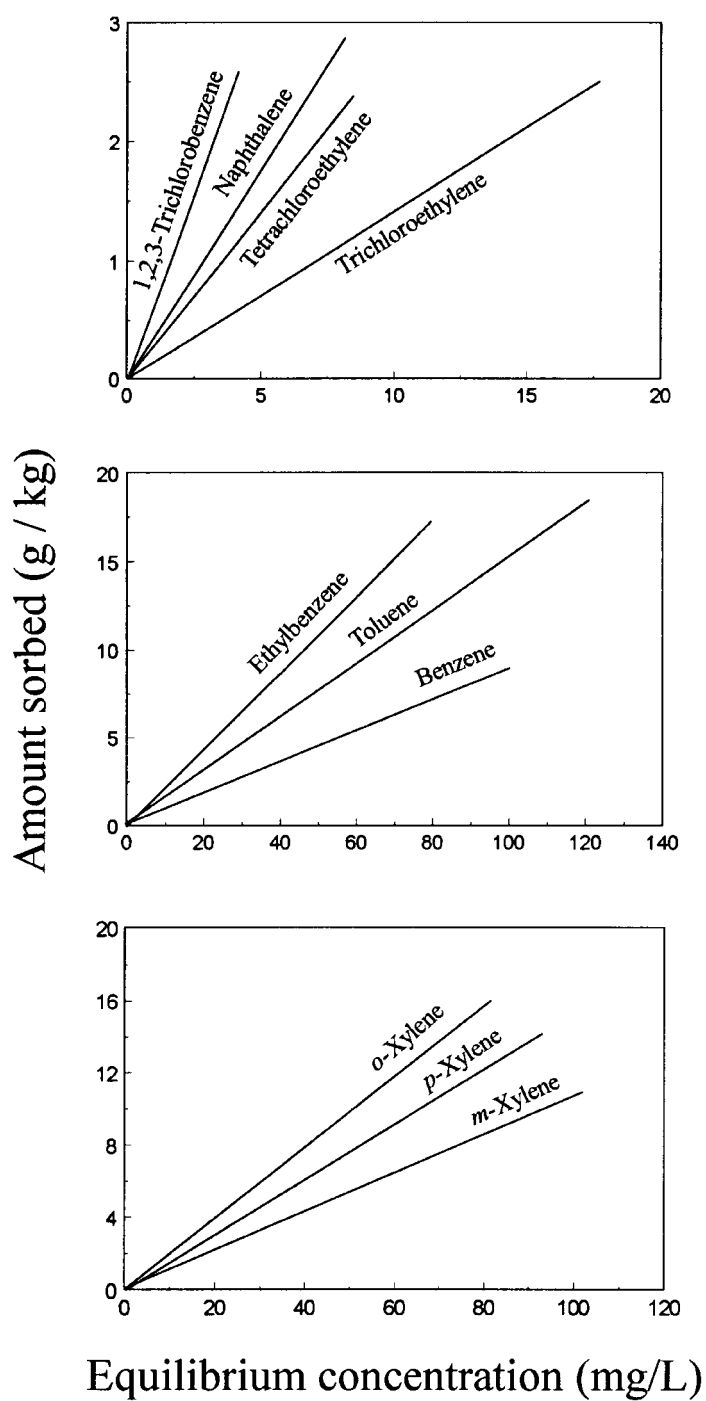


Figure 3. Isotherms for the sorption of hydrophobic organic compounds at 25 °C by the CMCD(3)-Mg/Al LDH intercalate. All isotherms had regression coefficients (R^2) greater than 0.97.

higher degree of sorption. Because of the high linearity of the sorption isotherms, an effort was made to normalize the K_{iw} values according to the organic matter content and the organic-matter-normalized $\log K_{iw}$ (designated as $\log K_{om}$) are shown in Table I. Except for trichloroethylene and benzene, $\log K_{om}$ values are all smaller than the corresponding logarithm of the octanol/water partition coefficient (K_{ow}) values. This result is due in part to the fact that the glycosidic oxygen bridge gives the cyclodextrin cavity a polarity that is about the same as that of ethanol [15, 25]. This polarity causes the cyclodextrin cavity to have a lower capability for partitioning in comparison to ordinary organic solvents such as octanol, which results in lower sorption of some hydrophobic organic compounds [15]. However, for trichloroethylene and benzene, which have slightly higher $\log K_{om}$ values than $\log K_{ow}$ values, intermolecular retention was considered possible due to their relatively high aqueous solubilities. At an equilibrium concentration of 99.8 mg/L, the amount of benzene sorbed by CMCD(3)-Mg/Al LDH is 8.88 g/kg (Figure 3). If we take the guest molecule/cyclodextrin ratio of 0.2 for benzene [14], this value is nearly twice as much as the maximum sorption capacity (4.13 g/kg) which is estimated from the amount of CMCD(3). On the other hand, an additional one-point sorption at higher concentrations indicated that the amount of benzene sorbed by the CMCD(3)-Mg/Al LDH intercalate was 37.5g/kg at an equilibrium concentration of 833mg/L. Considering cyclodextrins usually form 1:1 inclusion complexes with guests in solution [14], the maximum sorption capacity is calculated to be 20.6 g/kg, less than 37.5 g/kg. This suggests that intermolecular space may contribute to the sorption of benzene (and, by inference, trichloroethylene). Kijima [26] has studied the inclusion behavior of benzoic acid towards intercalates of α - and γ -zirconium hydrogen phosphates with mono[6-(2-aminopropylamino)-6-deoxy]- β -cyclodextrin (Cdpn) and found that both intercalates sorbed benzoic acid by forming an inclusion complex with benzoic acid molecules embedded inside and outside the Cdpn cavity.

If we assume that the cyclodextrin cavity is the only sorption site, then only the cavity carbons make a contribution to the retention of organic compounds. A similar effort [15] was thus carried out to normalize the K_{iw} values according to the mass fraction of cavity carbon atoms, which is about 0.379 for CMCD(3), and the normalized $\log K_{iw}$ values (designated as $\log K_{cc}$) are also shown in Table I. It should be noted that $\log K_{om}$ values are very close to $\log K_{cc}$ values. In solution, CMCD(3) was found to be able to solubilize several low-polarity organic pollutants [16]. Based on the data curve of the reference [16], $\log K_{cc}$ was estimated to be around 3.13 for 1,2,3-trichlorobenzene, which is comparable to the $\log K_{cc}$ value obtained in this study. Since the estimated $\log K_{cc}$ value was based on the formation of a 1:1 inclusion complex, this comparability, to some extent, suggests that the intercalated cyclodextrin cavities act as sorption sites for organic compounds by forming 1:1 inclusion complexes. Therefore, it is assumed that, within the concentration range of this study, the cyclodextrin cavities may be the dominant sorption sites for organic compounds of relatively higher hydrophobicity.

A plot of $\log K_{om}$ versus $\log K_{ow}$ is shown in Figure 4, which reveals that, except for *p*-xylene and *m*-xylene, $\log K_{om}$ values are linearly proportional to $\log K_{ow}$ values ($\log K_{om} = 0.444 \log K_{ow} + 1.44$, $R^2 = 0.960$). This indicates uptake of hydrophobic organic compounds by the CMCD(3)-Mg/Al LDH intercalate is positively related to their hydrophobicities. A linear relationship could also be observed between $\log K_{iw}$ and $\log K_{ow}$. Wang and Brusseau [15] reported a similar linear equation between $\log K_{iw}$ and $\log K_{ow}$ in their studies of the enhancement of the apparent aqueous solubilities of low-polarity organic compounds by hydroxypropyl- β -cyclodextrin. The apparent correlation between K_{om} and K_{ow} supports the assumption that sorption is due to a partition process [24]. The deviation of *p*-xylene and *m*-xylene from the linear relationship is due, in addition to partitioning, to stereoselective or molecular size/shape effects that are also involved in the uptake of these organic compounds. The steric hindrance resulted in a lower affinity of the CMCD(3)-Mg/Al LDH intercalate for both *p*-xylene and *m*-xylene.

The theoretical estimation of thermodynamic parameters has suggested that van der Waals, dipole-dipole, hydrogen bonding, London, and hydrophobic forces cooperatively contribute to cyclodextrin-guest interactions [14, 26]. Previous studies indicated that hydrophobic interaction was the dominant mechanism in the complexation process of β -cyclodextrin with organic compounds [15, 27, 28]. The results reported in this study also indicated that the hydrophobic characteristics of the CMCD(3)-Mg/Al LDH and organic compounds contribute to their interaction.

The CMCD(3)-Mg/Al LDH complex can also be considered as a new type of organic-mineral complex. Thus, it would be of interest to contrast the sorption behavior of CMCD(3)-Mg/Al LDH with the more extensively studied conventional organic-clays, such as those with soils and montmorillonite. The $\log K_{iw}$ and $\log K_{om}$ values of most of the organic compounds used in this study were larger than those obtained from cyclododecyltrimethylammonium-smectites, but smaller than hexadecyltrimethylammonium-smectites [29–31], indicating there are differences between CMCD(3)-Mg/Al LDH and organo-clays for hydrophobic organic compounds.

In aqueous solutions, CMCD(3) was found to simultaneously increase the apparent aqueous solubilities of selected low-polarity organic compounds and complex with heavy metals [16]. The intercalation of CMCD(3) into Mg/Al LDH interlayers would make the cyclodextrin cavity less accessible to target molecules in comparison to that in free aqueous solutions. However, this study showed that the intercalated CMCD(3) molecules were still accessible to guest species, suggesting the potential usefulness of the CMCD(3)-Mg/Al LDH intercalate in extracting hydrophobic organic compounds from water, as well as for use in chromatographic applications. The inclusion characteristics of hydrophobic organic compounds by CMCD(3)-Mg/Al LDH suggested that CMCD(3) molecules probably formed a staggered perpendicular bilayer coverage within the Mg/Al LDH interlayers.

The above results were obtained using a macroscopic method (i.e., sorption isotherms), therefore, it is difficult to characterize the relative contribution of the

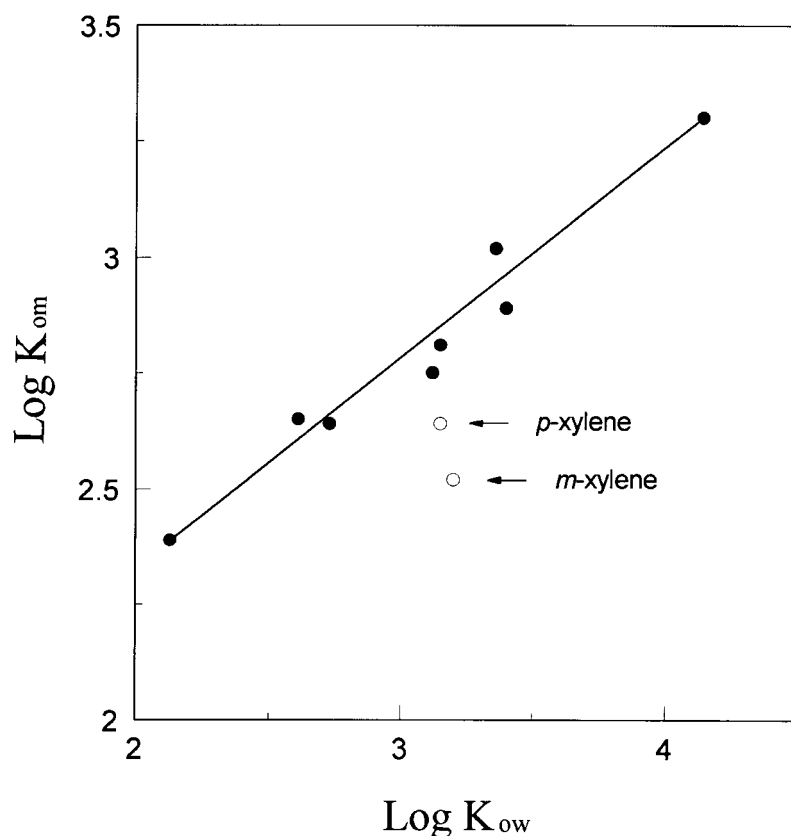


Figure 4. Linear relationship between $\log K_{om}$ and $\log K_{ow}$ for organic compounds, trichloroethylene, tetrachloroethylene, benzene, toluene, *o*-xylene, ethylbenzene, 1,2,3-trichlorobenzene and naphthalene, sorbed by CMCD(3)-Mg/Al LDH. Both *m*- and *p*-xylene were not included in determining the linear relationship.

cyclodextrin cavity and the inter-cyclodextrin micropore. Definitive explanation of the sorption sites, the contribution of the intermolecular space and the resolution of the structural arrangement must await further work by using other molecular scale techniques.

4. Conclusions

CMCD(3) was intercalated at 65 °C 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 intercalate could be further expanded in aqueous solution and was capable of retaining various nonionic, hydrophobic organic pollutants (trichloroethylene, tetrachloroethylene, benzene, toluene, *o*-, *p*-, *m*-xylenes, ethylbenzene, naphthalene and 1,2,3-trichlorobenzene) from aqueous solution. The sorption affinity of the CMCD(3)-Mg/Al LDH intercalate for organic

compounds was positively related to their hydrophobicities. The host-guest interaction was attributed to a partition process of the hydrophobic organic compounds into the cyclodextrin cavities; however, the intermolecular spaces might also be a potential sorption site. Molecular size/shape effects are assumed to be involved in the uptake of *p*-xylene and *m*-xylene, probably due to steric hindrance arising from the intercalation reaction. The novel CMCD(3)/Mg-Al LDH complexes may be useful for removing hydrophobic organic compounds from water, as well as for the development of new chromatographic applications.

Acknowledgements

This work was supported by a student research grant from the Clay Minerals Society to H. Zhao and a multidisciplinary grant from the U.S. Air Force (93-NA-187). We wish to thank American Cerestar Company (Hammond, IN) for generously supplying the cyclodextrin materials and Mark Sanderson, Western Research Institute, University of Wyoming for technical assistance with TGA analysis.

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