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Intercalation of carboxymethyl-β-cyclodextrin into magnesium–aluminum layered double hydroxide†

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New intercalated compounds have been prepared by incorporating carboxymethyl-β-cyclodextrin (CMCD) into magnesium–aluminum layered double hydroxide (Mg/Al LDH). The sorptive uptake of CMCD(3) and CMCD(14), with a degree of carboxymethyl substitution of 3 and 14, respectively, by Mg/Al LDH was examined at 65 °C, and the resulting complexes were characterized using X-ray diffraction (XRD) and FT-IR spectroscopy. Results indicated that Mg/Al LDH retained approximately twice as much CMCD(3) as compared to CMCD(14). Results of XRD and FT-IR spectroscopy confirmed that both CMCD(14) and CMCD(3) could be intercalated into Mg/Al LDH interlayers due to an ion-exchange process. After exposure to CMCD(14) and CMCD(3), the *d*-spacing of Mg/Al LDH expanded from 8.74 to 15.48 and 20.63 Å, respectively. Intercalated CMCD(14) molecules formed monolayer coverage in the Mg/Al LDH interlayers, with the cavity axis perpendicular to the LDH layer, while CMCD(3) molecules adopted either a parallel-monolayered arrangement or a perpendicular-bilayer-like coverage. Both CMCD(14) and CMCD(3) molecules were believed to be loosely packed within the Mg/Al LDH interlayers.

Layered double hydroxides (LDHs), also known as anionic clays, are an important class of materials currently receiving considerable attention in view of their potential technological importance as catalysts, ion exchangers, optical hosts, ceramic precursors and antacids.[1] They are considered antitypes of 2/1 clay minerals (three-layered clay minerals) and consist of positively charged metal oxide/hydroxide sheets with intercalated anions and water molecules. At present, they are the only layered materials with positively charged layers, in contrast to a large variety of materials with negative layers. They have considerably higher ion-exchange capacities than do smectitic clays. The general chemical composition of LDHs is:[1] $[M_{1-x}M^{III}_{x}(OH)_2]^{\xi+}X^{n-}_{\xi/n}\cdot zH_2O$, where M can be Li^+ or one of several divalent cations (Ca^{2+}, Mg^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+} or Cu^{2+}), M^{III} is a trivalent cation (Al^{3+}, Cr^{3+}, Co^{3+}, Ni^{3+}, Mn^{3+} or Fe^{3+}), and X is an interlayer anion (*e.g.*, Cl^-, NO_3^-, ClO_4^-, CO_3^{2-}, SO_4^{2-}, or other inorganic anion). The interlayer charge is $\xi = x$ for M = divalent cations and $\xi = 2x - 1$ for M = monovalent cations. The $M^2 : M^{3+}$ ratio is usually between 1 and 5.

With positively charged LDH structures, several anionic species have been intercalated into the gallery region of LDH layers, with the resulting intercalates used for several applications in various fields. These include anionic surfactants, metallophthalocyanine tetrasulfonates, and silicate anions,[1–4] as well as large polyoxometalates[5–8] and various organic acids and polymers.[9–12]

Cyclodextrins are cyclic oligosaccharides of D-glucopyranose that possess a unique non-polar cylindrical cavity. They 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 a side chain of comparable size, to form crystalline inclusion complexes.[13] Cyclodextrins and their derivatives are very useful as micro-encapsulating agents for stabilizing volatile or toxic organic compounds. These compounds have found prospective applications in the food industry, pharmaceutical industry, production of organic chemicals, agriculture, cosmetics, tobacco industry, environmental protection, and in various other fields.[13–15] Modified β-cyclodextrins have been incorporated into montmorillonite,[16–19] α- and γ-zirconium phosphates,[20–22] as well as zeolitic structures.[23] However, to our knowledge, no information is currently available on the intercalation of cyclodextrins into LDH structures. Because carboxymethyl-β-cyclodextrin (CMCD) (in the form of a sodium salt) is a derivative of β-cyclodextrin and could easily disassociate into its negatively-charged species, we hypothesize that CMCD molecules may be sorbed into the interlayers of LDH structures. The inclusion of cyclodextrin molecules as interlayer guest species in LDHs would appear to be intriguing because the host–guest interaction could impart unique structural features and physicochemical properties to the complex. Cyclodextrin–LDH complexes would also appear to be a novel use of LDHs as well as cyclodextrin molecules.

The objective of this study was, therefore, to develop a novel family of inclusion compounds by examining the uptake and intercalation properties of carboxymethyl-β-cyclodextrin by magnesium aluminum hydroxide (Mg/Al LDH), and to explore potential uses of LDHs and cyclodextrins in catalysis reactions and in adsorption technology.

Experimental

Preparation of layered double hydroxide

Magnesium–aluminum layered double hydroxide with an ideal formula[1] of $[Mg_3Al(OH)_8]NO_3\cdot 2H_2O$ was selected for our intercalation studies. Nitrate was used as the charge balancing anion because carbonate anions are often difficult to exchange in Mg/Al, Ca/Al and Ni/Al hydroxides.[1,24]

The Mg/Al LDH was prepared by a procedure similar to that described by Meyn *et al.*[1] A solution of $Mg(NO_3)_2\cdot 6H_2O$ (64 g, 0.250 mol) and $Al(NO_3)_3\cdot 9H_2O$ (23.4 g, 0.125 mol) in distilled, deionized water (250 cm^3) was added dropwise over 1 h to a solution of NaOH (25.0 g, 0.62 mol) and $NaNO_3$ (36.4 g, 0.42 mol) in water (290 cm^3). The mixture was held at 65 °C for 16 d. The precipitate was separated by centrifugation, dialysed and dried at 40 °C.

Reagents

Reagent grade, hydrated metal nitrates were purchased from Aldrich (Milwaukee, WI) or Sigma (St. Louis, MO) and used as

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† *Non-SI unit employed*: M = mol dm^{-3}.

received. Carboxymethyl-β-cyclodextrins (CMCDs) with different substitution degrees (3 and 14) were generously supplied by the American Cerestar Company (Hammond, IN) and used without further purification. The CMCD has an empirical formula of $(C_{42}H_{70-n}O_{35})\cdot(CH_2COONa)_n$. The average degree of carboxymethyl substitution (n) is 3 for CMCD(3) and 14 for CMCD(14). The average molecular weight for CMCD(3) and CMCD(14) is 1375 and 2255, respectively.

Sorption/desorption isotherms

Isotherm sorption experiments were conducted using the batch method. The LDHs (100 mg) were weighed into screw-top Corex glass centrifuge tubes that were filled with aqueous CMCD solutions (25 cm^3) with concentrations ranging from 5.95×10^{-2} to 3.57 mM for CMCD(14) and from 5.95×10^{-2} to 12.2 mM for CMCD(3). The suspensions were shaken intermittently at 65 °C for 24 h, centrifuged, and the cyclodextrin concentrations in the supernatant solutions measured using a Shimadzu TOC-5000 (Total Organic Carbon) Analyzer. Two sets of the adsorption experiments were carried out simultaneously. After centrifugation, one set was used for desorption studies to examine the reversibility of cyclodextrin sorption, and the other one was washed with water extensively, centrifuged, and dried at 40 °C for X-ray diffraction (XRD) and FT-IR analysis.

The desorption studies were conducted using the dilution method as follows: after the sorption experiments, some of the equilibrated cyclodextrin solution (10–20 cm^3) was removed and distilled, deionized water (10–20 cm^3) added. Samples were shaken intermittently for 24 h at 65 °C, centrifuged, and the supernatant analysed for cyclodextrin. The desorption procedure was completed three times for each sample.

Instrumental and analytical

X-Ray diffraction patterns were obtained using a Scintag XDS 2000^{TM} diffractometer, with Cu-Kα radiation (40 kV and 30 mV) and a scanning rate of 1° min^{-1}. Sample slides were prepared by pipetting the CMCD–Mg/Al LDH complex suspensions onto glass slides, which were dried at 40 °C for 24 h before analysis. Infrared spectra were obtained by using the KBr disc (1–2% w/w) method and a Michelson Series FT-IR spectrometer with 2 cm^{-1} resolution and 35 scans.

Results

Isotherm sorption

The sorption isotherms of carboxymethyl-β-cyclodextrin by Mg/Al LDH are shown in Fig. 1, which indicates Mg/Al LDH has a stronger affinity for CMCD(3) than CMCD(14). The average maximum sorption capacity (calculated from the sorption plateau) for CMCD(3) was 415 ± 24 mmol kg^{-1} ($n = 4$), and 222 ± 13 mmol kg^{-1} ($n = 5$) for CMCD(14), indicating that Mg/Al LDH could sorb approximately twice as much CMCD(3) as compared to CMCD(14).

Desorption experiments indicated that 12.1 ± 5.5% ($n = 4$) of the CMCD(14) retained by Mg/Al LDH was desorbed at the lower concentration range, while no desorption was observed for samples with maximum sorption. This, to some extent, suggests there was intercalation of CMCD(14) into the Mg/Al LDH interlayers. Similar desorption tendencies were also found for CMCD(3).

X-Ray diffraction

The X-ray diffraction patterns of the original Mg/Al LDH, its complexes with CMCD(14) (obtained at 3.57 mM solution at 65 °C) and with CMCD(3) (obtained at 12.2 mM solution at 65 °C) are shown in Fig. 2. The original Mg/Al LDH exhibited XRD patterns similar to those reported previously,[25,26] with an interlayer spacing (d_{003}) of 8.74 Å; however, Meyn *et al.*[1] reported a basal spacing of 7.4 Å. In addition, the original Mg/Al LDH contained a small amount of particles with lower interlayer spacings of 7.57 Å [Fig. 2(*a*)]. The Mg/Al LDH had greater basal spacings, as compared with the values observed for halogen ($Cl^- = 7.85$, $Br^- = 7.95$ Å) and carbonate-containing (7.65 Å) LDHs.[26,27] Presumably, the monovalent NO_3^- occupies a space corresponding to three oxygens and is greater than that occupied by other anions such as Cl^- and Br^-.[26] Nitrate was apparently forced to adopt an arrangement that favoured the closest possible packing. This can lead to strong repulsion inside the interlayer region when the concentration of nitrate increases. Consequently, the LDH exchanged with nitrate had a higher basal spacing value,[26] which would presumably favour the CMCD incorporation. The original Mg/Al LDH also had a peak at 4.82 Å, which was interpreted as an indication of some degree of cation ordering in Mg/Al LDH.[28]

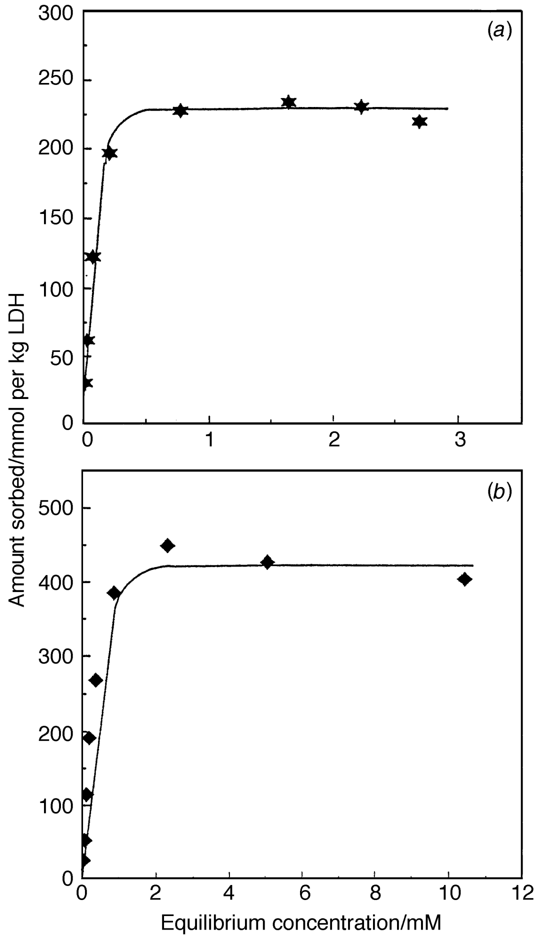

Fig. 1 Adsorption of (*a*) CMCD(14) and (*b*) CMCD(3) by Mg/Al LDH at 65 °C. Note that the scales are different

The XRD results indicated that, for both CMCDs (3 and 14), little *d*-spacing change was observed until retention reached the sorption plateau, suggesting they could only be intercalated into Mg/Al LDH interlayers at higher concentrations. At higher CMCD loadings, the Mg/Al LDH basal spacing (d_{003}) expanded from 8.74 to 15.48 Å for CMCD(14), and to 20.63 Å for CMCD(3).

FT-IR spectra

The FT-IR spectra of pure CMCD(3), Mg/Al LDH, and CMCD(3)–Mg/Al LDH complex are shown in Fig. 3. Because CMCD(14) and its complex with Mg/Al LDH exhibited the same patterns, they are not shown here. The assignment of major bands of CMCD(3) [Fig. 3(*b*)] was made by reference to the study on β-cyclodextrin by Wiedenhof *et al.*[29] and are as

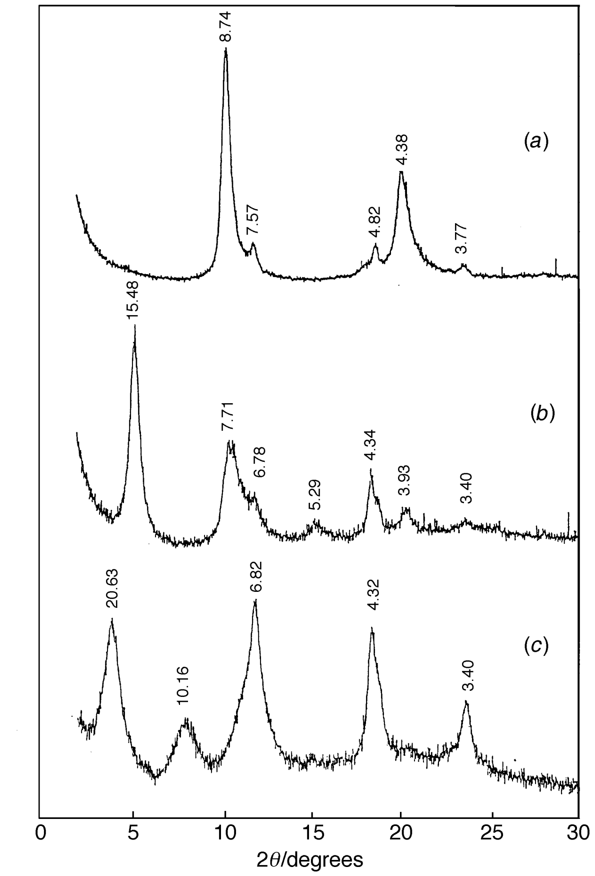

Fig. 2 X-Ray diffraction patterns of (*a*) Mg/Al LDH, (*b*) CMCD(14)–Mg/Al LDH complex, and (*c*) CMCD(3)–Mg/Al LDH complex

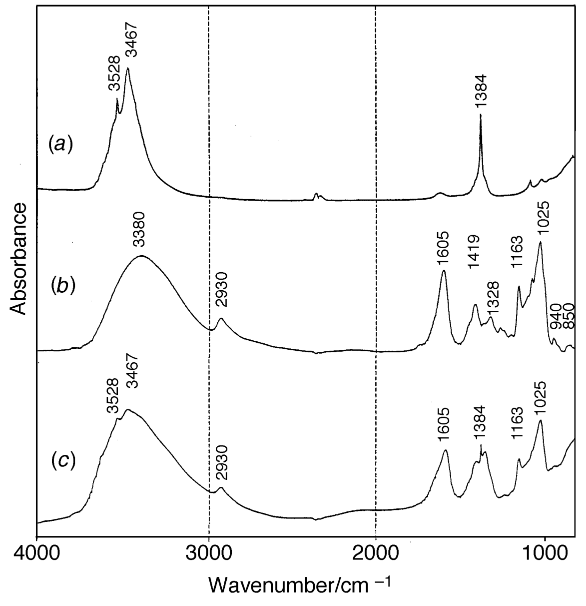

Fig. 3 The FT-IR spectra of (*a*) Mg/Al LDH, (*b*) CMCD(3) and (*c*) CMCD(3)–Mg/Al LDH complex

follows: 3380 (OH stretching), 2930 (CH stretching), 1605 [ionized carboxyl group, ν_{asym}(CO)], 1419 (CH deformation) and 1163–940 (CO/CC stretching). The FT-IR spectrum of the Mg/Al LDH displayed the characteristics bands of LDHs and was analogous to that reported by Miyata.[26] The absorption at 3500–3600 cm^{-1} is attributed to the H-bond stretching vibrations of the OH group in the brucite-like layer. In the 600–1800 cm^{-1} region, there were some bands related to vibrations of the anions and to cation-oxygen vibrations. The major absorption band of NO_3^- appeared at 1384 cm^{-1}. Miyata[26] has reported band splitting in some LDHs containing different anions and suggested that the NO_3^- could exist in the interlayer region of Mg/Al LDH as a mono- or a bi-dentate complex.

After the Mg/Al LDH was exposed to CMCD(3), its FT-IR spectrum [Fig. 3(*c*)] clearly demonstrated that CMCD(3) had been adsorbed by Mg/Al LDH. The principal change occurred with the major peak of NO_3^- (1384 cm^{-1}), which decreased sharply due to its exchange by CMCD(3), while the band of ionized carboxyl group (1605 cm^{-1}) significantly increased. This indicates that CMCD(3) was adsorbed by Mg/Al LDH through an ion-exchange reaction and that the carboxyl group of CMCD(3) was held through electrostatic attraction between the negative charge of the carboxyl group and the positive charge of the Mg/Al LDH layers. The same conclusions also hold for CMCD(14).

Discussion

Previous studies[1,9] have indicated that LDHs react easily with various types of organic anions. However, because hydrotalcite-type clays have considerably higher charge densities than silicate-based clays, it was expected that hydrotalcites would be more difficult to swell and for exchange processes to occur. Earlier work[30] has shown that the anion-exchange reactions of hydrotalcite proceed with greater difficulty as the charge density of the material increases (*i.e.*, as the Mg:Al atomic ratio decreases) due to increased electrostatic attraction. This was confirmed in our preliminary studies that indicated Ca/Al LDH, which has a higher charge density than Mg/Al LDH,[1] had little affinity for CMCD and could not intercalate CMCD molecules. On the contrary, Mg/Al LDH was capable of intercalating CMCD molecules at higher loadings, while the uptake of CMCD at lower concentrations might be contributed to sorption onto the external surfaces of Mg/Al LDH.

Cyclodextrin should be regarded as a truncated cone rather than a cylinder.[13] There are seven primary and 14 secondary hydroxyl groups along the β-cyclodextrin cavity. On the side where the secondary hydroxyl groups are situated, the diameter of the cavity is larger than on the side with the primary hydroxyls, since free rotation of the latter around the C^5–C^6 bond reduces the effective diameter of the cavity. β-Cyclodextrin has an approximate torus thickness of 7.8, an outer diameter of 15.3 and an inner diameter of 7.8 Å (as shown in Fig. 4). Primary hydroxyl groups are more readily substituted than are the secondary hydroxyl groups, and the secondary hydroxyls at C^3 are much less reactive than those at C^2.[13] Therefore, for CMCD(3), the three carboxymethyl groups were assumed to be located on the narrow side of the cyclodextrin ring, while for CMCD(14), both primary and secondary hydroxyls at C^2 have been substituted by carboxymethyl groups.

In deducing the geometry of CMCD between Mg/Al LDH interlayers, we first considered the brucite layer thickness of 4.78 Å,[31,32] which left a spacing occupied by CMCD of 10.7 Å for CMCD(14) and of 15.8 Å for CMCD(3). Considering the dimensions of the β-cyclodextrin molecules, the CMCD(14) molecules could only adopt a monolayered arrangement [Fig. 4(*a*)] with its cavity axes perpendicular to the LDH layer and carboxymethyl groups on both sides of the cyclodextrin cavity attached to the Mg/Al LDH surfaces. As the equivalent area (area per charge)[1] for ideal Mg/Al LDH is 32.4 $Å^2$, the theoretical internal surface area of one face can be estimated[33] to be $[(6.02 \times 10^{23}) \times 32.4]/(333.9 \times 10^{20}) = 584\ m^2$ per g LDH {333.9 is equal to the molecular mass of $[Mg_3Al(OH)_8]NO_3{\cdot}2H_2O$}. Assuming that cyclodextrin molecules are hexagonally close-packed in the monolayer phase, the effective area per molecules was estimated[17] to be 203 $Å^2$, therefore, CMCD(14) content is $(584 \times 10^{20})/203[(6.02 \times 10^{23}) \times 10^3] = 478$ mmol per kg LDH, which is nearly twice the observed value of 222 ± 13 mmol per kg LDH. Alternatively, based on charge balance, we could also obtain a value of 428 mmol per kg LDH by assuming that all of

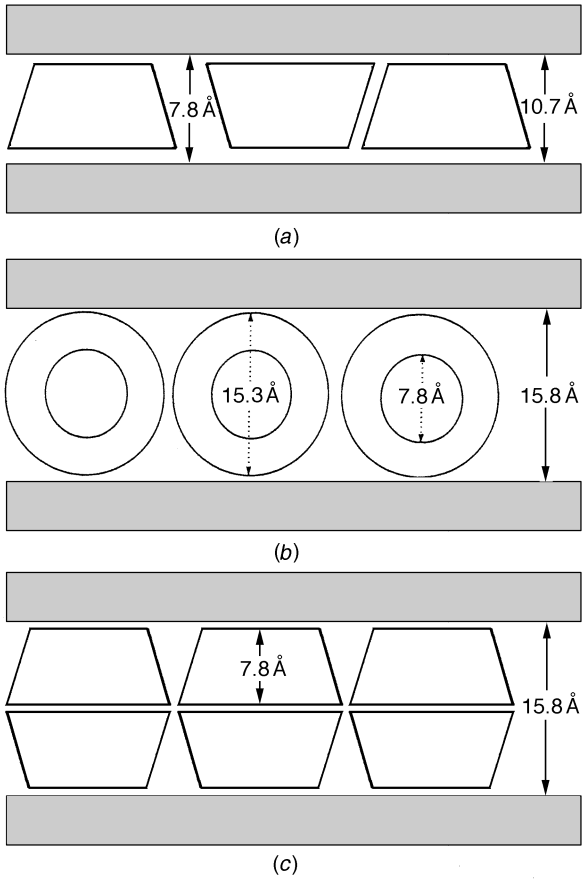

Fig. 4 Schematic representation (not to scale) of the possible arrangements for (*a*) a perpendicular monolayer CMCD(14)–Mg/Al LDH complex, (*b*) a parallel-monolayer CMCD(3)–Mg/Al LDH complex, and (*c*) a perpendicular-bilayer CMCD(3)–Mg/Al LDH complex

the charge sites are occupied by carboxymethyl groups. Therefore, it would be reasonable to assume that the CMCD(14) molecules were loosely packed and existed as discrete isolated entities within the LDH interlayers, calculated to be approximately 6.5 Å apart from each other. This could be due to the conformation of carboxymethyl groups. As none of the cyclodextrin hydroxyls points into the cavity and the C^6–O^6 bonds are preferentially directed away from the centre of the ring,[13,34–36] then the carboxymethyl groups could orient towards the exchange sites outside the cavity, leaving the exchange sites above or below the cavities inaccessible for carboxymethyl groups. This conformation would make the effective area of cyclodextrin larger than 203 Å^2. Hence, the larger effective area of cyclodextrin and the competition for exchange sites, as well as the steric hindrance effect, would result in the loose packing of CMCD(14) molecules. By subtracting the surface area occupied by cyclodextrin, we obtained a fairly close value to the observed data, confirming the above reasoning. The thickness of this packing model is 2.9 Å greater than the cyclodextrin torus thickness, which might be ascribed to the carboxymethyl groups along the sides of the cavity. The contribution of carboxymethyl groups on both sides of the cavity was estimated to be 5.5 Å[1] (observed value is 2.9 Å). The difference of 2.6 Å might be attributed to the flexibility or the outwards conformation of the carboxymethyl groups.

In regard to the CMCD(3) molecules, the space occupied by CMCD(3) is 15.8 Å, which is about twice the torus thickness or equivalent to its outer diameter. Therefore, two types of arrangements are possible: a parallel-monolayered arrangement [Fig. 4(*b*)] and a perpendicular-bilayer-like coverage [Fig. 4(*c*)]. Using the same evaluation method described above, the CMCDC(3) content for both the bilayer phase and parallel-monolayer phase amounts to 940 and 813 mmol per kg LDH, respectively, which was nearly twice as much as the observed data (415 ± 24 mmol per kg LDH). This suggests that CMCD(3) molecules are also loosely packed, owing to the reason described above. However, it is difficult to predict the relative spatial arrangement among CMCD(3) molecules due to the uncertainty of the position and the flexibility of the carboxymethyl groups on the ring side. Based on charge balance, the estimated CMCD(3) content could be as high as 1996 mmol per kg LDH, which is about four times the observed value, indicating that nearly 80% of the charge sites were unoccupied by carboxymethyl groups. This could also be attributed to the blocking of exchange sites by cyclodextrin, as well as the low substitution degree of CMCD(3). In the parallel-monolayer phase, the three carboxymethyl groups could presumably be attached to both LDH layers. In a bilayer-like model, because the CMCD(3) molecules would associate face-to-face with hydrogen bonds between their secondary hydroxyl groups, as observed in several cyclodextrin inclusion compounds,[17,36] the contribution of carboxymethyl groups together with the intermolecular hydrogen bonds that have a length[17] of 2.8 Å would make the thickness of the bilayer more than twice that of the torus thickness, or larger than the observed 15.8 Å. Thus, we suggest the parallel-monolayered model is more likely to occur than the bilayer-like model, although a randomly staggered bilayer phase also seems plausible. A definitive explanation, however, awaits further work.

Conclusion

The following conclusions are apparent from this study. First, carboxymethyl-β-cyclodextrin can be adsorbed by Mg/Al LDH with the retention of CMCD(3) approximately twice that of CMCD(14). Secondly, Mg/Al LDH was able to intercalate CMCD molecules with the intercalated CMCD(14) molecules adopting a monolayer arrangement, with the axis of the cavity perpendicular to the LDH surfaces. Thirdly, Mg/Al LDH and CMCD(3) formed a complex that contained either a perpendicular-bilayer or a parallel-monolayer coverage within the interlayers. Fourthly, both CMCD(14) and CMCD(3) molecules were believed to be loosely packed within the interlayers. Finally, the novel CMCD–Mg/Al LDH intercalates may be of potential use in many aspects. Studies are now in progress to examine the possible use of CMCD–Mg/Al LDH complexes in removal of organic pollutants and chromatographic applications.

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