Preferential intercalation of isomers of anthraquinone sulfonate ions into layered double hydroxides

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Intercalation compounds of anthraquinone sulfonate ions into layered double hydroxides (LDHs) have been directly synthesized. From the X-ray diffraction data and the guest size, the orientation of the intercalated anthraquinone sulfonate ions was determined. The intercalated anthraquinone-1,5-disulfonate (AQ15) and anthraquinone-2,6-disulfonate (AQ26) are arranged with their molecular planes and their sulfonate group axes tilted to the perpendicular of the hydroxide layer. Intercalated anthraquinone-2-sulfonate (AQ2) is arranged with the molecular plane and its sulfonate axis also perpendicular to the hydroxide layer with an antiparallel pattern. The product from a mixture of AQ2, AQ15 and AQ26 was also prepared; 86.8% of AQ2 and 13.2% of AQ26 were co-intercalated, whereas AQ15 was not intercalated into the LDH. These results indicate the possibility of a molecular recognition ability of LDH.

Layered double hydroxides (LDHs) are minerals and synthetic materials with positively charged brucite-type layers of mixed-metal hydroxides. Exchangeable anions located in the interlayer spaces compensate for the positive charge of the brucite-type layers. The chemical composition of LDHs is generally expressed as $[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2]^{x+}[(A^{n-})_{x/n}H_2O]^{x-}$ with $x=[M^{3+}]/([M^{2+}]+[M^{3+}])$ ($M^{2+}=Mg^{2+}$, Co^{2+}, Ni^{2+}, *etc.*; $M^{3+}=Al^{3+}$, Cr^{3+}, *etc.*, and A^{n-} is an interlayer exchangeable anion such as $CO_3{}^{2-}$, Cl^-, *etc.*). These ionic layered materials also have been termed 'hydrotalcite-like' compounds in reference to the structural similarity to the mineral hydrotalcite, $[Mg_6Al_2(OH)_{16}]^{2+}CO_3{}^{2-}\cdot 4H_2O$, or termed 'anionic clays' in mirror image resemblance to the cationic clays whose negative charges of the aluminosilicate layers are counterbalanced by intercalated cations. LDHs are an important class of materials currently receiving considerable attention. The preparation, properties and applications of LDH materials have been studied extensively.[1–7] They are used as adsorbents, catalysts, catalyst precursors, aninoic exchangers, and antacid drugs.[8–11] LDHs are also attractive as host materials owing to the possibility of new nanoscale organic–inorganic hybrid composites, through intercalation. There have been several reports on the intercalation of organic anions into LDHs[12–16] with the main synthetic route *via* anionic exchange. However, preferential intercalation of isomeric organic anions into LDHs has scarcely been studied. Tagaya *et al.* reported the preferential intercalation of isomers of naphthalene carboxylate ions into LDH by anion exchange.[17] In the present work, intercalation compounds of isomers of anthraquinone sulfonates into an LDH were directly synthesized. Results of the preferential intercalation of isomers of anthraquinone sulfonate ions into the LDH are also described.

Experimental

Materials

The compounds $ZnCl_2$ and $AlCl_3$ were of guaranteed reagent grade. Anthraquinone-1,5-disulfonic acid disodium salt (AQ15), anthraquinone-2,6-disulfonic acid disodium salt (AQ26) and anthraquinone-2-sulfonic acid sodium salt (AQ2) were obtained from Aldrich and used without further purification.

Direct synthesis of LDH intercalation compounds

The layered double hydroxide of aluminium with zinc (Zn/Al-LDH) was synthesized by hydrolysis of the mixed aqueous solutions of $ZnCl_2$ (1.0 mol dm^{-3}) and $AlCl_3$ (0.5 mol dm^{-3}) at $pH=7.5\pm0.2$ by dropwise addition of an aqueous NaOH solution (1.0 mol dm^{-3}) with vigorous stirring under a nitrogen atmosphere. The molar ratio of aluminium to zinc was 0.33. The precipitate was aged at 60 °C for 24 h, filtered, washed with decarboxylated water, and air dried at 80 °C for 18 h. The intercalation compound of an anthraquinone-1,5-disulfonate (AQ15) into the LDH of aluminium with zinc (LDH-AQ15) was directly synthesized by hydrolysis of a mixed aqueous solutions of $ZnCl_2$ (0.05 mol dm^{-3}), $AlCl_3$ (0.025 mol dm^{-3}) and anthraquinone-1,5-disulfonate (AQ15) (0.0125 mol dm^{-3}) at $pH=7.5\pm0.2$ by dropwise addition of an aqueous NaOH solution (1.0 mol dm^{-3}) with vigorous stirring under a nitrogen atmosphere. The precipitate was aged at 70 °C for 7 days, filtered, washed with decarboxylated water, and air dried at 80 °C for 18 h. Intercalation compounds of anthraquinone-2,6-disulfonate (AQ26) and anthraquinone-2-sulfonate (AQ2) into the LDH (LDH-AQ26, LDH-AQ2) were directly synthesized by a similar method to LDH-AQ15. The amount of AQ15, which form two anions, corresponded to same number of equivalents of the stoichiometric interlayer anions calculated from the aluminium content. For the synthesis of LDH-AQ2, 0.025 mol dm^{-3} of anthraquinone-2-sulfonate was used to retain the same number of equivalents. For the synthesis of the mixed intercalation compound of AQ15, AQ26 and AQ2, the same number of equivalents of AQ15, AQ26 and AQ2 was added to a mixed aqueous solution of $ZnCl_2$ and $AlCl_3$ at $pH=7.5$.

Characterization

Chemical analysis for Zn and Al was carried out by using an inductively coupled plasma atomic emission spectrometer (ARL Model 3410 ICP-AES). IR spectra were recorded on a Midac Prospect FTIR spectrometer. X-Ray diffraction spectra were obtained with a Rigaku diffractometer using Cu-Kα radiation. The amounts of intercalated anthraquinone sulfonate ions were also determined using an Vario EL CHN analyzer. For the case of intercalation of a mixture of AQ15, AQ26 and AQ2 ions into the LDH, the amounts of intercalated anthraquinone sulfonate ions were determined by HPLC, after dissociating the intercalated LDH with a few drops of acid (2 M HCl), by calibration with known composition. The Shimadzu HPLC equipment used included two LC-10AD pumps, an SCL-10A controller, SPD-10AV UV–VIS detector (254 nm), and a C-R7A recorder. The mobile phases were prepared by mixing 50% methanol and 50% 0.005 M tetrabutylammonium hydrogensulfate aqueous solution. Tetrabutylammonium hydrogen-sulfate acts as an ion-pairing reagent. If an ion-pairing reagent is added to the mobile phase, it is possible to achieve efficient and rapid separations of a number of aromatic sulfonic acids.[18] The retention times of dissociated AQ15, AQ26 and AQ2 on C_{18} columns are 3.5, 4.0 and 13.0 min, respectively.

Results and Discussion

Intercalation of AQ15, AQ26 and AQ2 ions

The layered double hydroxides of Al and Zn (Zn/Al-LDH) were directly synthesized by the hydrolysis of $ZnCl_2$ and $AlCl_3$ with an NaOH solution and the interlayer anion is Cl^-. The intercalation compound between anthraquinone-1,5-disulfonate and a layered double hydroxide (LDH-AQ15) was directly synthesized by the hydrolysis of $ZnCl_2$, $AlCl_3$ and anthraquinone-1,5-disulfonate with NaOH solution. A similar method was applied with LDH-AQ26 and LDH-AQ2. The X-ray diffraction patterns of the LDH and intercalated compounds of LDH with anthraquinone sulfonates are displayed in Fig. 1 and the indexing of the patterns is listed in Table 1. Fig. 1(A) shows the X-ray diffraction pattern of the LDH. The indexing of the diffraction peaks was obtained by comparison with the diagram reported for synthetic hydrotalcite.[19] The *a* parameter of the hexagonal unit cell corresponds to the distance between two metals in adjacent octahedral sites while the *c* parameter corresponds to three times the distance between adjacent hydroxy layers. The *c*-axis parameter was calculated to be 22.86 Å from the positions of the (003) and (006) peaks. The *a*-axis parameter was calculated to be 3.08 Å from the (110) peak. Since the *c*-axis parameter is 22.86 Å, the basal spacing of the LDH is 7.62 Å. The gallery height of the LDH is 2.84 Å when the thickness of the mixed aluminium/zinc hydroxide layers (4.78 Å) is subtracted.[20]

Fig. 1(B) shows the X-ray diffraction pattern of LDH-AQ15. The (003) diffraction peak and the higher-order peaks of the LDH-AQ15 shifted to lower 2θ angles compared to those of the Zn/Al-LDH. The *c*-axis parameter of LDH-AQ15 was calculated to be 47.04 Å from the (003) and (006) peaks. The basal spacing of the LDH-AQ15 increased from 7.62 Å (LDH) to 15.68 Å. Therefore, the gallery height of the LDH-AQ15 was 10.90 Å. This increase in the gallery height strongly indicated the intercalation of AQ15 into the LDH. The IR spectrum of LDH-AQ15 was similar to those of anthraquinone-1,5-disulfonate in the range 1700–1000 cm^{-1}. This also indicated that anthraquinone-1,5-disulfonate was intercalated into LDH-AQ15. Fig. 1(C) shows the X-ray diffraction pattern of LDH-AQ26 and is similar to LDH-AQ15 with a calculated gallery height of 13.58 Å. Fig. 1(D) shows the X-ray diffraction pattern of LDH-AQ2. The (003) and higher-order peaks of LDH-AQ2 shifted to lower 2θ angles compared to those of the LDH-AQ26 and the gallery height of 15.11 Å is larger than that of LDH-AQ26. Therefore the gallery heights of the intercalated Zn/Al-LDH with the three anthraquinone sulfonates differ upon changing the position of substitution of SO_3^- groups on the anthraquinone moiety.

Table 1 Indexing of the XRD patterns of intercalated products

	LDH-AQ15	LDH-AQ26	LDH-AQ2	LDH-AQ mixture
hkl	*d*/Å	*d*/Å	*d*/Å	*d*/Å
003	15.66	18.31	19.80	20.16
006	7.85	9.20	9.99	10.06
009	5.27	6.20	6.68	6.60
0012	3.99	4.66	5.00	5.00
0015		3.73	3.94	3.99
0018				3.30
003[a]				7.62

[a](003) peak of unreacted Zn/Al-LDH.

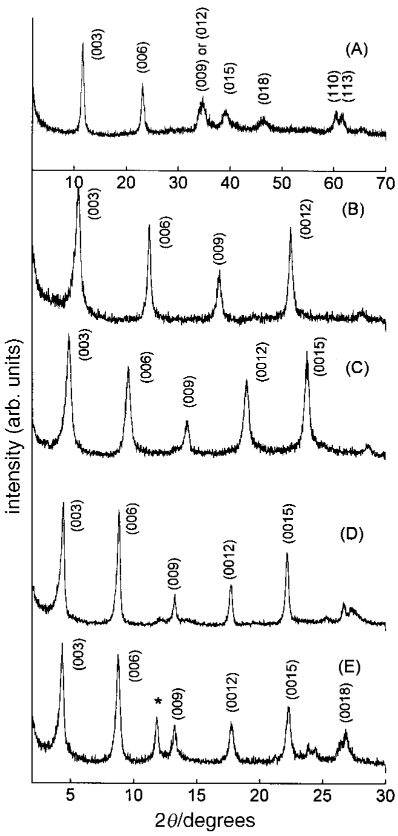

Fig. 1 X-Ray diffraction patterns and Miller indices of (A) Zn/Al-LDH, (B) LDH-AQ15, (C) LDH-AQ26, (D) LDH-AQ2 and (E) a mixture of AQ26, AQ15 and AQ2 within the LDH

Kanezaki *et al.* have recently reported a comparative study on the intercalation of AQ26 in a synthetic Mg/Al-LDH.[21] Two values of enhanced interlayer distance in the intercalate are observed. Owing to the intercalation of AQ26 with the Mg/Al-LDH, the interplanar spacing increased from 7.72 to *ca.* 19 Å or to *ca.* 12 Å. It was interpreted that steric hindrance of the bulky anthraquinone moiety is responsible for the differences in packing of the interlayer molecules. Products containing intercalated AQ15, AQ18 or AQ27 in Mg/Al-LDH did not show a dual interlayer distance nor was such behaviour seen in this work. An explanation of the dual interlayer distance upon intercalation of AQ26 into Mg/Al-LDH requires a more extensive investigation.

The elemental composition of LDH-AQ15 was measured by ICP–AES and CHNS elemental analysis. The ratio of zinc to aluminium in the directly synthesized LDH was 0.63 : 0.37, slightly different from the initial mixing ratio. The ideal formula of LDH-AQ15, based on the zinc to aluminium ratio, would be $[Zn_{0.63}Al_{0.37}(OH)_2](AQ15)_{0.185}\cdot mH_2O$. The validity of this formula was checked by CHNS elemental analysis (H data could not be utilized owing to the presence of water). The % C and S values {Found: C, 17.80; S, 6.66. Calc. for $[Zn_{0.63}Al_{0.37}(OH)_2][(AQ15)_{0.185}]$ based on the Al content (6.53%): C, 20.32; S, 7.76%} were slightly lower than the ideal values. The formula of LDH-AQ15, based on the zinc to aluminium ratio, can be written $[Zn_{0.63}Al_{0.37}(OH)_2](AQ15)_{0.16}Cl^-{}_{0.05}\cdot mH_2O]$ with the anthraquinone-1,5-disulfonate content corresponding to about half of the stoichiometric aluminium content of LDH. This fact indicates that one of two sulfonate groups of the anthraquinone-1,5-disulfonate is attached to the positively charged upper hydroxide layer, the other sulfonate group is attached to another positively charged lower hydroxide layer. The formulae of LDH-AQ26 and LDH-AQ2 were $[Zn_{0.64}Al_{0.36}(OH)_2](AQ26)_{0.17}Cl^-_{0.02}\cdot mH_2O$ and $[Zn_{0.65}Al_{0.35}(OH)_2](AQ2)_{0.29}Cl^-_{0.06}\cdot mH_2O$, respectively. The anthraquinone-2-sulfonate contents are almost equal to the stoichiometric aluminium content of LDH.

From X-ray diffraction studies, the orientation of the intercalated species can be roughly estimated. The size of anthraquinone-2,6-disulfonate was calculated using the Alchemy program. The length of AQ26 is 14.3 Å, assuming a van der Waals radius of oxygen of 1.4 Å[22] while the gallery height of LDH-AQ26 measured from the X-ray diffraction peaks is 13.58 Å. The gallery height is smaller than the estimated length of the anthraquinone-2,6-disulfonate and therefore, the molecular plane of the anthraquinone ions and its sulfonate groups shows a tilt angle of 18°. The tilt angle is the angle of the sulfonate group axes to the normal of the layer surface. A schematic illustration of the arrangement of the anthraquinone-2,6-disulfonate in the LDH is shown in Fig. 2(A). The results for LDH-AQ15 are very similar to those of the LDH-AQ26, with the sulfonate group axis of the AQ15 lying perpendicular to the hydroxide layer with a tilt angle of 34°. AQ2 has a length of 12.9 Å assuming van der Waals radii of oxygen and hydrogen of 1.4 and 1.2 Å, respectively,[22] while the gallery height of LDH-AQ2 measured from X-ray diffraction is 15.11 Å. Here the gallery height is larger than the estimated length of the anthraquinone-2-sulfonate. AQ2 contains one sulfonate group whereas the interlayer of LDH possesses top and bottom cationic surfaces. Since the sulfonate group of AQ2 attached to the positively charged LDH layer, an antiparallel pattern is anticipated. Therefore, the molecular plane of AQ2 and its sulfonate group axis also lie perpendicular to the hydroxide layers as shown in Fig. 2(B). The gallery heights of the intercalated products along with elemental analysis values are listed in Table 2.

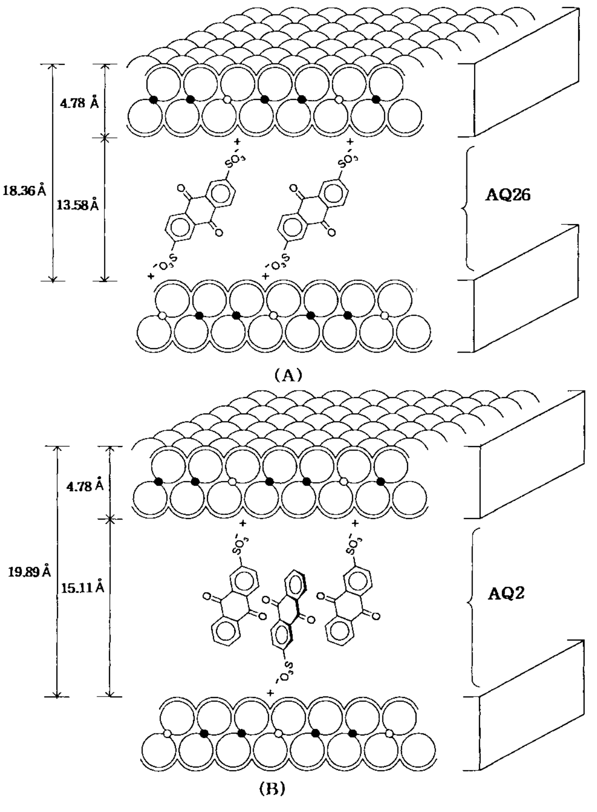

Fig. 2 Schematic illustration of the orientation of (A) LDH-AQ26 and (B) LDH-AQ2 (OH layers shown by large circles; •, Zn; ◦, Al)

Intercalation of a mixture of AQ15, AQ26 and AQ2 ions

The intercalation compound from a mixture of AQ15, AQ26 and AQ2 ions into the layered double hydroxide was directly synthesized by hydrolysis of $ZnCl_2$, $AlCl_3$ and a mixture of AQ15, AQ26 and AQ2 ions (1 : 1 : 1 equivalent) with NaOH. Fig. 1(E) shows the X-ray diffraction pattern of the intercalation compound of a mixture of AQ15, AQ26 and AQ2 ions into the LDH and is similar to those obtained with LDH-AQ2. The asterisked peak at $2\theta = 11.6°$ is the (003) diffraction peak of unreacted Zn/Al-LDH. The (003) diffraction peak and higher-order peaks of LDH-AQ26 and LDH-AQ15 were not observed in Fig. 1(E). It seems that the only AQ2 is intercalated into the LDH. Since the gallery height of the LDH-AQ2 is larger than those of LDH-AQ26 and LDH-AQ15, there is, however, a possibility that small amounts of AQ15 and AQ26 were co-inserted into the interlayer site of AQ2 with LDH.

It is difficult to determine the amount of each of the intercalated anthraquinone ions into the LDH from XRD and CHNS analysis data. Therefore, the amount of intercalated anthraquinone ions was determined by HPLC. Although XRD shows no evidence for AQ26, HPLC data show that 86.8% of AQ2 and 13.2% of AQ26 are co-intercalated, whereas AQ15 is not intercalated. The gallery height is expanded to a value of 15 Å upon intercalation of AQ2 and then the similarly sized AQ26 is co-intercalated into the gallery. Since the gallery height of LDH-AQ15 is much smaller than that of LDH-AQ2, AQ15 is easily de-intercalated from the interlayer spacing of LDH-AQ2 and LDH-AQ26. From the present experiment, it is considered that AQ2 strongly interacts with the Zn/Al-LDH. Therefore, it is possible that intermolecular forces between the host and the guest causes preferential intercalation. To confirm the preferential intercalation from the intercalation compound itself, the intercalation compound of a mixture of AQ15 and AQ26 was synthesized. In this case, 11.5% AQ15 and 88.5% AQ26 were co-intercalated. Since AQ15 and AQ26 are isomers with the same negative charge, this preferential intercalation indicates the presence of a molecular recognition ability of the LDH. The intercalation compound of a mixture of AQ15 and AQ2 was also synthesized. In this case, only AQ2 was intercalated whereas AQ15 was not. Therefore, preferential intercalation was observed for Zn/Al-LDH; the ability of intercalation into Zn/Al-LDH is in the order AQ2 > AQ26 ≫ AQ15.

The results indicate that the electron density of the anthraquinone sulfonate is important for intercalation, and here ions having low negative charge are intercalated in preference to ions having high negative charges. These results are quite different from those obtained with naphthalene carboxylate ions, where 2,6-naphthalene dicarboxylate ion was more easily intercalated than 2-naphthalene carboxylate ion.[17] In this case, the amount of intercalated carboxylate ion was small, because

Table 2 Experimental results for the intercalated products

	LDH-AQ15	LDH-AQ26	LDH-AQ2
gallery height l^a/Å	10.90	13.58	15.11
guest size l^b/Å	13.1	14.3	12.9
tilt angle θ^c/°	34	18	0
composition	$[Zn_{0.63}Al_{0.37}(OH)_2]/(AQ15)_{0.16}Cl_{0.05}^-\cdot mH_2O$	$[Zn_{0.64}Al_{0.36}(OH)_2]/(AQ26)_{0.17}Cl_{0.02}^-\cdot mH_2O$	$[Zn_{0.65}Al_{0.35}(OH)_2]/(AQ2)_{0.29}Cl_{0.06}^-\cdot mH_2O$

[a] The remainder after subtracting the thickness of a layer (4.78 Å) from the interlayer spacing, which is calcualted from averaging of the (003) and (006) peaks in XRD, see text. [b] Interatomic distance between two oxygen atoms in the different SO_3^- groups for AQ15 and AQ26, see text. [c] Tilt angle of the guest molecule axis to the normal of the layer surface, see text.

an excess of host to guest was used; layer expansions were only 2.8–3.4 Å. It was interpreted that the plane of the naphthalene carboxylate ion here was parallel to the plane of the host layer. Therefore, the different behavior of preferential intercalation arises from the different intercalated geometries between anthraquinone sulfonates and naphthalene carboxylates. To elucidate the mechanism of preferential intercalation, an experiment using a large amount of intercalated carboxylate ion must be carried out. While the mechanism of the molecular recognition is still not clear, we can confirm the existence of a molecular recognition ability and preferential intercalation of LDH.

Conclusions

We have synthesized the intercalation compounds of AQ15, AQ26 and AQ2 ions with Zn/Al-LDH and X-ray diffraction data revealed the orientation of the intercalated anthraquinone sulfonate ions. For AQ15 and AQ26, the molecular plane and sulfonate group axes are tilted relative to the normal of the hydroxide layer. For AQ2, a similar orientation was adopted but with the molecules adopting an antiparallel pattern. We succeeded in establishing a preferential intercalation of anthraquinone sulfonate ions into the LDH indicating the existence of a molecular recognition ability of the layered double hydroxide.

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