

# Articles

## Preferential Intercalation of Organic Anions into Layered Double Hydroxide

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Intercalation compounds of organic anions into layered double hydroxides (LDH) are synthesized by the coprecipitation route. X-ray diffraction data reveal that the intercalated terephthalate (TP), naphthalene-2,6-disulfonate (NA26), and anthraquinone-2,6-disulfonate (AQ26) are arranged with their molecular planes perpendicular to the hydroxide layer. HPLC data show that 26.2% of TP and 73.8% of AQ26 are co-intercalated, whereas NA26 is not intercalated into the Zn/Al-LDH. These results indicate the possibility of a molecular recognition ability of Zn/Al-LDH. The molecular recognition ability of intercalation into Zn/Al-LDH is in the order AQ26 > TP >> NA26.

### Introduction

Layered inorganic solids have been of interest in a variety of areas due to their adsorptive and catalytic properties. These materials are essentially two dimensional in character in the sense that the bonding forces within the layers are much stronger than those between layers. These materials exhibit the ability to exchange or intercalate organic molecules. In this study, we have focused on the preferential intercalation of organic anions into layered double hydroxides (LDHs). LDHs consist of layers of  $M^{2+}$  and  $M^{3+}$  cations coordinated octahedrally by six oxygen atoms, as hydroxides. These layers exist with a similar layered structure of brucite,  $Mg(OH)_2$ . The substitution of  $M^{3+}$  cations into the position of the  $M^{2+}$  cations in the layers creates the positively charged layers. Exchangeable anions located in the interlayer spaces compensate for the positive charge of the brucite-type layers. The chemical composition of the 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.). LDHs are an important class of materials currently receiving considerable attention. LDHs are attractive as host materials owing to the possibility of a new nanoscale organic-inorganic composite, through intercalation. The preparation, properties and applications of intercalated LDH materials have been studied extensively.<sup>1-7</sup> They are used as adsorbents, catalysts, catalyst precursors, anionic exchangers, and antacid drugs.<sup>8-11</sup>

LDH containing organic anions have been mainly prepared by anionic exchange reactions.<sup>12-16</sup> Large expansions of the LDH interlayer were observed depending on the size and the stereochemistry of organic molecules. In this manner, LDHs intercalated with terephthalate, naphthalenedisulfonate, or anthraquinonedisulfonate were investigated.<sup>17-20</sup> However, preferential intercalation of 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.<sup>21</sup> Their results indicated that the charge density of naphthalene

carboxylate ions was important for the intercalation, and ions having high negative charges were intercalated in preference to ones having low negative charges. However, in these cases the amount of intercalated naphthalene anions was small because an excess of LDH to naphthalene anions was used. Upon insertion of naphthalene anions into the LDH, the interlayer spacings are close to those of the LDH itself. It was interpreted that the plane of the naphthalene anions was parallel to the plane of the LDH layers. However, the reaction was finished within 2 hours, which was not enough for the intercalation. These results may come from the possibility of adsorption of naphthalene anions on the surface of the LDH rather than those of intercalation into the LDH interlayer. Sato *et al.* reported the selective adsorption behaviour of various benzene-carboxylate ions into LDH by using the chemical reaction of magnesium aluminium oxide.<sup>22</sup> They reported that the selectivity of anion uptake increased with increasing charge density of the ions. In a previous paper we reported the preferential intercalation of isomers of anthraquinone sulfonates into LDH.<sup>23</sup> Our results showed that ions having low negative charges are intercalated in preference to ones having high negative charges, which are in contrast to those obtained with naphthalene anions by Tagaya *et al.* These studies have focused on the effect of the electric charge density of anion on the intercalation behaviour. To examine the preferential intercalation behaviours depending on the shape or the size of organic anions, a more systematic study of the interactions between the LDH and organic anions with the same charge is also required. In this work, we report on the preferential intercalation of organic anions having the same charges into the LDH, which indicates the existence of a molecular recognition ability of the LDH.

### Experimental

**Materials.** The compounds  $ZnCl_2$  and  $AlCl_3$  were of guaranteed reagent grade. Terephthalic acid, disodium salt (TP), 2,6-naphthalenedisulfonic acid, disodium salt (NA26)

and anthraquinone-2,6-disulfonic acid, disodium salt (AQ26) were obtained from Aldrich and used without further purification.

#### Direct Synthesis of Intercalated LDH Compounds.

The synthesis of intercalation compounds of LDH has been described in detail in an earlier paper,<sup>23</sup> so only a brief description will be given here. Layered double hydroxide of aluminium with zinc (Zn/Al-LDH) was synthesized by hydrolysis of the mixed aqueous solutions of  $\text{ZnCl}_2$  ( $1.0 \text{ mol dm}^{-3}$ ) and  $\text{AlCl}_3$  ( $0.33 \text{ mol dm}^{-3}$ ) at  $\text{pH}=7.5 \pm 0.2$  with  $\text{NaOH}$  solution ( $1.0 \text{ mol dm}^{-3}$ ) under a nitrogen atmosphere. The mole fraction of aluminium to zinc was 0.25. The intercalation compound of an organic anion into the Zn/Al-LDH was directly synthesized by coprecipitation of a mixed aqueous solution of  $\text{ZnCl}_2$  ( $0.10 \text{ mol dm}^{-3}$ ),  $\text{AlCl}_3$  ( $0.033 \text{ mol dm}^{-3}$ ) in the presence of organic anions ( $0.017 \text{ mol dm}^{-3}$ ) at  $\text{pH}=7.5$  by dropwise addition of  $\text{NaOH}$  solution ( $1.0 \text{ mol dm}^{-3}$ ) with vigorous stirring under a nitrogen atmosphere. The precipitate was aged at  $70^\circ\text{C}$  for 7 days, filtered, washed with decarbonated water, and dried at  $80^\circ\text{C}$  for 18 hours. Hereafter intercalation compounds of terephthalate (TP), naphthalene-2,6-disulfonate (NA26), and anthraquinone-2,6-disulfonate (AQ26) into the Zn/Al-LDH are referred to as LDH-TP, LDH-NA26, and LDH-AQ26, respectively. For the synthesis of the intercalation derivative with mixed organic anions, the same concentrations of TP, NA26, and AQ26 were added to a mixed aqueous solution of  $\text{ZnCl}_2$  and  $\text{AlCl}_3$  at  $\text{pH}=7.5$ . Since TP, NA26, and AQ26 are highly soluble disodium salts, the solubility of these anions does not play a role in the intercalation process.

**Characterization.** X-ray powder diffraction profiles were recorded on a Rigaku diffractometer using  $\text{Cu-K}_\alpha$  radiation (40 kV and 20 mA) and a scan speed of  $3^\circ$  in  $2\theta$ /min. For the case of intercalation of a mixture of TP, NA26, and AQ26 ions into the LDH, the amounts of intercalated organic anions were determined using HPLC, after dissolving the LDH layers with a few drops of acid (2 M HCl), by calibration with a known composition. Since LDH is very weak in acidic conditions, most of the intercalated organic anions are easily released by acid treatment. Shimadzu HPLC equipped with two LC-10AD pumps, SCL-10A controller, SPD-10AV UV-Vis detector (254 nm), and a C-R7A recorder was used. The mobile phases were prepared by mixing 50% (v/v) acetonitrile and 0.01 M tetrabutylammonium hydrogensulfate aqueous solution. Tetrabutylammonium hydrogensulfate acts as an ion-pairing reagent. If an ion-pairing reagent is added to the mobile phase, it is possible to achieve efficient separations of a number of aromatic acids.<sup>24</sup> The retention times of TP, NA26, and AQ26 on  $\text{C}_{18}$  columns are 2.31, 3.11, and 3.64 min, respectively.

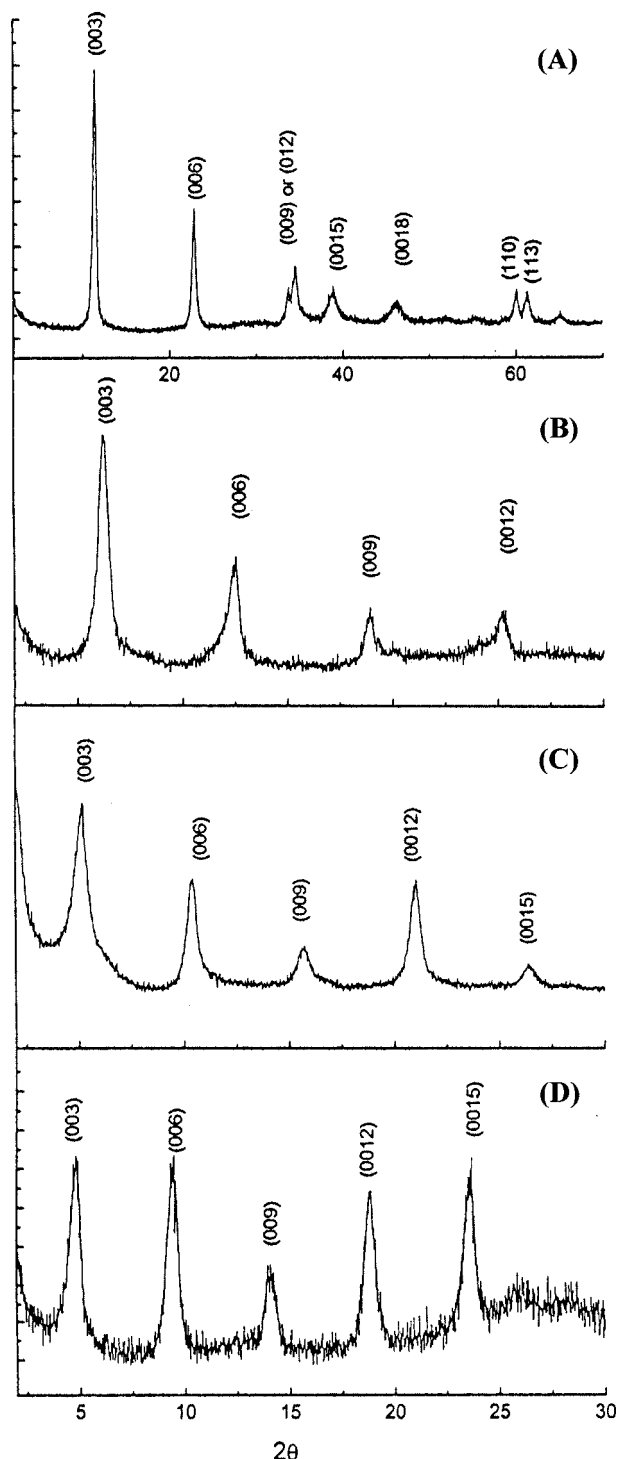
## Results and Discussion

#### Intercalation of Each TP, NA26, and AQ26 Ion.

The layered double hydroxide of Al and Zn (Zn/Al-LDH) was directly synthesized through the hydrolysis of  $\text{ZnCl}_2$  and  $\text{AlCl}_3$  with  $\text{NaOH}$  solution. The intercalation derivative with an organic anion was also prepared by the coprecipitation of  $\text{ZnCl}_2$ ,  $\text{AlCl}_3$  and an organic anion with  $\text{NaOH}$  solution. The X-ray powder diffraction patterns of

the LDH and organic intercalated ones are displayed in Figure 1. Figure 1(A) shows the X-ray diffraction pattern of the Zn/Al-LDH. The  $c$ -axis parameter was calculated to be  $23.3 \text{ \AA}$  from the positions of the (003) and (006) peaks. Since the  $c$ -axis parameter is  $23.3 \text{ \AA}$ , the basal spacing of the Zn/Al-LDH is  $7.8 \text{ \AA}$ . The gallery height of the Zn/Al-LDH is  $3.0 \text{ \AA}$  when the thickness of the mixed aluminum/zinc hydroxide layers ( $4.8 \text{ \AA}$ ) is subtracted.<sup>25</sup>

Figure 1(B) shows the X-ray diffraction pattern of LDH-

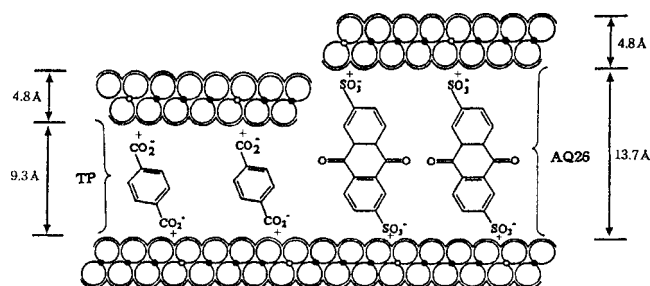


**Figure 1.** X-ray diffraction patterns and Miller indices of (A) Zn/Al-LDH, (B) LDH-TP, (C) LDH-NA26, and (D) LDH-AQ26.

TP. The (003) diffraction peak and the higher-order peaks of the LDH-TP shifted to lower  $2\theta$  angles compared with those of the Zn/Al-LDH. The  $c$ -axis parameter of LDH-TP was calculated to be 42.3 Å from the (003) and (006) peaks, suggesting that the gallery height of the LDH-TP was 9.3 Å. Drezdron and Kanazaki *et al.* also reported similar studies on the intercalation of TP in a Mg/Al-LDH.<sup>18,19</sup> The gallery heights of Mg/Al-LDH-TP are 9.4 Å and 9.5 Å, respectively, and agree with our experimental data. Figure 1(C) shows the X-ray diffraction pattern of LDH-NA26 with the gallery height of 12.3 Å. Kanazaki *et al.* also reported a study on the intercalation of NA26 in a Zn/Al-LDH.<sup>18</sup> The gallery height of the LDH-NA26 is 10.6 Å and smaller than that of our data. Figure 1(D) shows the X-ray diffraction pattern of LDH-AQ26. The calculated gallery height of LDH-AQ26 is 13.7 Å. Mousty *et al.* reported a study on the intercalation of AQ26 in a Zn/Cr-LDH.<sup>20</sup> The gallery height of the LDH-AQ26 is 14.1 Å and agrees with our experimental data within experimental error.

From X-ray diffraction studies, the orientation of the intercalated species can be roughly estimated. The size of terephthalate was calculated using the Alchemy program.<sup>26</sup> The molecular length of TP is 10.3 Å, assuming a van der Waals radius of oxygen of 1.4 Å,<sup>27</sup> while the gallery height of LDH-TP measured by X-ray diffraction peaks is 9.3 Å. Therefore, the molecular line which connects the two anionic oxygen atoms in the two carboxylate groups of terephthalate is nearly perpendicular to the hydroxide layers. Similarly calculated molecular length of NA26 is 12.4 Å, while the one measured from the X-ray diffraction is 12.3 Å, indicating also that the NA26 molecules are arranged perpendicularly to the hydroxide layers. AQ26 has a length of 14.3 Å, while the gallery height of the LDH-AQ26 measured from the X-ray diffraction is 13.7 Å. Therefore, the molecular plane of AQ26 also lies nearly perpendicular to the hydroxide layers. Schematic illustrations of the LDH-TP and LDH-AQ26 are shown in Figure 2.

**Intercalation of a Mixture of TP, NA26, and AQ26 Ions.** There have been several reports on the preferential adsorption of organic anions into the LDH. Sato and Tagaya *et al.* reported the preferential adsorption behaviour of various benzene carboxylate and naphthalene carboxylate ions into the LDH.<sup>21,22</sup> Their results indicated that the charge density of benzene carboxylate and naphthalene carboxylate were important for the adsorption, and ions having a high charge density were adsorbed in preference to ones having a low charge density. However,

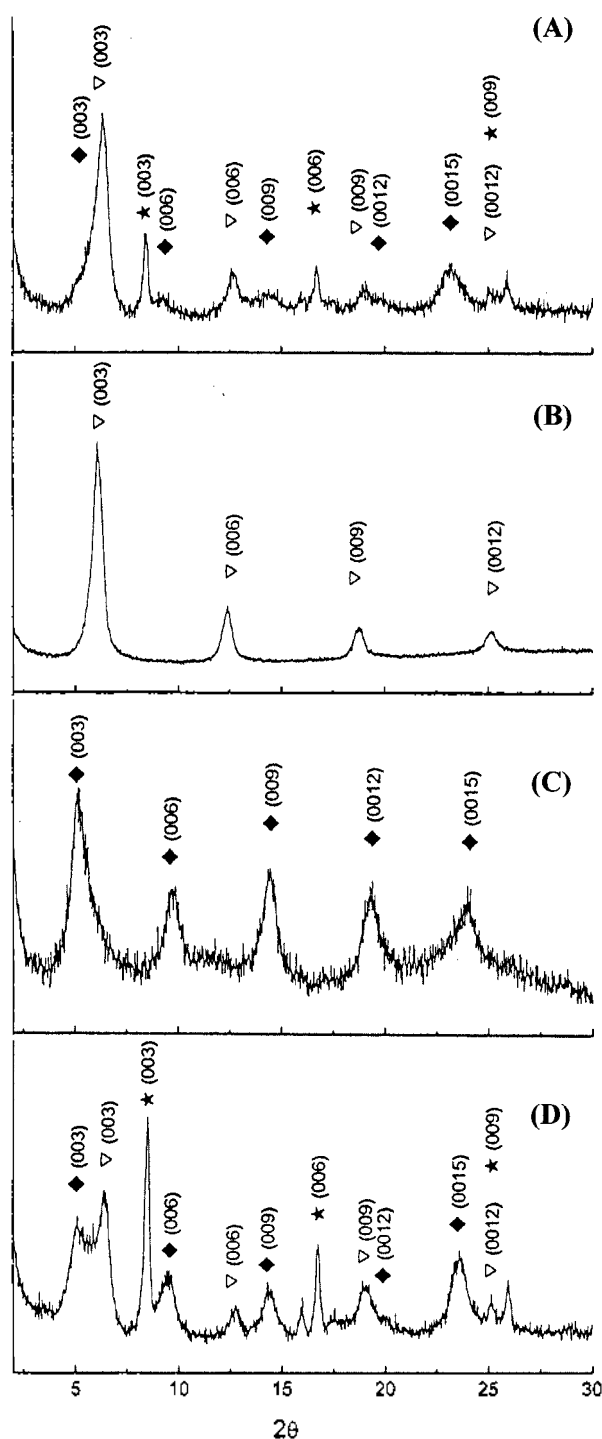


**Figure 2.** Schematic illustrations of the orientation of TP and AQ26 which are co-intercalated into the Zn/Al-LDH. (OH layers shown by large circles; ●, Zn; ○, Al).

we reported the preferential intercalation of isomers of anthraquinone sulfonates into LDH.<sup>23</sup> Our results show that ions having low negative charges are intercalated in preference to ones having high negative charges, which is in contrast to the preferential adsorption behaviour of benzene carboxylate and naphthalene carboxylate ions. It indicates that the mechanism of preferential intercalation into the LDH is different from that of adsorption. To examine the preferential intercalation behaviours depending on the shape or the size of organic anions, the intercalation compound from a mixture of TP, NA26, and AQ26 ions into the Zn/Al-LDH is synthesized.

The intercalation compound from a mixture of TP, NA26, and AQ26 ions was directly synthesized by coprecipitation of ZnCl<sub>2</sub> and AlCl<sub>3</sub> with NaOH in the presence of a mixture of equal concentrations of TP, NA26 and AQ26 ions. The X-ray diffraction patterns of the intercalated compounds of LDH with mixtures of organic anions are displayed in Figure 3. Figure 3(A) shows the X-ray diffraction pattern of the intercalation compound of a mixture of TP, NA26, and AQ26 ions into the Zn/Al-LDH. The X-ray diffraction pattern is somewhat complicated and the major pattern is similar to those obtained with LDH-TP. The diffraction peaks due to the LDH-NA26 are not observed in Figure 3(A). Therefore, the X-ray pattern of a mixture of three organic anions is likely to be the sum of those of LDH-TP and LDH-AQ26. The unidentified three peaks are asterisked. This is thought to be from another form of intercalated LDH, because the characteristic (003), (006), and (009) peaks are present. The interplanar spacing of another intercalated LDH is 10.5 Å. Kanazaki *et al.* observed two values (*ca.* 19 Å or *ca.* 12 Å) of enhanced interlayer distance in the intercalate of AQ26 in a Mg/Al-LDH.<sup>17</sup> It was interpreted that steric hindrance of the bulky anthraquinone moiety was responsible for the differences in the packing of the interlayer molecules. However, we observed only an 18.5 Å interlayer distance in a Zn/Al-LDH with AQ26 as shown in Figure 1(D). We tentatively conclude that the three unidentified peaks may arise from the AQ26 in LDH with more tilt in the interlayer space, which is likely to be the form of *ca.* 12 Å of the enhanced interlayer distance in the intercalate of AQ26 in a Mg/Al-LDH. Judging from the X-ray diffraction pattern of a mixture of three organic anions, the TP is mostly intercalated into the Zn/Al-LDH. However, it is difficult to measure the amount of each of the intercalated anions into the LDH from the X-ray diffraction pattern. The amount of intercalated anions could be determined by HPLC, after dissolving the LDH layers with a few drops of acid. The retention times of TP, NA26, and AQ26 on C<sub>18</sub> columns are 2.31, 3.11, and 3.64 min, respectively. HPLC data showed that 26.2% of TP and 73.8% of AQ26 are co-intercalated, whereas NA26 is not intercalated into the LDH. From the HPLC data, we conclude that the AQ26 is mostly intercalated into the Zn/Al-LDH. Moreover, HPLC data showed only two peaks with TP and AQ26 positions. The three unidentified peaks in Figure 3(A) must have arisen from TP or AQ26. Therefore, the three unidentified peaks may have arisen from the AQ26 in LDH with a more tilted form.

To confirm the preferential intercalation, the intercalation



**Figure 3.** X-ray diffraction patterns and Miller indices of (A) a mixture of TP, NA26, and AQ26, (B) a mixture of TP and NA26, (C) a mixture of NA26 and AQ26, and (D) a mixture of TP and AQ26 into the Zn/Al-LDH. (▽, ◆ and ★ represent the XRD peaks of LDH-TP, LDH-AQ26, and LDH-AQ26 (with more tilted form), respectively.

compound of a mixture of TP and NA26 was also synthesized. Figure 3(B) shows the XRD of the intercalation compound of a mixture of TP and NA26 into the Zn/Al-LDH. The (003) diffraction peak and the higher-order peaks of the LDH-NA26 are not observed in Figure 3(B). It seems that the only TP is intercalated into the Zn/Al-LDH.

**Table 1.** Preferential intercalation of three different organic anions into the interlayer of Zn/Al-LDH

mixtures of organic anions	Intercalated organic anions into the Zn/Al-LDH, mol %		
	TP	NA26	AQ26
TP+NA26+AQ26	26.2	0	73.8
TP+NA26	100	0	-
NA26+AQ26	-	0	100
TP+AQ26	24.8	-	75.2

HPLC data show that 100% of the TP is intercalated. It indicates that the shape and size of the anion play an important role in the specific interaction between LDH and guest anions. Since the product was aged for 7 days, the XRD patterns of the product come from the final step of the intercalation processes. Figure 3(C) shows the XRD of the intercalation compound of a mixture of NA26 and AQ26 into the Zn/Al-LDH. The (003) diffraction peak and the higher-order peaks of the LDH-AQ26 are only observed in Figure 3(C). AQ26 is more strongly intercalated than NA26 into the LDH. HPLC data showed that AQ26 is only intercalated, which confirms the XRD data in Figure 3(C). Therefore, we conclude that the molecular interaction of NA26 into the Zn/Al-LDH is much weaker than those of TP and AQ26. Figure 3(D) shows the XRD of the intercalation compound of a mixture of TP and AQ26 into the LDH. The X-ray diffraction pattern is complicated as is the sum of those of LDH-TP and LDH-AQ26 with another tilted form of LDH-AQ26, which are asterisked. HPLC data show that 24.8% of the TP and 75.2% of the AQ26 are co-intercalated. This HPLC data is similar to that obtained with a mixture of TP, NA26, and AQ26, whereas the XRD line intensities in Figure 3(A) are different from those in Figure 3(D). Therefore, we observed the preferential intercalations of organic anions for Zn/Al-LDH, as shown in Table 1.

This preferential intercalation indicates the presence of a molecular recognition ability of the Zn/Al-LDH and the ability of intercalation into Zn/Al-LDH is in the order AQ26 > TP >> NA26. From this experiment, it is considered that the AQ26 strongly interacts with the Zn/Al-LDH, whereas NA26 interacts little with the Zn/Al-LDH. Since AQ26, NA26, and TP have the same negative charge per molecule, the anion charge does not play an important role in the intercalation into LDH. Whereas the molecular size of the anion is in the order AQ26 > NA26 > TP, the ability of intercalation into LDH is in the order AQ26 > TP >> NA26. The mechanism of preferential intercalation depending on the shape of guest anions is still under investigation.

## Conclusions

We have synthesized the intercalated compounds of TP, NA26, and AQ26 into the Zn/Al-LDH, and X-ray diffraction data reveal that the intercalated anions are arranged with their molecular planes perpendicular to the hydroxide layer. Therefore, the molecular line which connects the two oxygen atoms in the two sulfonate (or carboxylate) groups of intercalated anions is nearly perpendicular to the layer of the double hydroxides. Preferential intercalations of organic

anions were observed for Zn/Al-LDH. A molecular recognition ability of intercalation into Zn/Al-LDH is in the order AQ26 > TP >> NA26. The shape of the anion plays an important role in the specific intercalation.

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## Studies on Solvent Extraction and Flotation Technique Using Metal-Dithizone Complexes(II). Determination of Trace Elements in Water Samples by Solvent Sublation

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The preconcentration and determination of trace elements in water samples were studied by a solvent sublation utilizing dithizonate complexation. After metal dithizonates were formed, trace amounts of cadmium, cobalt, copper and lead were floated and extracted into small volume of a water-immiscible organic solvent on the surface of sample solution and determined in the solvent directly by GF-AAS. Several experimental conditions as formation condition of metal-dithizonate complexes, pH of solution, amount of dithizone, stirring time, the type and amount of surfactants, N<sub>2</sub> bubbling rate and so on were optimized for the complete formation and effective flotation of the complexes. And also four kinds of light solvents were compared each other to extract the floated complexes, effectively. After the pH was adjusted to 4.0 with 5 M HNO<sub>3</sub>, 8.0 mL of 0.05% acetone solution of dithizone was added to 1.00 L water sample. The dithizonate complexes were floated and extracted into the upper methyl isobutylketone (MIBK) layer by the addition of 2.0 mL 0.2% ethanolic sodium lauryl sulfate solution and with the aid of small nitrogen gas bubbles. And this solvent sublation method was applied to the analysis of real water samples and good results of more than 85% recoveries were obtained in spiked samples.

### Introduction

At present, an importance and necessity of accurate informations about trace elements in various kinds of

samples increases with the industrial development in our society. Spectrochemical, electrochemical and radiochemical methods are widely used for the determination of trace elements to get the information. But although such methods