Direct Synthesis of Intercalation Compounds between a Layered Double Hydroxide and an Anionic Dye

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Intercalation compounds between a layered double hydroxide and an anionic dye were directly synthesized by hydrolysis of mixed solutions of aluminium nitrate, magnesium nitrate, and the anionic dyes (indigo carmine or new coccine). The intercalated indigo carmine anions are possibly arranged with their molecular planes perpendicular to the hydroxide layers. The basal spacings of the new coccine intercalates suggested that the configuration of the new coccine anions in the interlayers changed upon washing. Intercalation of the dyes by anion exchange from layered double hydroxides with NO_3^- or Cl^- as the interlayer anions was also conducted for comparison.

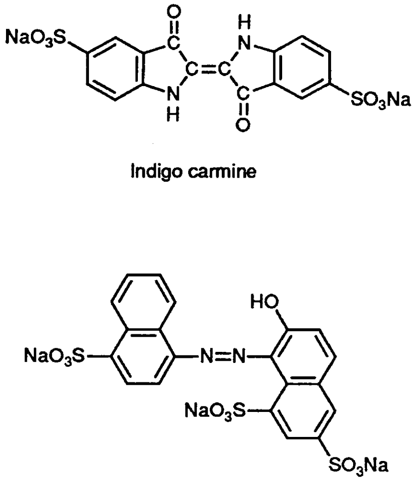
Layered double hydroxides (l.d.h.s) are hydrotalcite-like compounds, and those of magnesium and aluminium, for example, are expressed according to the formula $[Mg_{1-x}Al_x(OH)_2(A^{n-})_{x/n}]\cdot mH_2O$, where $0.2 < x \leqslant 0.33$ and A is the interlayer anion.[1] The crystal structures consist of positively charged brucite-like octahedral hydroxide layers and negatively charged interlayers. The interlayers are composed of anions, which are exchangeable, and water molecules. Several divalent and trivalent cations can form l.d.h.s with various interlayer anions (A). Since the synthesis of l.d.h.s was developed by Feitknecht and Fischer,[2] these compounds have been extensively investigated as anion exchangers, catalysts, adsorbents, and so on.[3,4]

There have been several reports on the intercalation of organic anions into l.d.h.s.[5–13] The main synthetic route has been by anion exchange. Only a few studies have been carried out using direct synthesis, in spite of the possibility of preparing novel intercalation compounds using this method that are not accessible by anion exchange. Layered double hydroxides of aluminium with zinc, magnesium, and nickel, intercalated respectively with dicarboxylates,[5] terephthalate,[11] and sebacate[13] have been investigated so far. Among the various organic substances used as the interlayer guest species, dyes are one of the most interesting materials because their host–guest interaction may provide unique structural features and physicochemical properties. Several papers have already appeared on the synthesis of clay–dye intercalation compounds and their significant spectral properties highlighted.[14–17] Intercalation compounds between a layered double hydroxide and an anionic dye [l.d.h. (A = anionic dye)] are expected to have several uses such as in pigments and in the recovery of anionic dyes from waste water. However, with regard to the intercalation of anionic dyes into l.d.h.s, Miyata[3] reported only the anion exchange of Naphthol Yellow S and found that the dianion had a high ion selectivity despite its large ionic size.

In this study, two anionic dyes, indigo carmine and new coccine, which are known to be colour additives for food, have been selected. Intercalation of these dyes into l.d.h.s was attempted by both direct synthesis and anion exchange.

Experimental

Materials.—The compounds $MgCl_2\cdot6H_2O$, $Mg(NO_3)_2\cdot6H_2O$, $AlCl_3\cdot6H_2O$, and $Al(NO_3)_3\cdot9H_2O$ were of guaranteed reagent grade. Indigo carmine {disodium 2-(1,3-dihydro-3-oxo-5-sulpho-2*H*-indol-2-ylidene)-2,3-dihydro-3-oxo-1*H*-indole-5-sulphonate} was obtained from Kanto Chemical Co., Inc. and new coccine {trisodium 7-hydroxy-8-[(4-sulpho-1-naphthalenyl)azo]-1,3-naphthalenedisulphonate} from Junsei Chemical Co., Ltd. These dyes were used without further purification.


Indigo carmine

New coccine

Scheme.

Direct Synthesis of l.d.h (A = Anionic Dye) Intercalation Compounds.—The l.d.h (A = anionic dye) intercalation compounds were directly synthesized by hydrolysis of the mixed aqueous solutions of magnesium nitrate (0.075 mol dm^{-3}), aluminium nitrate (0.025 mol dm^{-3}), and an anionic dye (0.025 mol dm^{-3}) at pH 10—11 by dropwise addition of an aqueous sodium hydroxide solution (0.5 mol dm^{-3}) with vigorous stirring under a nitrogen atmosphere. The amounts of indigo carmine and new coccine, which form 2− and 3− anions, corresponded to 2 and 3 equivalents of the stoicheiometric interlayer anions calculated from the aluminium contents, respectively. After the suspensions were aged to 60 °C for 2 d, the products were washed with decarboxylated water and dried under reduced pressure at ambient temperature in order to reduce the effect of carbonate anions.

Preparation of l.d.h.s (A = Anionic Dye) by Anion Exchange.—A l.d.h. with NO_3^- as the interlayer anion [l.d.h. (A = NO_3^-)] was prepared by adding an aqueous sodium hydroxide solution

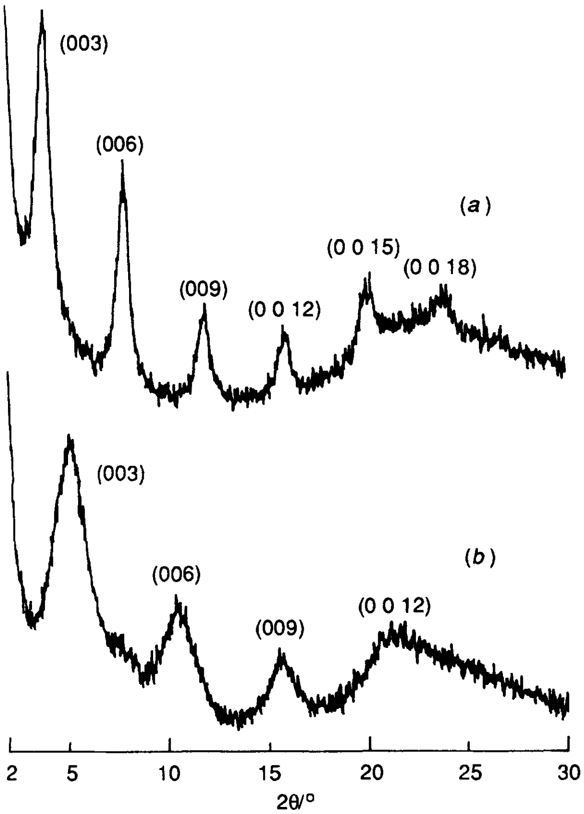


Figure 1. *X*-Ray diffraction patterns of oriented samples (after washing) formed by direct synthesis: (*a*) l.d.h. (A = ic) and (*b*) l.d.h. (A = nc) intercalation compounds

Table. Basal spacings of the l.d.h. (A = anionic dye) intercalation compounds

		Basal spacing/Å	
		L.d.h (A = ic)	L.d.h. (A = nc)
Direct synthesis	Unwashed	22.2	22.4
	Washed	22.2	16.8
Anion exchange	Unwashed	21.9	22.2
	Washed	21.2	16.5

(1 mol dm^{-3}) to a mixed aqueous solution of magnesium nitrate and aluminium nitrate at pH 10—11 under a nitrogen atmosphere. The total cation content was 0.4 mol dm^{-3} and Al/(Mg + Al) = 0.25. The precipitate was aged at 80 °C for 2 d, washed with decarboxylated water, and dried under reduced pressure at ambient temperature.

The analogue l.d.h. (A = Cl^-) was prepared in a similar manner from magnesium chloride and aluminium chloride. In addition, the l.d.h. (A = CO_3^{2-}) was also prepared by this method, using a mixed aqueous solution of sodium hydroxide (1 mol dm^{-3}) and sodium carbonate (0.2 mol dm^{-3}), and a mixed aqueous solution of magnesium chloride and aluminium chloride. This time, the experiment was conducted in air and deionized water used throughout. The formation of the l.d.h.s (A = NO_3^-, Cl^-, or CO_3^{2-}) was confirmed by *X*-ray diffraction, i.r. spectroscopy, and chemical and thermal gravimetric (t.g.) analyses.

The anion-exchange capacities of the l.d.h.s (A = NO_3^- or Cl^-) were *ca.* 2.5 mequiv. g^{-1}, which were about 85% of the calculated values based on the aluminium contents. The remaining interlayer anions may be carbonates. The l.d.h. (A = NO_3^-, Cl^-, or CO_3^{2-}) was introduced into the anionic dye aqueous solutions (0.2 mol dm^{-3}, *i.e.* five times the anion-exchange capacities of l.d.h.s), and stirred at 60 °C for 3 d. The suspensions were washed with decarboxylated water and dried under reduced pressure at ambient temperature.

Characterization.—Oriented samples of the l.d.h.s (A = anionic dye) were prepared by drying suspensions onto glass slides for *X*-ray diffraction measurements, which were obtained with a Rigaku RAD-IC diffractometer using Ni-filtered Cu-K_α radiation. Infrared spectra were recorded on a Perkin-Elmer FT-IR 1640 spectrometer using KBr pellets, u.v.-visible spectra on a Hitachi U-3200 spectrophotometer, and t.g. curves on a Shimadzu DT-40 apparatus at a heating rate of 10 °C min^{-1} in air. The aluminium and magnesium contents of the products were determined using an inductively coupled argon plasma emission spectrometer (Nippon Jarrell-Ash ICAP-575II) and the chloride and nitrate contents using an ion-chromatographic analyser (Yokogawa IC-100). The dye content of the products was calculated by C, H, and N elemental analyses.

Results and Discussion

Intercalation compounds between a layered double hydroxide and an anionic dye were formed by the hydrolysis of mixed solutions of aluminium nitrate, magnesium nitrate, and the anionic dye with a sodium hydroxide solution. Figure 1 shows the *X*-ray diffraction patterns of the oriented samples after washing. Compared to l.d.h.s with small interlayer anions such as Cl^-, NO_3^-, or CO_3^{2-},[3] both the (003) diffraction peaks and the higher order peaks shifted to lower 2θ angles.

The *X*-ray diffraction patterns of the dye-exchanged samples obtained from the l.d.h.s (A = NO_3^- or Cl^-) were similar to those of the compounds synthesized directly. When the l.d.h. (A = CO_3^{2-}) was employed as a starting material, no change in the diffraction pattern was evident, indicating that an anion-exchange reaction had not occurred. This can be explained by the smaller dissociation constant of the l.d.h. (A = CO_3^{2-}) compared with those with NO_3^- or Cl^- interlayer anions.

The basal spacings (d_{003}) of the l.d.h.s (A = anionic dye) prepared by direct synthesis and anion exchange are listed in the Table. The basal spacings of the dye-exchanged materials were similar to those of the compounds synthesized directly and the basal spacings of the indigo carmine intercalates changed little before and after washing. The length of the indigo carmine anion, estimated from the distance between sulphonate groups in the anion, is *ca.* 17.2 Å, when the van der Waals radius of oxygen is assumed to be 1.4 Å. The area occupied by the molecular plane of the indigo carmine anions was estimated to be *ca.* 110 Å^2. From the relation between the lattice parameters *vs.* the composition x[= Al/(Mg + Al)] in the Mg–Al system,[1] the charge density in the hydroxide layer was *ca.* 30 Å^2 per unit negative charge, when x = 0.26—0.27. Based on the basal spacings, the ionic size, and the layer charge density, it is suggested that the indigo carmine anions are arranged with their C=C axes nearly perpendicular to the brucite layers.

The basal spacings of the l.d.h. (A = nc, anion of new coccine) intercalation compounds diminished appreciably by washing. The length of the new coccine anion was calculated to be *ca.* 17.5 Å using the distance between the more remote sulphonate groups in the anion, and the width of the new coccine molecular plane was estimated to be *ca.* 10.5 Å. Although the area calculated from the length and the width is *ca.* 180 Å^2, the discrete area occupied by the anion was estimated to be *ca.* 140 Å^2. The gallery height between the

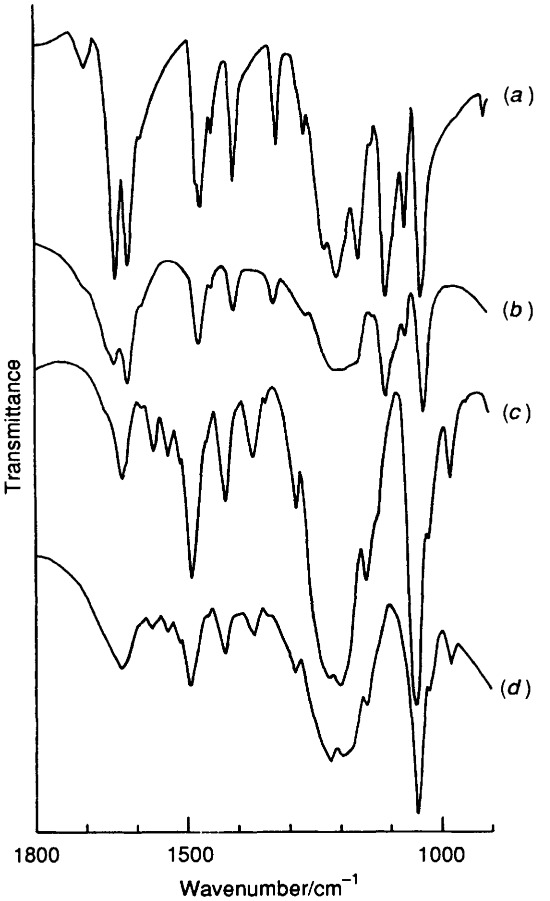


Figure 2. I.r. spectra of (*a*) indigo carmine, (*b*) the l.d.h. (A = ic) intercalation compound, (*c*) new coccine, and (*d*) the l.d.h. (A = nc) intercalation compound

hydroxide layers of the unwashed l.d.h. (A = nc) sample corresponds approximately to the length described above. Therefore, from the basal spacing, the ionic size, and the charge density in the brucite layer, the new coccine anions in the unwashed compounds may be arranged with the connecting lines between two side sulphonate groups vertical to the hydroxide layers. On the other hand, the gallery height of the washed sample nearly corresponded to the width of the new coccine molecular plane. The reason for this alteration may be explained by the assumption that the excess of intercalated dye was removed during washing and the dissociated middle sulphonate group may play a role in the interaction with the hydroxide layers.

The i.r. spectra of the anionic dyes and the l.d.h. (A = anionic dye) intercalation compounds are shown in Figure 2. The i.r. absorption bands of the intercalation compounds corresponded to those of the dye salts. The sulphonate absorption bands of the intercalation compounds at 1 050—1 025 cm^{-1} shifted slightly to lower frequency regions, in comparison with those of the dye salts. This fact indicates that the interactions between the intercalated dye anions and the hydroxide layers are different from those in the dye salts.

The u.v.-visible diffuse reflectance spectra of the intercalation compounds in the solid state were similar to those of the solid-state dye salts but different from the visible absorption spectra of the aqueous dye-salt solutions. These facts suggest that the dye anions are rather closely packed in the interlayer spaces.

The ratios of magnesium to aluminium in the l.d.h.s (A = anionic dye) synthesized directly were 0.74:0.26 (A = ic, anion of indigo carmine) and 0.73:0.27 (A = nc), which were slightly different from the initial mixing ratios. The total water contents were 16.5 (A = ic) and 11.0 wt.% (A = nc), respectively. The water contents obtained from the first weight losses contained the adsorbed and the interlayer waters, which could not be measured separately by t.g. analysis. However, the water contents did not affect the basal spacings, confirmed by the fact that the basal spacings of the heat-treated l.d.h.s (A = anionic dye) at 300 °C did not change. The ideal formulae of the intercalation compounds, based on the magnesium to aluminium ratios, can thus be expressed as $[Mg_{0.74}Al_{0.26}(OH)_2(ic)_{0.13}]\cdot mH_2O$ and $[Mg_{0.73}Al_{0.27}(OH)_2(nc)_{0.09}]\cdot mH_2O$. The validity of these formulae was confirmed by C, H, and N elemental analyses and although the H data could not be utilized because of the presence of water, the C and N values were compatible with the calculated ones {Found: C, 17.9; N, 2.55. Calc. for $[Mg_{0.74}Al_{0.26}(OH)_2(ic)_{0.13}]\cdot mH_2O$ based on the Al content (5.13%): C, 18.3; N, 2.65. Found: C, 17.0; N, 2.25. Calc. for $[Mg_{0.73}Al_{0.27}(OH)_2(nc)_{0.09}]\cdot mH_2O$ based on the Al content (6.39%): C, 18.9; N, 2.20%}. The i.r. spectra of these compounds did not show the presence of carbonate anions.

The organic contents of the l.d.h. (A = anionic dye) intercalation compounds prepared by anion exchange nearly corresponded to the anion-exchange capacities of the l.d.h. (A = NO_3^- or Cl^-) starting materials. Thus the anionic dyes were easily intercalated into the l.d.h.s, although they are large in size. However, when the l.d.h. (A = Cl^-) was anion-exchanged in an indigo carmine solution, where the amount of dye was twice the anion-exchange capacity of the l.d.h., the unreacted l.d.h. (A = Cl^-) phase was detected by *X*-ray diffraction analysis. Based on the intensities of the (003) diffraction lines of the l.d.h. (A = ic) and the unreacted l.d.h. (A = Cl^-), the intercalated-dye content was estimated to be *ca.* 75% of the anion-exchange capacity. Thus, the l.d.h. (A = ic) synthesized directly could accommodate a greater amount of dye than that formed by anion exchange. In our recent publication,[12] when the l.d.h. (A = Cl^-) was used as the starting material, monovalent acrylate anions were exchanged only in a highly concentrated solution. However, the present dye anions were easily exchanged when l.d.h. (A = Cl^-) was used. This different exchange property may be mainly due to the difference between their ion selectivities arising from the different charges of the intercalated anions.

In conclusion, l.d.h. (A = anionic dye) intercalation compounds have been formed by direct synthesis and anion exchange. The compounds synthesized directly contain few carbonate anions, and the intercalated dye contents correspond to the layer charges based on the aluminium contents. The dye contents of the anion-exchanged products nearly correspond to the anion-exchange capacities. From the present experiment, it is considered that the dianion of indigo carmine and the trianion of new coccine used as anionic dyes possess high ion selectivities, despite their large size.

Acknowledgements

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