

## Intercalation of Dyes Containing SO<sub>3</sub>H Groups into Zn–Al Layered Double Hydroxide

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### Abstract

The intercalates of Naphthol Yellow S, Tropaeolin 000, and Tropaeolin 00 were prepared by heating [Zn<sub>0.67</sub>Al<sub>0.33</sub>(OH)<sub>2</sub>](CO<sub>3</sub>)<sub>0.165</sub> · 0.5H<sub>2</sub>O with acidic forms of the dye solutions in an open reaction vessel. The intercalates were characterized by chemical and thermal analysis, X-ray powder diffraction and UV–VIS spectroscopy. A possible arrangement of the dye molecules in the intercalates was suggested on the basis of their chemical compositions and interlayer distances, by taking into account van der Waals dimensions of the guest molecules and by assuming that the structure of the host layers is not changed during the intercalation process.

### Introduction

Hydrotalcite-like compounds (HTlcs) or layered double hydroxides (LDHs) are host materials that are of interest because of their potential application as catalysts, sorbents, hosts for nanoscale reactions as well as in medicine as antacids [1–5]. In general HTlcs may be represented by the general formula [M<sup>II</sup><sub>(1-x)</sub>M<sup>III</sup><sub>x</sub>(OH)<sub>2</sub>][x/nA<sup>n-</sup>] · mH<sub>2</sub>O, where M<sup>II</sup> (typically Mg, Zn, Ni, and Co) and M<sup>III</sup> (Al, Cr, or Fe) are divalent and trivalent cations, respectively. A<sup>n-</sup> are exchangeable anions of charge *n* which compensate positive charge induced by the presence of M<sup>III</sup> in the layers. The anions are accommodated in the interlayer region, where water molecules are also located. Therefore, functional organic or organometallic species with anionic groups (carboxylate, phosphonate, sulfonate) can be intercalated in this class of layered hosts.

Three main methods for the preparation of intercalates with relatively large organic guest have been reported. The first one is a conventional anion exchange [6–9]. It is known that the carbonate anions are strongly held in the interlayer region and it is difficult to replace them with other counter anions [10]. So HTlcs containing chloride or perchlorate anions are usually used as precursors for the exchange reactions. Secondly, organic cations may be incorporated directly by coprecipitation [1, 11, 12]. The third method is based on the fact that M<sup>II</sup>–M<sup>III</sup> mixed oxides, obtained by calcination of a HTlc at about 500 °C, adsorb anions from their aqueous

solutions during the reconstruction of the HTlc structure (the so-called memory effect) [4, 13–16].

In this work, intercalations of Naphthol Yellow S (2,4-dinitro-1-naphthol-7-sulfonic acid sodium salt), Tropaeolin 000 (4-(4-hydroxy-1-naphthylazo)benzenesulfonic acid sodium salt), and Tropaeolin 00 (4-[(4-anilinophenyl)azo]benzenesulfonic acid sodium salt) into [Zn<sub>0.67</sub>Al<sub>0.33</sub>(OH)<sub>2</sub>](CO<sub>3</sub>)<sub>0.165</sub> · 0.5H<sub>2</sub>O are reported. Structural formulas of the anions intercalated are given in Figure 1.

### Experimental

A large amount of Zn–Al–CO<sub>3</sub>, with the formula [Zn<sub>0.67</sub>Al<sub>0.33</sub>(OH)<sub>2</sub>](CO<sub>3</sub>)<sub>0.165</sub> · 0.5H<sub>2</sub>O, was prepared by an urea method [17]. A solution obtained by mixing 100 mL of 0.5 M AlCl<sub>3</sub>, 200 mL of 0.5 M ZnCl<sub>2</sub> and 30 g of urea was refluxed for 2 days. The precipitate obtained was filtered, washed with distilled water and equilibrated with 100 mL of 0.1 M Na<sub>2</sub>CO<sub>3</sub> for one day. Then the solid was recovered by filtration, washed with distilled water and dried in air.

Sodium salts of the dyes were converted into their acid forms by stirring their aqueous solution with an Amberlite IR 120 ion-exchange resin. All intercalates were prepared by reaction of 1.23 g (2 mmol) of Zn–Al–CO<sub>3</sub> with the solutions of the acid forms of the dyes. The reaction mixtures were heated at 90 °C with stirring in an open vessel for 48 h. The volume of the reaction mixture (400 mL) was kept constant by an automatic addition of distilled water [18]. The intercalates prepared were filtered, washed with CO<sub>2</sub>-free distilled water and

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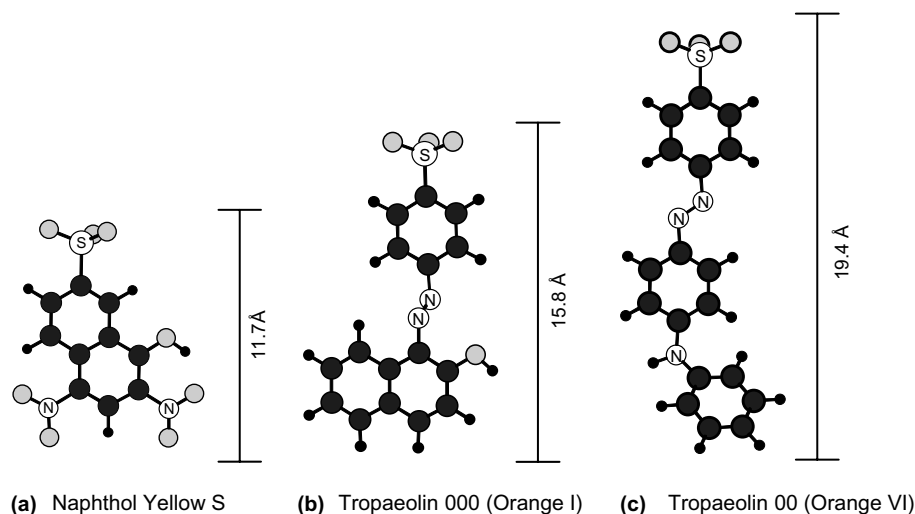


Figure 1. Structural formulas of the anions of the dyes used.

dried. An excess of the dye was removed from the surface of the intercalates by extraction with ethanol. After extraction, the samples were kept in a desiccator containing a NaBr saturated solution (58% RH). The contents of zinc, aluminium and sulfur were determined by an energy-dispersive X-ray spectrometry (EDX) microanalysis. The contents of carbonate and the dye anions were determined by elemental analysis (C, H, N, S) and water contents were calculated from thermogravimetry. The amounts of the dyes (sodium salts) used for the intercalation together with the results of elemental analysis are given in Table 1.

Samples with the dye adsorbed on surface were prepared by stirring of Zn–Al–CO<sub>3</sub> with a solution of sodium salt of the corresponding dye at room temperature overnight. The samples prepared were filtered, washed with small amount of distilled water and dried.

Powder X-ray diffraction data were obtained with a D8-Advance diffractometer (Bruker AXE, Germany) using CuK $\alpha$  radiation with secondary graphite monochromator. Diffraction angles were measured from 2 to 70° (2 $\theta$ ). In-situ temperature XRD measurement was carried out in a MRI chamber from 30 to 320 °C. Diffraction angles were measured from 2 to 25° (2 $\theta$ ). The TG analyses were performed using a Derivatograph C (MOM Budapest, Hungary). The measurements were

carried out in air between 20 and 900 °C at a heating rate of 5 K min<sup>-1</sup>. UV–VIS absorption spectra of the solids were measured using a Perkin-Elmer Lambda 12 spectrometer in a nujol suspension containing 15% of the sample.

## Results and discussion

None of the dyes studied could be intercalated into Zn–Al–CO<sub>3</sub> using sodium salt of the corresponding dye. Only in the case of Tropaeoline 00, partial exchange of carbonate was observed when Zn–Al–CO<sub>3</sub> was heated with a Tropaeoline 00 sodium salt solution. The carbonate ions are strongly held in the interlayer region and it is difficult to replace them with other anions. This replacement could be favored by removing the carbonate ions from the solution. This could be done easily by heating Zn–Al–CO<sub>3</sub> with the acidic form of the dye solution in an open reaction vessel. Single-phase products were prepared by this way. The compositions of the intercalates obtained from elemental analysis and TGA are given in Table 1. As can be seen from the formulas, all intercalates prepared contained some carbonate anions.

Table 1. Formulas of the intercalates prepared and the results of elemental analysis

Dye	Dye amount (g)	Formula	Found/calculated				
			C	H	N	S	Weight loss
Tropaeolin 00	2.25 (6 mmol)	Zn <sub>0.67</sub> Al <sub>0.33</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>0.05</sub> (C <sub>18</sub> H <sub>14</sub> N <sub>3</sub> O <sub>3</sub> S) <sub>0.23</sub> ·0.5H <sub>2</sub> O	27.22/27.96	3.15/3.61	5.40/5.37	3.99/4.10	58.9/60.4
Tropaeolin 000	2.10 (6 mmol)	Zn <sub>0.67</sub> Al <sub>0.33</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>0.04</sub> (C <sub>16</sub> H <sub>11</sub> N <sub>2</sub> O <sub>4</sub> S) <sub>0.25</sub> ·0.5H <sub>2</sub> O	26.33/26.96	3.09/3.22	4.08/3.90	4.39/4.45	61.6/60.4
Naphthol Yellow	1.87 (6 mmol)	Zn <sub>0.67</sub> Al <sub>0.33</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>0.10</sub> (C <sub>10</sub> H <sub>5</sub> N <sub>2</sub> O <sub>8</sub> S) <sub>0.13</sub> ·0.5H <sub>2</sub> O	11.53/11.82	2.49/2.52	2.84/2.56	3.03/2.93	50.6/49.9

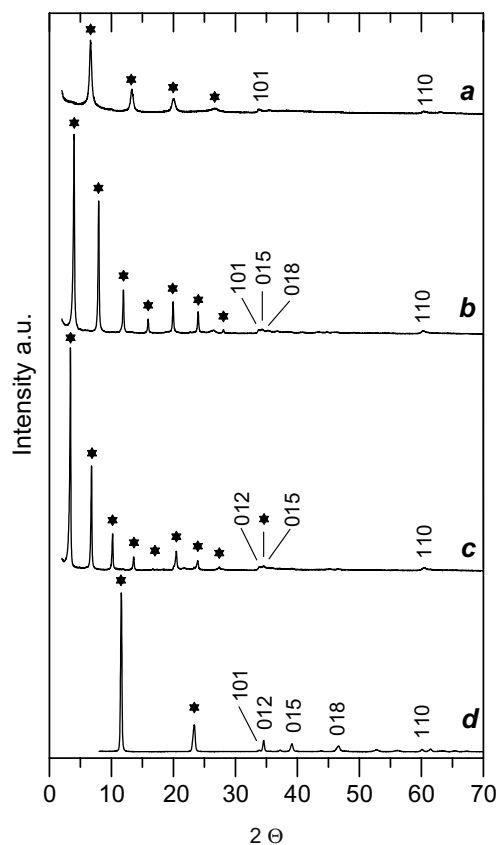


Figure 2. X-ray diffractograms of Naphthol Yellow (a), Tropaeolin 000 (b), Tropaeolin 00 (c) intercalates, and pure  $[\text{Zn}_{0.67}\text{Al}_{0.33}(\text{OH})_2(\text{CO}_3)_{0.165} \cdot 0.5\text{H}_2\text{O}]$  (d). (0 0  $l$ ) reflections are marked with an asterisk.

The intercalates prepared were crystalline solids. Figure 2 shows typical X-ray diffractograms of the intercalates prepared together with the diffractogram of the pure host. The 7.60 Å reflection corresponding to the most intensive (0 0 3) line of the pure host was not observed in the diffractograms of the intercalates. A series of sharp intensive (0 0  $l$ ) diffraction lines was observed in the diffractograms together with several ( $h k l$ ) lines with low intensity. All diffraction lines could be indexed in a hexagonal lattice with lattice parameters given in Table 2. As follows from XRD, if the carbonate anions are present in the intercalates, then they occur in the interlayer space together with the dye anions. The found value of basal spacing of the Naphthol Yellow intercalate (13.35 Å) is very similar to the value observed

Table 2. Lattice parameters of the intercalates prepared, the increase of the basal spacing and the van der Waals lengths of the dye anions

Dye	$a$ (Å)	$c$ (Å)	$\Delta d^a$ (Å)	$l$ (Å)
Tropaeolin 00	3.069 (1)	77.97 (8)	21.53	19.4
Tropaeolin 000	3.070 (1)	66.80 (3)	17.81	15.8
Naphthol Yellow	3.068 (2)	40.06 (9)	8.89	11.7

<sup>a</sup> $\Delta d = c/3 - d_l$  where  $c/3$  is the basal spacing and  $d_l$  is the thickness of the host layer (4.46 Å).

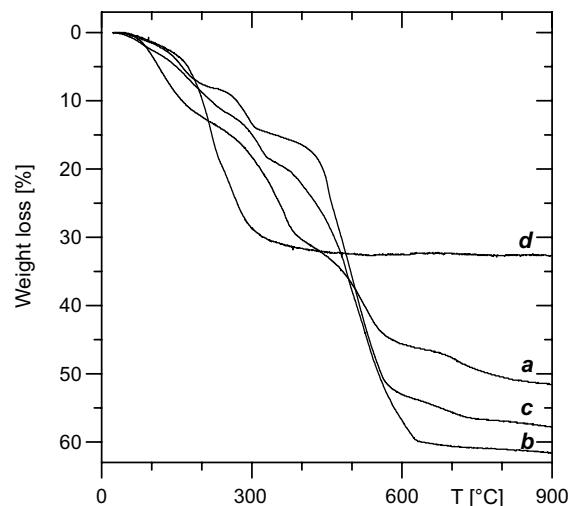


Figure 3. Thermogravimetric curves of Naphthol Yellow (a), Tropaeolin 000 (b), Tropaeolin 00 (c) intercalates, and pure  $[\text{Zn}_{0.67}\text{Al}_{0.33}(\text{OH})_2(\text{CO}_3)_{0.165} \cdot 0.5\text{H}_2\text{O}]$  (d).

by Miyata [8] for Mg–Al–Cl HTlc exchanged with Naphthol Yellow (13.00 Å).

The thermogravimetric curves of the intercalates and the parent host are shown in Figure 3. Zn–Al–CO<sub>3</sub> decomposed in one step so that it was not possible to distinguish weight losses caused by the release of interlayer water, CO<sub>2</sub> from the carbonate anions, and water from dehydroxylation of HTlc. The intercalates decomposed in three steps. The first two weight losses were probably caused by a release of both types of water and CO<sub>2</sub>. The decomposition of the intercalated dyes occurred in the third step above 300 °C.

The thermal behavior of the intercalates was followed by in situ X-ray diffraction. The thermal dependences of the basal spacing are given in Figure 4. In the case of the Naphthol Yellow intercalate, the basal spacing decreased from 13.35 Å at room temperature to 13.01 Å at 100 °C.

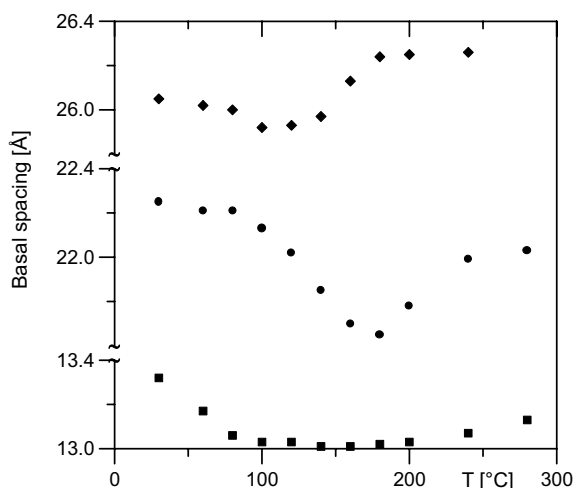


Figure 4. Temperature dependences of the basal spacing of Naphthol Yellow (squares), Tropaeolin 000 (circles), Tropaeolin 00 (diamonds).

Above this temperature, the diffraction lines were broadened and their intensities decreased. In the case of the Tropaeolin 00 intercalate, a small decrease of the basal spacing (from 26.05 to 25.92 Å) was observed up to 100 °C. The basal spacing significantly increased from 140 to 180 °C (26.24 Å at 180 °C). The phase formed at 180 °C was still a well-crystalline solid as follows from the sharp and intensive (0 0 *l*) lines. The Tropaeolin 000 intercalate behaved similarly. A significant decrease of the basal spacing (from 22.25 to 21.65 Å) was observed between 80 and 180 °C. The basal spacing increased from 180 to 240 °C (22.00 Å at 240 °C). The phase formed at 240 °C was still a well crystalline solid. The decrease of the basal spacing of all three intercalates was probably caused by a release of cointercalated water. This dehydration process was reversible. The samples regained their original weight and basal spacing when kept at relative humidity of 76%.

Absorption spectra of the dyes in a water solution and in a solid state (pure dye salt, adsorbed or intercalated

in the Zn–Al–HTlc) are shown in Figure 5. The spectrum of the Naphthol Yellow solution had two maxima at 392 and 429 nm. In the intercalate, these maxima were shifted to the higher wavelength (404 and 442 nm). The maximum of absorbance of surface adsorbed Naphthol Yellow was shifted to the lower wavelength. The spectrum of the Tropaeolin 000 solution had a maximum at 483 nm. In the spectra of both intercalated and adsorbed dyes, this maximum was shifted to the lower wavelength (424 nm for intercalated, 392 nm for adsorbed) and a shoulder at 525 and 500 nm, respectively, appeared. The spectrum of the Tropaeolin 00 solution had a maximum at 440 nm. The surface-adsorbed dye had an absorption maximum at 380 nm and its spectrum was similar to that of the pure solid dye. In the case of the intercalated dye, the absorption band was very broadened (380–500 nm).

A possible arrangement of the guest molecules in the intercalates was suggested on the basis of their chemical compositions and interlayer distances, by taking into account the van der Waals dimensions of the guest molecules and by assuming that the structure of the host layers was not changed during intercalation process. Geometry of the dye anions was optimized using Hyperchem. The van der Waals lengths of the molecules of the dyes are given in Figure 1. Taking into account the tetrahedral geometry of the terminal  $\text{SO}_3^-$  group, the oxygens of which presumably lie on the surface of the layer in a plane parallel to the plane of the host layers, the S–C bond of the dye could be almost perpendicular to the layer similarly as in the case of Methyl Orange intercalated Zn–Al–HTlc [7]. As follows from the comparison of the van der Waals lengths of the molecules and the increase of the basal spacing  $\Delta d$  (see Table 2),

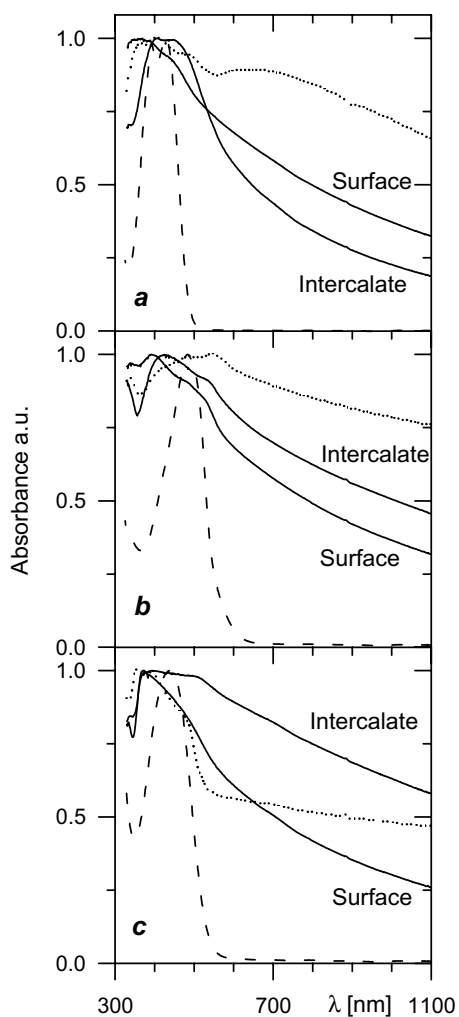


Figure 5. Normalized absorption spectra of the dye adsorbed on the Zn–Al–HTlc, intercalated in the Zn–Al–HTlc, the solid dye (dotted line) and a water solution of a dye at pH = 7 (dashed line) for Naphthol Yellow (a), Tropaeolin 000 (b) and Tropaeolin 00 (c).

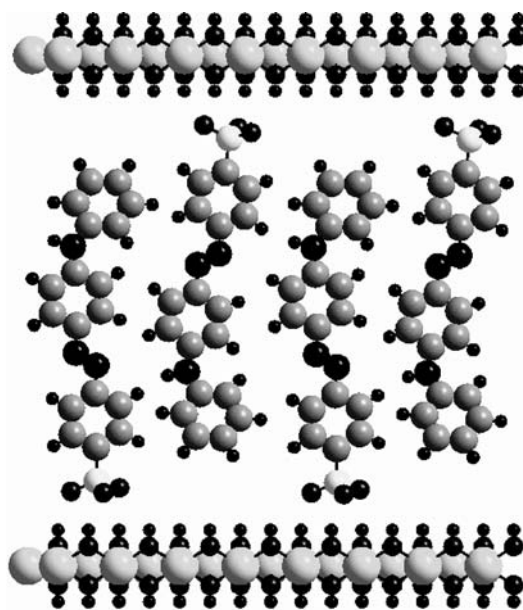


Figure 6. Probable arrangement of Tropaeolin 00 molecules in the interlayer space.

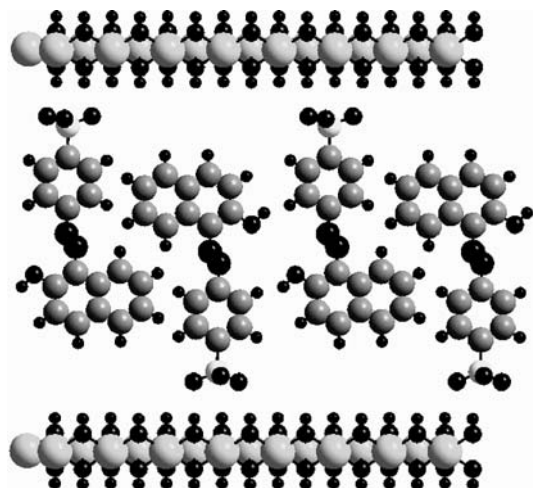


Figure 7. Probable arrangement of Tropaeolin 000 molecules in the interlayer space.

this arrangement is possible for both Tropaeolin molecules but it is not possible for Naphthol Yellow molecules for which this length is higher than  $\Delta d$ . The probable arrangements of the Tropaeolin 00 and Tropaeolin 000 molecules are shown in Figures 6 and 7, respectively. The molecules of both Tropaeolins form a monolayer of partially interdigitated species and the charge balancing  $\text{SO}_3^-$  groups lie alternately above and below the layer. As the cross section of both anions is larger than an “equivalent area” surrounding each positive charge in the brucite-like sheet ( $3 \cdot a^2 \cdot \sin 60^\circ = 25 \text{ \AA}^2$ ) [7], all positive charges cannot be compensated by the dye anions so that a part of positive charges is compensated by non-exchanged carbonate anions. These anions together with cointercalated water molecules are placed in cavities between the host layers and the guest molecules. In the case of the Naphthol Yellow intercalate, the dye molecules probably form bilayers with their naphthalene rings parallel to the host layer.

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