

Original Research Article

## Intercalation of 2-Naphthol-3,6-disulfonate, 9,10-Anthraquinone-2,6-disulfonate, and 9,10-Anthraquinone-2-sulfonate Anions into Zn–Al Layered Double Hydroxide

LUDVÍK BENEŠ\*, VÍTĚZSLAV ZIMA, JAN SVOBODA and KLÁRA MELÁNOVÁ

Joint Laboratory of Solid State Chemistry of the Institute of Macromolecular Chemistry of Academy of Sciences and University of Pardubice, Studentská 84, 532 10 Pardubice, Czech Republic

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### Abstract

The intercalates of 9,10-anthraquinone-2,6-disulfonate, 9,10-anthraquinone-2-sulfonate, and 2-naphthol-3,6-disulfonate anions were prepared by heating  $[\text{Zn}_{0.67}\text{Al}_{0.33}(\text{OH})_2](\text{CO}_3)_{0.165} \cdot 0.5\text{H}_2\text{O}$  with a solution of corresponding acid in an open reaction vessel. The intercalates were characterized by chemical and thermal analysis, X-ray powder diffraction and UV-vis spectroscopy. Thermal behavior of the intercalates prepared was followed by *in situ* X-ray diffraction. Dehydration was reversible for all three intercalates. If the samples dehydrated at 400 °C reacted with water, brucite-like layers of the host were reconstructed.

### Introduction

Layered double hydroxides (LDHs), which are often termed hydrotalcite-like compounds (HTLcs), have found use as catalysts, anion-exchangers, sorbents, hosts for nanoscale reactions as well as components of drugs in pharmaceutical industry [1–5]. HTLcs have a structure derived from that of brucite,  $\text{Mg}(\text{OH})_2$ , in which octahedra of  $\text{Mg}^{2+}$  coordinated to OH groups share their edges to form infinite sheets. When a trivalent ion is substituted for a  $\text{Mg}^{2+}$  ion, a positive charge is generated in the sheet. This charge is compensated by a counteranion placed in the interlayer region of HTlc. The hydrotalcite-like compounds have the general formula  $[\text{M}^{\text{II}}_{(1-x)}\text{M}^{\text{III}}_x(\text{OH})_2][x/n\text{A}^{n-}] \cdot m\text{H}_2\text{O}$ , where  $\text{M}^{\text{II}}$  (typically Mg, Zn, Ni, and Co) and  $\text{M}^{\text{III}}$  (Al, Cr, or Fe) are divalent and trivalent cations, respectively and  $\text{A}^{n-}$  are exchangeable anions of charge  $n$  which compensate positive charge induced by the presence of  $\text{M}^{\text{III}}$  in the layers. The anions are accommodated in the interlayer region, where water molecules are also located and together with them can be considered intercalated guest species. As the counteranions, most often carbonates but also chlorides, sulfates, nitrates etc. can serve. Regarding organic anions, functional organic or organometallic species with anionic groups (carboxylate, phosphonate, and sulfonate) can be used 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. Secondly, organic cations may be incorporated directly by coprecipitation. Thirdly,  $\text{M}^{\text{II}}\text{–}\text{M}^{\text{III}}$  mixed oxides, obtained by calcination of a HTlc, adsorb anions from their aqueous solutions during the reconstruction of the HTlc structure (the so-called memory effect).

Many reports have investigated intercalations of sulfonates into HTlc. Anthraquinone disulfonate and anthraquinone-2-sulfonate ions were intercalated into Mg–Al or Zn–Al HTLcs using coprecipitation method [6–8]. The intercalates of 2-naphthol-3,6-disulfonate were prepared by reaction of mixed Mg–Al and Zn–Al oxides with a guest solution [9].

In this work, intercalations of 9,10-anthraquinone-2,6-disulfonate (ADS), 9,10-anthraquinone-2-sulfonate (AS), and 2-naphthol-3,6-disulfonate (NDS) anions into  $[\text{Zn}_{0.67}\text{Al}_{0.33}(\text{OH})_2](\text{CO}_3)_{0.165} \cdot 0.5\text{H}_2\text{O}$  via an anion-exchange are reported and the intercalates prepared are characterized.

### Experimental

A large amount of Zn–Al– $\text{CO}_3$ , with the formula  $[\text{Zn}_{0.67}\text{Al}_{0.33}(\text{OH})_2](\text{CO}_3)_{0.165} \cdot 0.5\text{H}_2\text{O}$ , was prepared by an urea method [10]. An aqueous solution obtained by mixing 100 mL of 0.5 M  $\text{AlCl}_3$ , 200 mL of 0.5 M  $\text{ZnCl}_2$  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  $\text{Na}_2\text{CO}_3$

\* Author for correspondence. E-mail: ludvik.benes@upce.cz

Table 1. Composition and lattice parameters of the intercalates prepared

Guest	Formula	$a$ [Å]	$c$ [Å]
NDS	$[\text{Zn}_{0.67}\text{Al}_{0.33}(\text{OH})_2](\text{C}_{10}\text{H}_5\text{O}_7\text{S}_2)_{0.11} \cdot 1.5\text{H}_2\text{O}$	3.073(1)	49.05(1)
ADS	$[\text{Zn}_{0.67}\text{Al}_{0.33}(\text{OH})_2](\text{C}_{14}\text{H}_6\text{O}_8\text{S}_2)_{0.165} \cdot 2.5\text{H}_2\text{O}$	3.072(1)	56.64(3)
AS	$[\text{Zn}_{0.67}\text{Al}_{0.33}(\text{OH})_2](\text{C}_{14}\text{H}_7\text{O}_5\text{S})_{0.33} \cdot \text{H}_2\text{O}$	3.072(1)	59.72(3)

for one day. Then the solid was recovered by filtration, washed with distilled water and dried in air.

Sodium salts of the guests were converted into their acid forms by stirring their aqueous solutions with an Amberlite IR 120 ion-exchange resin. The intercalates were prepared by reactions of 1.23 g (2 mmol) of Zn–Al–CO<sub>3</sub> with the solutions of the corresponding sulfonic acids. The reaction mixtures (molar ratio Al/S = 1/2) were heated at 90 °C with stirring in an open vessel for 48 h. The volume of the reaction mixture (500 mL for NDS and ADS; 1000 mL for AS) was kept constant by an automatic addition of distilled water [11]. The intercalates prepared were filtered, washed with CO<sub>2</sub>-free distilled water and dried. An excess of the guest was removed from the surface of the intercalates by extraction with ethanol. After extraction, the samples were kept in a desiccator containing a saturated solution of NaCl to achieve 76% relative humidity (RH). The contents of zinc, aluminum and sulfur were determined by an energy-dispersive X-ray spectrometry (EDX) microanalysis. The contents of carbonate and the guest anions were determined by elemental analysis (C, H, S) and water contents were calculated from the thermogravimetry data.

The samples with the guest adsorbed on their surface were prepared by stirring Zn–Al–CO<sub>3</sub> (1.23 g) with 250 mL of a solution of sodium salt of the corresponding acid (molar ratio Al/S = 1/1) at room temperature overnight. The samples prepared were filtered, washed with a small amount of distilled water and dried.

Powder X-ray diffraction data were obtained with a D8-Advance diffractometer (Bruker AXE, Germany) using CuK<sub>α</sub> radiation with secondary graphite monochromator. Diffraction angles were measured from 2 to 70° (2θ). *In-situ* temperature XRD measurements were carried out in a MRI chamber from 30 to 320 °C. Diffraction angles were measured from 2 to 25° (2θ). 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 intercalate.

## Results and discussion

Carbonate ions are strongly held in the interlayer region of starting Zn–Al–CO<sub>3</sub> and it is difficult to replace them with other anions. Therefore, none of the guests studied

could be intercalated into Zn–Al–CO<sub>3</sub> using sodium salt of the corresponding acid. On the other hand, carbonates can be replaced by desired organic anions used in their acidic forms. This reaction is favored by removing the carbonate ions from the solution. This could be done easily by heating Zn–Al–CO<sub>3</sub> with a solution of the corresponding acid in an open reaction vessel. The products prepared in this way were single phases. The compositions of the intercalates obtained from elemental analysis and TGA are given in Table 1.

The intercalates prepared were crystalline solids. Figure 1 shows typical X-ray diffractograms of the intercalates prepared together with the diffractogram of the pure host. A series of sharp intensive (00 $l$ ) diffraction lines was observed in the diffractograms together with several ( $hkl$ ) lines with low intensity. All diffraction lines could be indexed in a hexagonal lattice with lattice parameters given in Table 1. The 7.60 Å reflection corresponding to the most intensive (003) line of the pure host was not observed in the diffractograms of the intercalates.

The found value of basal spacing of the ADS intercalate (18.88 Å) is similar to the value observed

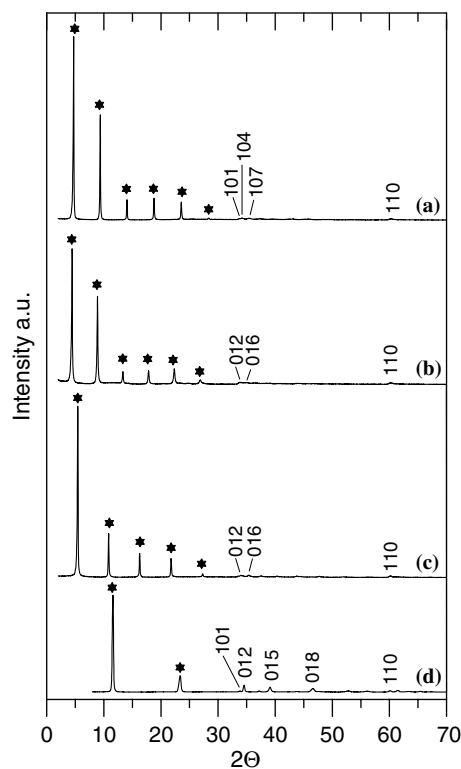


Figure 1. X-ray diffractograms of the ADS (a), AS (b), NDS (c) intercalates, and pure  $[\text{Zn}_{0.67}\text{Al}_{0.33}(\text{OH})_2](\text{CO}_3)_{0.165} \cdot 0.5\text{H}_2\text{O}$  (d). The (00 $l$ ) reflections are marked with an asterisk.

by Kuk and Huh [8] for nearly the same intercalate prepared by coprecipitation (18.31 Å). A phase with the basal spacing of 12 Å similar to the MgAl-ADS intercalate reported by Kanezaki [6] was not observed. The AS intercalate (basal spacing 19.91 Å) is very similar to that prepared via coprecipitation by Kuk (basal spacing 19.80 Å) [8].

The basal spacings of the NDS and ADS intercalates depend on relative humidity (RH) of the surrounding atmosphere. The diffractograms of both intercalates kept at 33% RH or 0% RH are given in Figure 2. Cointercalated water molecules were released from the ADS intercalate and a new phase with the basal spacing of 15.62 Å was formed at 33% RH. The basal spacing of the new phase decreased with decreasing RH and achieved 13.78 Å at 0% RH. Diffraction lines (003), (006), (009), and (0012) could be observed in the diffractogram of this phase. On the other hand, only one new reflection  $d = 13.46$  Å was present in the diffractogram of the NDS intercalate kept at 33% RH. In the diffractogram of this intercalate kept at 0% RH, the reflections were remarkably broadened and their positions were shifted. This phenomenon could be caused by a formation of a Hendricks-Teller disordered layered lattice [12, 13]. The basal spacing of the AS intercalate did not change with relative humidity.

Thermogravimetric curves of all the intercalates are shown in Figure 3. The ADS intercalate stored at 76% RH decomposed in three steps. Interlayer water was released in the first step up to 200 °C and a dehydroxylation occurred between 200 and 400 °C. Observed weight losses 23% and 9% were in good agreement with the values of 23.4% and 9.4% calculated for the sample containing 2.5 molecules of H<sub>2</sub>O per formula unit. The decomposition of intercalated ADS occurred in the third slow step above 400 °C. The total weight loss (61.2%)

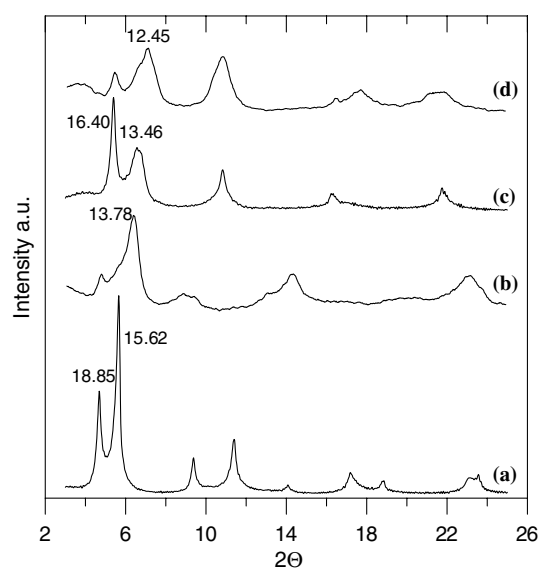


Figure 2. X-ray diffractograms of the ADS intercalate at 33% RH (a), the ADS intercalate at 0% RH (b), the NDS intercalate at 33% RH (c) and the NDS intercalate at 0% RH (d).

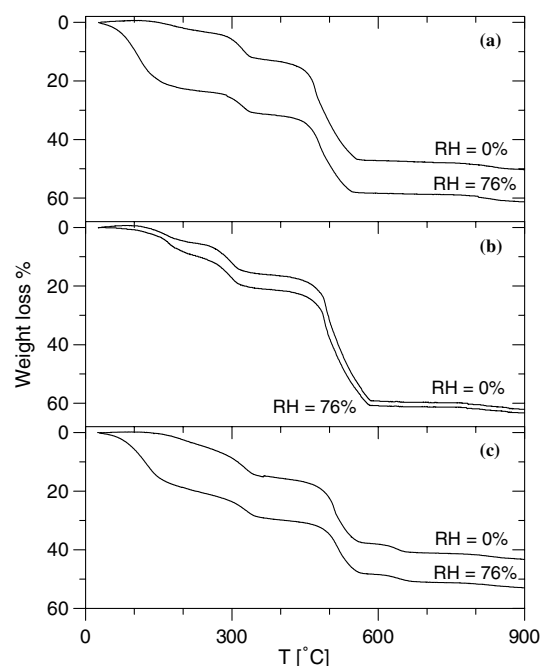


Figure 3. Thermogravimetric curves of the ADS (a), AS (b), NDS (c) intercalates kept at 76 or 0% RH.

was in good agreement with the value of 62.9% calculated for  $Zn_{0.67}Al_{0.33}(OH)_2(C_{14}H_6O_8S_2)_{0.165} \cdot 2.5-H_2O$ . The sample stored over P<sub>2</sub>O<sub>5</sub> in vacuum did not contain interlayer water. It decomposed in two steps, the first one to 400 °C (observed 13%, calculated 12.2%) corresponded to the dehydroxylation, and the second one to 600 °C corresponded to the thermal decomposition of intercalated ADS. The total weight loss (50%) was in good agreement with the value of 51.4% calculated for  $Zn_{0.67}Al_{0.33}(OH)_2(C_{14}H_6O_8S_2)_{0.165}$ .

The AS intercalate stored at 76% RH decomposed in three steps. Interlayer water was released in the first step up to 220 °C and the dehydroxylation occurred between 220 and 350 °C. The observed weight losses of 9.5% and 11% were in good agreement with the values of 9% and 9% calculated for the sample containing 1.0 molecule of H<sub>2</sub>O per formula unit. The decomposition of intercalated AS occurred in the third slow step above 420 °C. The total weight loss (63.3%) was in good agreement with the value of 64.2% calculated for  $Zn_{0.67}Al_{0.33}(OH)_2(C_{14}H_7O_5S)_{0.33} \cdot H_2O$ . The sample stored over P<sub>2</sub>O<sub>5</sub> in vacuum lost about one half of interlayer water. It decomposed in three steps, interlayer water was released in the first step (observed 5%, calculated 4.7%), the second one (observed 10%, calculated 9.4%) corresponded to the dehydroxylation, and the third one corresponded to the thermal decomposition of intercalated AS.

The NDS intercalate stored at 76% RH decomposed in three steps. Interlayer water was released in the first step up to 210 °C and the dehydroxylation occurred between 220 and 400 °C. The observed weight losses 19.5% and 10.5% were in good agreement with the values of 18.4% and 12.2% calculated for the

sample containing 1.5 H<sub>2</sub>O per formula unit. The decomposition of intercalated NDS occurred in the third slow step above 400 °C. The total weight loss (52.9%) was in good agreement with the value of 51.4% calculated for Zn<sub>0.67</sub>Al<sub>0.33</sub>(OH)<sub>2</sub>(C<sub>10</sub>H<sub>5</sub>O<sub>7</sub>S<sub>2</sub>)<sub>0.11</sub> · 1.5-H<sub>2</sub>O. The sample stored over P<sub>2</sub>O<sub>5</sub> in vacuum did not contain interlayer water. It decomposed in two steps, first one (observed 15.2%, calculated 15.0%) corresponded to the dehydroxylation, and the second one corresponded to a thermal decomposition of intercalated NDS. The total weight loss (43%) was in good agreement with the value of 40.5% calculated for Zn<sub>0.67</sub>Al<sub>0.33</sub>(OH)<sub>2</sub>(C<sub>10</sub>H<sub>5</sub>O<sub>7</sub>S<sub>2</sub>)<sub>0.11</sub>.

The thermal behavior of the intercalates was followed by the *in situ* X-ray diffraction. The dependence of the basal spacing on temperature is given in Figure 4. The ADS intercalate did not change up to 50 °C, a new phase with lower basal spacing appeared at 60 °C. The basal spacing of this phase significantly decreased up to 140 °C. As follows from TGA, this decrease of the basal spacing was probably caused by a release of interlayer water. A small decrease of the basal spacing connected with broadening of the (00 $l$ ) diffraction lines and with the decrease of their intensities was probably caused by a dehydroxylation of the HTlc layers. The sample was amorphous above 320 °C. In the case of the AS intercalate, the basal spacing did not change up to 80 °C and then slowly decreased. A formation of a new phase with lower basal spacing was not observed. The sample was amorphous above 320 °C. The NDS intercalate did not change up to 80 °C, when a new phase with a lower basal spacing appeared. The basal spacing of this phase slowly decreased up to 320 °C. The sample was amorphous above 320 °C.

The first two dehydration steps were reversible for all three intercalates. If the samples dehydrated at 400 °C

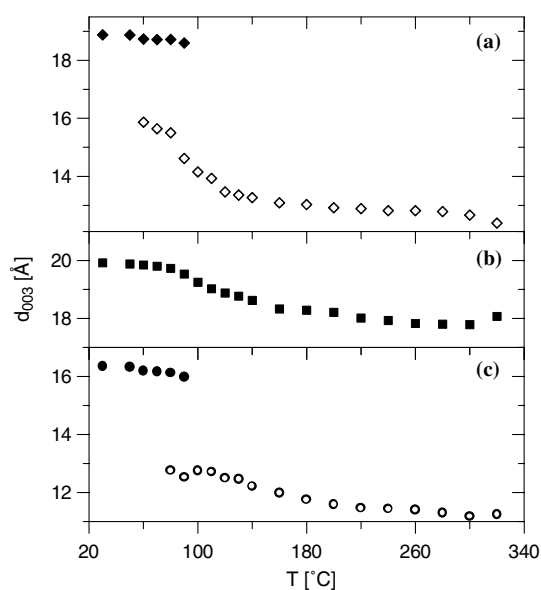


Figure 4. Thermal dependence of basal spacing of the ADS (a), AS (b), NDS (c) intercalates.

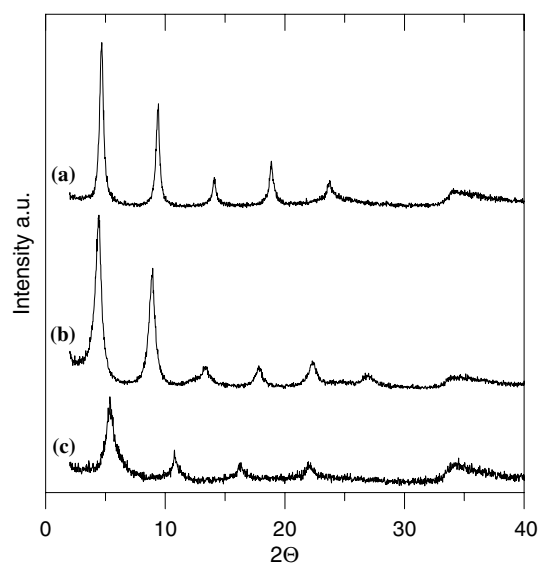


Figure 5. X-ray diffractograms of the ADS (a), AS (b), NDS (c) intercalates formed by rehydration of samples dehydrated at 400 °C.

were stirred in water overnight, the amorphous samples became crystalline with the same basal spacing as before the dehydration. As can be seen from Figure 5, the (00 $l$ ) reflections of all recovered intercalates were markedly broadened in comparison with that of the parent intercalates (Figure 1). It is obvious that the brucite-like layers of the hosts were reconstructed, nevertheless crystallinity of the recovered samples was much worse than in the case of the parent intercalates.

The arrangement of the ADS and AS anions in the interlayer space was proposed by Kuk and Huh [8]. The ADS anions form a monolayer in the interlayer space and the planes of their aromatic rings are tilted to the host layers. This arrangement forms relatively large cavities among the ADS anions where water molecules could be placed. The AS anions form a monolayer of partially interdigitated species and the charge balancing SO<sub>3</sub><sup>-</sup> groups lie alternately above and below the layer. The planes of their aromatic rings are perpendicular to the host layers. The cointercalated water molecules could be placed in the cavities between the host layers and the guest molecules.

As follows from the composition of the NDS intercalate, NDS must be present as a trianion in the interlayer space, that means that in addition to both SO<sub>3</sub>H groups also OH group is dissociated similarly as in the case of the fluorescein intercalate [14]. Schematic illustration of the arrangement of the NDS anions is given in Figure 6. The van der Waals length of the NDS anion is smaller than the gallery height of the intercalate, so that the naphthalene planes of the NDS anions can be perpendicular to the host layers. A cross-section area of NDS projected on the sheets of the host layers is 68 Å<sup>2</sup>. An “equivalent area” surrounding each positive charge in the brucite-like sheet is  $3a^2 \sin 60^\circ = 25 \text{ Å}^2$  [14]. As every NDS trianion is compensated by three positive charges of the host layers, the area available for one

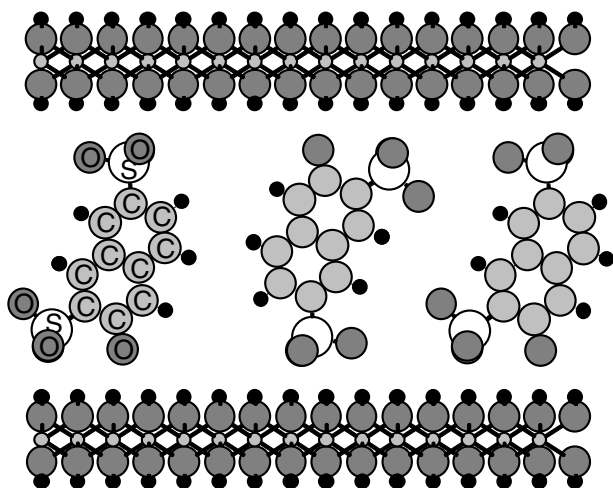


Figure 6. Probable arrangement of NDS anions in the interlayer space.

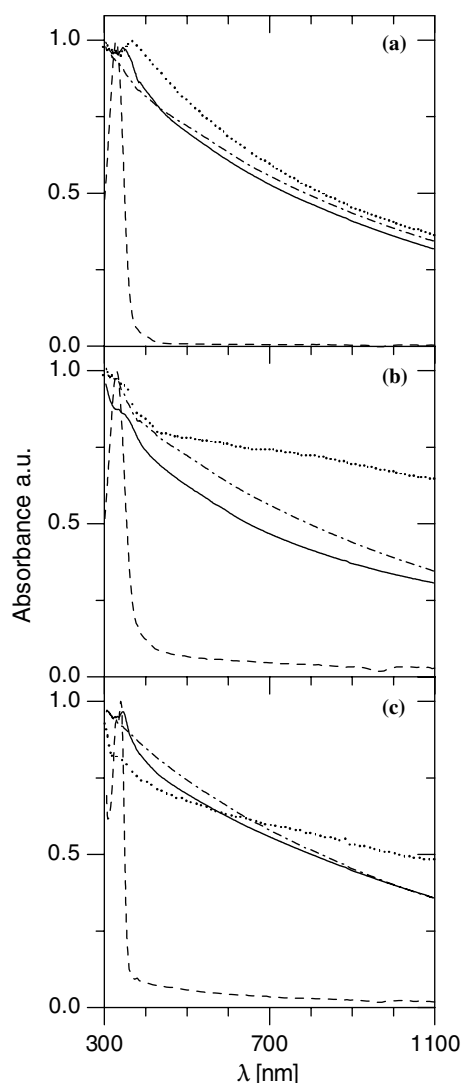


Figure 7. Normalized absorption spectra of the guest adsorbed on the Zn-Al-HTlc (dot-and-dash line), intercalated in the Zn-Al-HTlc (solid line), the solid dye (dotted line) and the water solution of the guest at pH = 7 (dashed line) for ADS (a), AS (b) and NDS (c).

NDS trianion is  $3 \times 25 = 75 \text{ \AA}$  which is more than the cross-section area of the guest molecule projected to the host layer. That means that there are relatively large cavities among the NDS anions where cointercalated water molecules could be placed.

Absorption spectra of the guests in a water solution and in a solid state (pure salts, adsorbed or intercalated in the Zn-Al-HTlc) are shown in Figure 7. The spectrum of the ADS solution had a band at 328 nm, solid ADS adsorbed at 367 nm. The maximum of absorbance of surface adsorbed ADS was shifted to the lower wavelength. In the intercalate, this band was found at 347 nm. Diffuse reflectance spectrum of ADS intercalated Mg-Al-HTlc was measured by Kanezaki *et al.* [6]. There were found two absorption bands at 320 and 518 nm, which were ascribed to  ${}^1B_{2u}(\pi, \pi^*) \leftarrow S_0$  and  ${}^1B_{1g}(n, \pi^*) \leftarrow S_0$  transitions, respectively. The weak band at about 518 nm was not observed in the spectrum of our ADS intercalate. Similarly, a band at 348 nm was observed in the spectrum of the AS intercalate.

The spectrum of the NDS solution had a maximum at 339 nm. The absorption band of surface adsorbed NDS was shifted below 300 nm. In the case of the intercalated NDS, two maxima at 299 and 344 nm were observed. Diffuse reflectance spectrum of naphthalene-1,5-disulfonate intercalated Zn-Al-HTlc was measured by Kanezaki [15]. There were found two absorption bands at 274–278 and 314–325 nm, which were ascribed to transitions to a  ${}^1B_{2u}(\pi, \pi^*)$  and a  ${}^1B_{3u}(\pi, \pi^*)$  in the naphthalene moiety, respectively.

## Conclusion

The advantage of the preparation method described consists in the possibility to work in an ambient atmosphere containing  $\text{CO}_2$ , which facilitates the synthesis. Our experience shows that this method cannot be used generally and does not work for guests containing only carboxylic group, for instance methyl red. Nevertheless, the method works well for guests containing sulphonic groups as was proved also by our other results [16, 17].

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