



Zn₂Al layered double hydroxides intercalated and adsorbed with anionic blue dyes: A physico-chemical characterization

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ABSTRACT

Three different anionic blue organic dyes have been intercalated into the structure of Zn₂Al layered double hydroxides, using the co-precipitation method at constant pH. Using the same synthetic procedure, Zn₂Al-Cl has been prepared and used as an adsorptive phase to retain the blue dyes from an aqueous solution. All the organic/inorganic (O/I) hybrid LDH compounds were analyzed by X-ray powder diffraction (XRPD), thermal analysis (TG/DTA), elemental analysis, solid state ¹³C nuclear magnetic resonance (CPMAS ¹³C NMR), and Fourier transform infrared spectroscopy (FTIR). In the adsorption experiments, Gibbs free energy ΔG values for the temperatures in a range between 10 and 40 °C were found to be negative, which indicates that the nature of adsorption is spontaneous and shows the affinity of LDH material towards the blue anionic dyes. Additionally a decrease in ΔG values at higher temperature further indicates that this process is even more favorable at these conditions. The enthalpy ΔH values were between physisorption and chemisorption, and it may be concluded that the process was a physical adsorption enhanced by a chemical effect, characterized by a combined adsorption/intercalation reaction, making these O/I assemblies reminiscent of the Maya blue.

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1. Introduction

Hybrid organic/inorganic (O/I) assemblies constitute a suitable approach for obtaining multifunctional materials. More specifically, concerning the intercalation of dye organic molecules into inorganic hosts, the interest stems from the peculiar molecular arrangement imposed by the host structure, the thermal stability supplied by the inorganic constituent, and the stability against the dissolution process, the whole contributing to maintain the optical properties of the intercalated dye.

In the domain of hybrid dye inorganic assemblies, we must note the outstanding longevity of Maya blue which comes from a synergistic effect. Indeed, Maya blue arises from a very stable organo-clay complex formed of a superlattice of palygorskite matrix with indigo molecules and is resistant to dilute mineral acid and alkaline solutions, solvent treatment, moderate heat, and even biocorrosion. Another example is the beautiful Caribbean Sea blue color which remains unaltered after centuries of exposure under drastic conditions of temperature and humidity of the tropical forest [1–3]. Whether the indigo molecules seal the channels in pa-

lygorskite clay or penetrate into the structure channels [4,5] and whether iron is present as nanoparticles as amorphous goethite [6] or in substitution in the clay [7] still remain controversial topics.

In the 1990s, there was a strong interest in the dyes and their incorporation into inorganic host structures. This was exemplified by immobilizing compounds into zeolite open frameworks and intercalation into layered smectite-type 2:1 clay minerals, as shown in some reviews [8–11] and aromatic molecules such as substituted stilbene, naphthalene, and phenanthrene into zeolite [12,13] and clay minerals [14–16]. Even if most of the studies related to dyes and mineral clays are currently devoted to environmental purposes and more specifically to their sorption from aqueous solutions [17–22], a renewed interest for new types of application has recently emerged. Indeed, exceptional properties may be found from the synergism of the two counterparts that neither the clay nor the organic dye alone exhibit as beautifully illustrated by the Maya blue and, more recently, by synthetic hybrid materials which can find a place in laser applications [23] or for the replacement of environmentally toxic metal-based pigments in the paint and pigment industry [24].

Besides that and from the point of view of the organic molecule, the inorganic part acts to position and orientate structurally the guest species. Such sandwiched inorganic organic stacked structures have been mostly illustrated by cationic smect-

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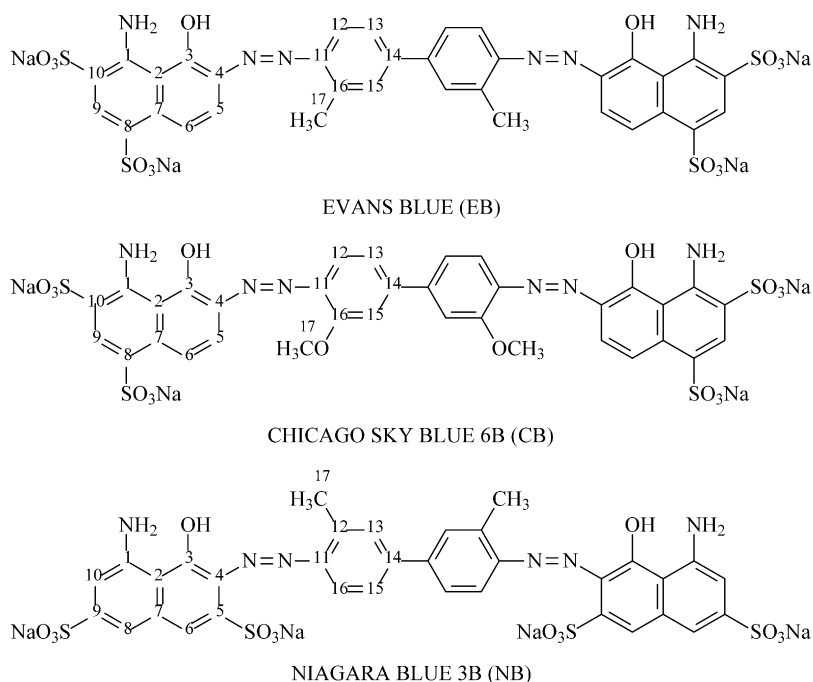


Fig. 1. Blue dyes molecular structures. Numbering of carbon atoms to attribution of ^{13}C nuclei NMR peaks.

ite-type mineral clays so far. Yet layered double hydroxides (LDH) and layered hydroxide salts (LHS) [25] also constitute two families of interest since they present a chemical versatility and a tunable layer charge density, ranging from 0.17 to 0.41 C m^{-2} in layered double hydroxides [26]. The LDH structure refers to the natural hydroxalite mineral, and this class of compounds is described with the ideal formula, $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2]_{\text{intra}}[\text{A}^m_{x/m}\cdot n\text{H}_2\text{O}]_{\text{inter}}$, where M^{II} and M^{III} are metal cations, A the anions, and *intra* and *inter* denote the intralayer and interlayer domains, respectively. The structure consists of brucite-like layers built up from edge-sharing $\text{M}(\text{OH})_6$ octahedra. A partial and isostructural M^{II} to M^{III} substitution induces a positive charge for these layers, balanced with the presence of the hydrated interlayer anions. Owing to their high charge density, LDH materials are sometimes considered less than ideal hosts for many applications of porous pillared materials [27]; however, they should be able to strongly orientate the molecular arrangement within the interlayer space in a highly stowed fashion as the anions must satisfy and compensate the forming layer charge and therefore supply potentially strong intermolecular interactions. Conversely the inorganic LDH blocks may consider the organic component as a textural agent, thus orientating the textural properties of the whole as reported for the intercalation of large macromolecules such as polymers [28–31] and biomacromolecules such as DNA [32–34]. Some studies have reported on multibranch tetrafunctionalized porphyrin-type macromolecules [35,36] and perylene-type chromophores intercalated into hydroxalite [37], as well as on the reversible color change of poly(diacetylenecarboxylates) incorporated into LDH [38], on the photo-sensitizing efficiency of intercalated 4-benzoyl benzoate for the oxidation of di-*n*-butylsulfide [39], or on the sunscreen effect of organic absorbents [40–42]. Some important findings were suggested by Costantino and co-workers on chromophores with donor acceptor properties [43], phenolphthalein [44], methyl orange [44,45], etc. Indeed, these authors have been pioneers in determining whether hydroxalite-type materials were able to intercalate large size dye and in obtaining information on the orientation/conformation of the dye by basal spacing measurements and photophysical properties [45,46]. They also observed shifts in the absorption spectra associated with intermolecular interactions;

yet, co-intercalation often occurred and ill-defined assemblies were obtained from the incorporation of large dye molecules [47,48].

Having successfully prepared polymer LDH assemblies by the so-called coprecipitation method [26], we have developed here a similar approach to incorporate three cumbersome commercially blue anionic dyes, Evans blue (EB), Chicago blue sky (CB), and Niagara blue (NB) presenting quite similar molecular structures, into Zn/Al layered double hydroxides. The process of immobilization was studied by direct coprecipitation synthesis and adsorption properties onto $\text{Zn}_2\text{Al}-\text{Cl}$ LDH were also examined. In the adsorption/intercalation experiments, thermodynamic data were obtained and attributed to adsorption/intercalation reactions.

2. Materials and methods

Dye sodium salts, Evans blue ($\text{C}_{34}\text{H}_{24}\text{O}_{14}\text{N}_6\text{S}_4\text{Na}_4$, direct blue 53, Aldrich, 40%) noted as EB, Chicago sky blue 6B ($\text{C}_{34}\text{H}_{24}\text{O}_{16}\text{N}_6\text{S}_4\text{Na}_4$, Aldrich 65%) noted as CB, Niagara blue 3B ($\text{C}_{34}\text{H}_{24}\text{O}_{14}\text{N}_6\text{S}_4\text{Na}_4$, Aldrich, 30%) noted as NB, and $\text{ZnCl}_2\cdot 5\text{H}_2\text{O}$ (Acros), $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (Acros, 99%), and NaOH (Acros, >97%) were used. The molecular structures of the used dyes are shown in Fig. 1.

The syntheses of the Zn/Al-dye LDH were carried out using the well-known coprecipitation method and previously described [49] and briefly reproduced below. The amount of dye molecule was optimized to 4 times the content of Al^{3+} cations, defined as the anionic exchange capacity of the LDH material. Typically, 10^{-2} mol of dye was dissolved into 500 ml of a solution of decarbonated water. To this solution, two other solutions were added dropwise, one containing 5×10^{-3} mol of $\text{ZnCl}_2\cdot 5\text{H}_2\text{O}$ and 2.5×10^{-3} mol of $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$, and the other NaOH, 1 mol/L. The addition was performed at constant pH of 9, under nitrogen atmosphere and vigorous stirring, and completed after 24 h. The precipitate was aged in the mother liquid for an additional period of time of 24 h under nitrogen atmosphere to avoid the contamination by carbonate, from the atmospheric CO_2 . The product was centrifuged and then washed five times with decarbonated water and dried at room temperature. The intercalation compounds are denoted as Zn_2Al -dye, where dye is the respective dye utilized in the synthesis.

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