



Layered double hydroxides intercalated with anionic surfactants/benzophenone as potential materials for sunscreens

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ABSTRACT

Layered double hydroxides intercalated with dodecylsulfate or dodecylbenzenesulfonate were synthesized by co-precipitation under alkaline conditions. After characterization by PXRD, FTIR, and TGA/DTA, the Zn_xAl/SUR compounds were reacted with neutral benzophenone, using different procedures. The products obtained from benzophenone adsolubilization were investigated by PXRD, FTIR, and DRUV–Vis spectroscopy before and after exposure to UV radiation. In general, the content of adsolubilized benzophenone was small and depended on the synthetic procedure. The best results were achieved under microwave irradiation, which furnished 9.09 wt% adsolubilized benzophenone. The products presented good adsorption in the full UV region, from UVC to UVA, and good stability to UV radiation. They did not cause skin irritation in tests conducted on rabbits, which makes them good candidates for the development of a new generation of sunscreens.

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1. Introduction

Layered double hydroxides (LDHs) are based on the brucite $(Mg(OH)_2)$ structure and have the generic formula $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}(A^{n-})_{x/n} \cdot yH_2O$. In LDHs, part of the M^{2+} cations is replaced with M^{3+} cations, which gives rise to a net positive charge in the layers, compensated by intercalation of A^{n-} anions in the interlayer domain [1].

Several anionic species, such as simple anions or even more complex structures like DNA and polymers, can be intercalated between the LDH layers [2–4]. In the literature, there are different studies on the intercalation of molecules displaying solar protection activity between the layers of clay minerals [5,6], LDHs [7–13], and layered hydroxide salts [14,15], which has led to a new class of sunscreens.

Sunscreen products stop the UV photons before the latter reach the skin and damage it. These products contain organic molecules capable of absorbing UV radiation as well as inorganic compounds that absorb, scatter, and reflect UV radiation. Most UV-active organic molecules used as ingredients in sunscreens can penetrate into the skin, causing cutaneous reactions such as contact

dermatitis, non-immunological phototoxic contact reactions, allergies, and photoallergic reactions, among other effects [16,17].

One way to reduce the absorption of organic sunscreens through the skin is to immobilize the organic UV absorber onto inorganic matrixes, and intercalation compounds are one of the best-known alternatives. After intercalation, the organic absorber retains its activity, whereas the majority of its molecules do not establish contact with the skin. This prevents many of the problems related to the absorption of these organic molecules, which enter the body through the skin.

Although many studies on the intercalation/adsorption of organic UV absorbers into layered compounds like clay minerals, LDHs, and layered hydroxide salts have been published, there are no reports on their adsolubilization. The latter process is interesting because a number of UV organic absorbers are neutral and cannot be intercalated into above mentioned compounds, since the species to be intercalated has to bear either positive or negative charge.

Adsolubilization or co-adsorption is a phenomenon analogous to micelle solubilization in aqueous solution [18]. It consists in the adsorption of surfactant molecules capable of assembling at the surface of the solid. As a result, the polarity of the surface is changed, improving the solubility of poorly soluble molecules that would not be adsorbed by the solid in the absence of the surfactant. In the case of layered compounds such as LDH, the organic phase, composed of an anionic surfactant like dodecylsulfate or

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dodecylbenzenesulfonate, is intercalated into a bidimensional environment, thereby altering the chemical characteristics of the layers and increasing their affinity for non-polar and non-ionic species [19]. Indeed, there are many examples of the adsolubilization of different organic molecules into LDH in the literature [20–22].

In previous works by our research group, we have described the intercalation of anionic UV-absorbers into different layered compounds. The present paper extends this work to neutral molecules and uses the adsolubilization process for entrapment of benzophenone.

Benzophenone absorbs UV radiation, provides broad-spectrum UVB and UVA protection, and is inexpensive. Moreover, according to the classification by the Food and Drug Administration (FDA) agency within the US Department of Health and Human Services, benzophenone-3 and benzophenone-4 are safe and effective, over-the-counter (OTC) sunscreen ingredients. Although benzophenone is considered to be safe, recent studies have associated it with photoallergic contact dermatitis [23]. Furthermore, there is evidence that benzophenone-3 is absorbed in the gastrointestinal tract and bioaccumulated in the human body [24], not to mention that it has been linked to endometriosis [25].

This work targeted the adsolubilization of benzophenone into anionic surfactants intercalated into LDH, in order to avoid the direct contact of this organic UV absorber with the skin, protect the molecule from photodegradation, and enhance its UV adsorption.

2. Materials and methods

Organic and inorganic reagents were analytical grade and were used without further purification. Benzophenone (Merck, purity >99%) was selected as a representative ultraviolet absorber, and sodium dodecylbenzenesulfonate (95%, Aldrich) or sodium dodecylsulfate (90%, Synth) was employed as the guest species. Inorganic starting materials such as zinc chloride (97%, Vetec), aluminum chloride hexahydrate (99.5%, Vetec), and sodium hydroxide (99%, Vetec) were of guaranteed reagent grade.

2.1. Synthesis of compounds containing intercalated anionic surfactants

LDHs were synthesized by co-precipitation in alkaline pH [26,27]. To control the density of the intercalated surfactant pillars and obtain different empty spaces for the adsolubilization of benzophenone, three synthetic procedures were carried out, using different Zn/Al molar ratios, 2:1, 3:1, and 4:1. The compounds were labeled Zn_xAl/SUR , where “x” corresponds to the proportion of Zn in the formula and SUR is the anion of the surfactant; that is, dodecylsulfate (DDS) or dodecylbenzenesulfonate (DBS).

A 1 Mol/L NaOH solution and a solution of the divalent and trivalent salts (Ex.: Zn^{+2}/Al^{+3} 2:1 –200 mL of 0.236 Mol/L of $ZnCl_2 + 0.118$ Mol/L of $AlCl_3 \cdot 6H_2O$) were prepared with distilled and decarbonated water (Table 1). Both solutions were added

dropwise to a reactor (around 3 h) containing the SUR sodium salt dissolved in 100 mL of water, which was calculated to be in excess of 4 times in relation to the content of M^{3+} . The reaction and the ripening process (24 h) were conducted at room temperature, under nitrogen flow, magnetic stirring, and virtually constant pH. The solid was isolated by centrifugation and redispersed with water in an ultrasonic bath. This process was repeated 5 times, and the solid was dried at 60 °C in a vacuum oven until constant weight.

2.2. Preparation of the adsolubilization compounds

The previously synthesized LDHs intercalated with SUR (2 mmol) were mixed with benzophenone (8 mmol) in three distinct batches of experiments. For the first batch, the mixture was added to a Teflon vessel placed inside a steel reactor and kept in a drying oven working at 80 °C, for 12 days. The products resulting from this batch were designated $Zn_xAl/SURbf$, where “b” refers to benzophenone and “f” to fused state. The second batch was prepared following the same procedure employed for the first batch, except that the benzophenone (8 mmol) was dissolved in diethyl ether. This sample was named $Zn_xAl/SURbe$, where “e” corresponds to ether. For the third batch, the reaction was accomplished in a domestic microwave oven for 2 min, with the power fixed at 40%. This sample was labeled $Zn_xAl/SURbm$, where “m” stands for microwave.

After the experiments, the compounds were double-washed with diethyl ether, centrifuged twice at 3000 rpm, and dried at room temperature in a rotary evaporator (rotavap).

2.3. Investigation of the UV photostability of the adsolubilization products

In order to verify the UV photostability of the adsolubilization products, some of the samples were submitted to UV irradiation for 2 h, and the spectra were collected by diffuse reflectance ultraviolet–visible spectroscopy (DRUV–Vis) in 30-min intervals. The radiation was generated with the aid of a 125-W mercury vapor bulb, without the protecting glass bulb. The samples were deposited on a glass sample holder and positioned 10 cm away from the UV source. The radiometer detected an intensity of 1.2 mV/cm².

2.4. Skin irritation test

The skin irritation tests were performed according to the guidelines published in the compendium of the Cosmetics Toiletries and Fragrance Association (CTFA) for the safe testing of cosmetics [28]. Specimens (10%, w/v) were prepared by dispersing the compounds in glycerol (Pharmanostra, Rio de Janeiro, Brazil), to ensure good contact with the skin. Each sample was tested in three male New Zealand white rabbits weighing 2–2.5 kg. The sample was applied on the dorsal area, which had been shaved on the previous day. The 6-cm² area of the skin was divided into four quadrants, two of them were superficially scratched using a sterile needle and the other two were kept intact. The tested substances were uniformly applied in the four quadrants, in a single dose. The application area was covered with gauze and porous tape for occlusive protection. The skin reactions, such as erythema or edema, were evaluated by means of the Draize score 4 h after application [29,30]. After the exposure time, the sample was removed with distilled water.

Primary skin irritation was assessed immediately after the test substance was removed, 24 h after the application, and on the next seven consecutive days. For evaluation of cumulative skin irritation, the product was removed and reapplied using the same procedure after 4 h of occlusion. The integrity of the skin was

Table 1

Mass of salts used and pH adjusted during the synthesis of the layered double hydroxides.

Samples	ZnCl ₂ (mmol)	AlCl ₃ ·6H ₂ O (mmol)	Surfactant Na salt (mmol)	pH
Zn ₂ Al/DDS	47.21	23.61	94.43	7.5
Zn ₃ Al/DDS	58.53	19.51	78.05	8.5
Zn ₄ Al/DDS	66.35	16.59	66.36	9.0
Zn ₂ Al/DBS	47.21	23.61	94.43	7.5
Zn ₃ Al/DBS	58.53	19.51	78.00	8.5
Zn ₄ Al/DBS	66.35	16.59	66.00	9.0

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