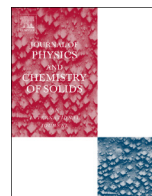




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Improved photostability of hydrophobic natural dye incorporated in organo-modified hydrotalcite

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ABSTRACT

β -carotene and annatto extract are typical carotenoids used as safe colorants for foods. However, the instability against irradiation limits their wide use. The improvement of stability was investigated by the intercalation of dye into the interlayer space of the anion-exchangeable clay, hydrotalcite. A hydrophobic environment was constructed in the interlayer space of the hydrotalcite by its modification with anionic surfactants (dodecyl sulfate and dodecylbenzene sulfonate). The lipophilic β -carotene and annatto dye were successfully incorporated into the organo-modified hydrotalcite, and the incorporated dyes exhibited improved photostability under visible irradiation from a 100 W halogen lamp (190 klux) in the air. The effect of the stabilization on the anionic annatto dye was higher by the incorporation in the modified hydrotalcite than that in the modified cation exchangeable clay, suggesting that the polarity of the clay sheet had some influence on the stabilization of the incorporated dye. The stabilization effect of β -carotene was not so significant as that of the annatto dye, because sufficient intercalation of non-polar β -carotene might require stronger hydrophobic environment. The π - π interaction between the β -carotene and the benzene ring of dodecylbenzene sulfonate was found to contribute to the stability enhancement.

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1. Introduction

Carotenoids are one of naturally occurring pigments and are widely present in plants and animals. They have a long polyene chain as a chromophore, resulting in their generally strong hydrophobicity. More than 700 types of carotenoids have ever been found in nature [1]. Among them, β -carotene is the most typical carotenoid. It is a member of carotenoid family, and possesses no other elements than hydrogen and carbon in its composition. The structure of β -carotene is shown in Fig. 1. Two six-membered rings are located at both ends of the polyene chain with 9 alternating single and double bonds. β -carotene is present in many vegetables and its contribution to the human health is well-known in recent years [2].

A series of compounds without the six-membered rings at the ends of the conjugated double bonds are generally called apocarotenoids. The annatto dye, which is extracted from the seed of *Bixa orellana* L., contains some kinds of apocarotenoids (bixin and norbixin) as the main components [3]. Structures of bixin and

norbixin are also shown in Fig. 1. The annatto dye, especially containing norbixin as a predominant component, is slightly water-soluble, but it is generally considered rather hydrophobic as β -carotene.

β -carotene and annatto dye are both used widely as non-toxic natural colorants of foods [4,5]. The oil-soluble nature of lipophilic dye is suitable for the coloration of processed dairy products or meats [6–8]. However, the instability of the dye limits its widespread use; carotenoids easily decompose through oxidation and lose their color [9]. Especially, annatto dye is known to be unstable under visible-light [10,11]. The improvement of stability will extend the usage of carotenoids as a general colorant.

For various purposes, some researchers have reported the improvement of stability by the incorporation of carotenoid molecules into other materials such as carbon nanotubes [12], polyacrylic acid [13] and cyclodextrin [14]. The inclusion of dye as a guest molecule into inorganic host materials is a promising approach, like the ancient Mayan people who used the composite of indigo and palygorskite clay for their colorant [15,16]. The intercalation of cationic or anionic dye molecule into the clay interlayer has been carried out to enhance the stability of the dye [17–24]. We have also reported the stability enhancement of natural dyes such as anthocyanin [25] and carmine [26] by their

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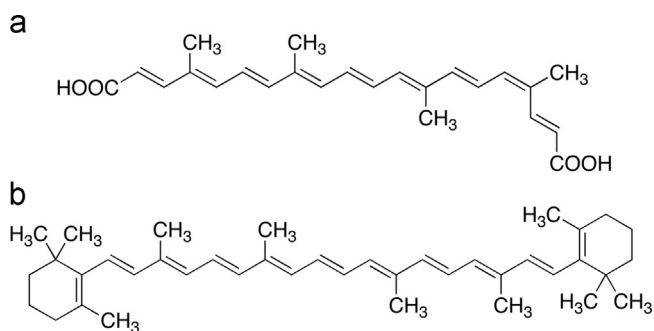


Fig. 1. Molecular structures of (a) norbixin, the main component of the annatto dye, and (b) β -carotene.

intercalation between clay layers. However, nonionic hydrophobic dyes are hardly intercalated into the polar clay interlayer space. In fact, we could not intercalate the lipophilic annatto dye between the layers of anion exchangeable hydrotalcite, although the annatto dye had carboxyl groups in its structure and exhibited anionic nature [26].

The polar and hydrophilic interlayer space of clays can be converted into hydrophobic one by the exchange of interlayer ions with suitable surfactant molecules. Such modified clays are called organoclays and have an ability to adsorb various organic molecules between the layers by the hydrophobic interaction [27,28]. The cation-exchangeable montmorillonite has been modified with the cationic alkylammonium surfactants and used for the inclusion of lipophilic β -carotene into the clay interlayer [29]. We have also been successful to intercalate and stabilize the annatto dye using montmorillonite modified with the cationic surfactant [30]. Therefore, it can be said that the cation-exchangeable clays can adsorb and stabilize the hydrophobic dye by the proper organo-modification.

Assuming that the stabilization effect comes from the intercalation caused by the hydrophobic interaction, the polarity of the original interlayer space (positive or negative charge of the clay sheet) is not expected to have a strong influence on the stability enhancement of the included dye molecules. In this study, we have investigated the possibility for the stabilization of β -carotene and the annatto dye with hydrotalcite modified with anionic surfactant. Hydrotalcite is a typical anion-exchangeable clay, having a layered structure made of Mg–Al double hydroxide. It is often used as an adsorbent or a host material of various anionic compounds [31,32] including dyes [33–36], and shows different properties from those of the cation-exchangeable montmorillonite. Therefore, the development of composite with hydrotalcite may expand the range of application for dyes as a colorant. In addition, the results obtained here will contribute to the evaluation of the generality of the idea that the intercalation into the clay layers can stabilize the included dye molecules.

2. Experimental

2.1. Materials

Hydrotalcite (denoted as HT) used in this study was supplied from Wako Chemical Co., whose chemical composition and anion exchange capacity (AEC) were $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ and 331 meq/100 g-HT, respectively. Silica (SIO) was supplied from Japan Catalysis Society (JRC-SIO-6) and used as a host material for the reference sample. The annatto dye (ANA) and β -carotene (BC) were both supplied from Wako Chemical and used as received. As anionic surfactants, sodium dodecyl sulfate (SDS) supplied from

Kishida Chemical Co. and sodium dodecylbenzene sulfonate (SDBS) from Tokyo Chemical Industry were employed.

The organo-modification of HT was carried out by a reconstruction method using the so-called “memory effect”, where the once calcined HT restored the original HT structure when mixed with aqueous solutions, incorporating various anions dissolved in the solutions between the layers [37,38]. First, 1 g of HT was calcined at 773 K for 2 h in air. Then, 6.6 mmol (200% vs. AEC) of each anionic surfactant (SDS or SDBS) was dissolved in 100 cm³ of deionized water, and the calcined HT was mixed with the aqueous solution and stirred for 18 h. The mixture was filtered and the sediment was collected to be dried at 343 K for 3 h. Thus obtained organo-modified HT was denoted as SDS/HT or SDBS/HT.

The composite sample of the dye with the organo-modified HT was prepared by immersing the host materials in the dye solution. The ethanolic solution (40 cm³) containing 20 mg of ANA or 10 mg of BC was mixed with 0.4 g of SDS/HT or SDBS/HT, stirred for 2 h and kept for 24 h in the dark. The amount of dye dissolved in the solution was 5 wt% (ANA) or 2.5 wt% (BC) with the modified HT. After the adsorption step, the sediment was filtered and the collected solid sample was dried at 323 K under reduced pressure in the dark. The obtained composite sample was represented as ANA/SDS/HT, ANA/SDBS/HT, BC/SDS/HT or BC/SDBS/HT.

As the reference samples, composites of ANA and BC with SIO were prepared. SIO was mixed with the solution of ANA dissolved in ethanol or with the solution of BC dissolved in petroleum ether. Dye molecules were forced to be immobilized on the SIO surface by drying up the solvent under the air stream in the dark. The loading amount of the dye was adjusted to 5 wt% (ANA) or 1 wt% (BC). The light absorption of ANA/SIO was about 20% of those of ANA/SDS/HT and ANA/SDBS/HT. This meant that the light absorption by ANA/SIO was smaller than those of ANA/SDS/HT and ANA/SDBS/HT so that the light fastness of ANA/SIO could be over-estimated. On the other hand, the absorption of BC/SIO was adjusted to be almost the same as those of the BC/SDS/HT and BC/SDBS/HT.

2.2. Measurements

XRD patterns were measured with a Rigaku MiniFlex X-ray diffractometer (CuK α , step angle and scan speed 0.05° and 2°/min, respectively, 15 mA, 30 kV). Transmittance UV–vis spectra were recorded with a Shimadzu UV-1700 spectrophotometer. Diffuse reflectance UV–vis spectra were collected with a JASCO V-550 spectrophotometer with an ISV-469 integrating sphere equipped to the spectrophotometer.

To investigate the light endurance of each sample, visible light was irradiated to the samples under ambient temperature and pressure. A 100 W halogen lamp (Schott Megalight 100) equipped with a 30 cm length flexible light guide was used as a visible light source. The powder samples were loaded in a plastic cell covered with a thin glass, and placed at a position of 1.1 cm from the aperture of the light guide. The light intensity was 190 klux at the sample position. The lamp emitted all the visible wavelength region, so that the colored samples were sufficiently irradiated to the absorbable light. The degree of the color fading was determined by the decrease in the main absorption peak of ANA or BC on the diffuse reflectance spectra of each composite material.

3. Results and discussion

3.1. Organo-modification of hydrotalcite and incorporation of dye

Fig. 2 illustrates XRD patterns of unmodified and organo-modified HT. The d_{003} reflection of unmodified HT was observed

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