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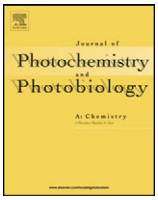

Photo-induced coloration of 2-hydroxychalcone in the clay interlayer

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ABSTRACT

2-Hydroxychalcones are known to be converted to the colored flavylium form under UV irradiation. In this study, the photochemical conversion of two 2-hydroxychalcone derivatives (4′-dimethylamino-2-hydroxychalcone and 4′-methoxy-2-hydroxychalcone) has been carried out in the solid matrix by the intercalation into the layer of the clay, montmorillonite. The 2-hydroxychalcone has been adsorbed on the clay by modifying the clay interlayer with a cationic surfactant, dodecyltrimethylammonium chloride. The addition of an acidic compound (benzenesulfonic acid) has induced the successful coloring reaction of the 2-hydroxychalcone derivatives by the conversion to the flavylium under UV irradiation between the clay interlayer. A delayed coloration has been observed on the short time irradiation of 4′-methoxy-2-hydroxychalcone included in the clay layer.

1. Introduction

2-Hydroxychalcone has been known as a photochromic compound that is converted by UV irradiation to the colored flavylium form [1–6]. The mechanism of the photochromic reaction is shown in Scheme 1 [1]. The colorless *trans*-2-hydroxychalcone (HC) is photochemically converted to *cis*-2-hydroxychalcone. The *cis*-form undergoes isomerization to become a hemiacetal form. Finally, dehydration of the hemiacetal results in the formation of the colored flavylium form (FV). Throughout the process, only the first step is the photochemical reaction, and the subsequent two are the thermal reactions requiring no irradiation. Since all species are colorless except for FV, the coloration means the formation of FV. The flavylium is regarded as a model compound of naturally occurring anthocyanins, because the flavylium has the same molecular structure as the natural anthocyanins [7,8]. Therefore, the impact of this photochromic system to the environment is expected to be small [9,10]. The colored flavylium form is not so stable that it is thermally discolored and returns to the original 2-hydroxychalcone at slightly elevated temperature. In addition, under neutral to basic pH, the 2-hydroxychalcone does not undergo the photochemical conversion to the colored flavylium, because the flavylium is only stable under acidic condition, as the natural anthocyanin is.

Pina and co-workers have extensively studied the chalcone–flavylium photochromic system for the application to an information recording system [4–6]. By applying the irradiation and pH jump, multistate switching recording has been successful with the 2-hydroxychalcone solution. Horiuchi et al. have reported the discoloration of the flavylium by irradiation with short wavelength UV light [11,12]. This implies the possibility of the all photon mode rewritable media with the present photochromic system.

Most of the reported examples about the photochromism between the chalcone and the flavylium concern the reaction in solutions. There are only a few reports considering the photochromic reaction in solid matrices. Matsushima et al. have reported reversible photochromic reaction between the chalcone and the flavylium in polymer [13,14] or silica gel matrices [15]. Galindo et al. have studied the multistate/multifunctional system in a polymer hydrogel [16]. Kawano et al. have been successful for the coloration under UV irradiation by the conversion of the chalcone to the flavylium on the silica surface [17]. The construction of the chalcone–flavylium photochromic system working in the solid state is essential for the practical use.

Here we report the photochemical coloration of the 2-hydroxychalcone derivatives incorporated between the clay interlayer. Incorporation into the clay layer makes available the application of the photochromic system to the devices in various states such as a film. There have been several reports concerning the photochromic reaction of azobenzene [18], diarylethene [19,20] or spiropyran [21,22] derivatives between the clay layers.

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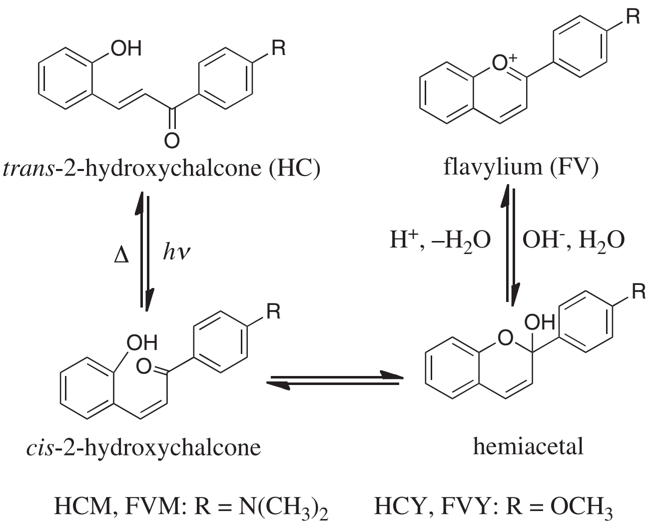

Scheme 1.

The clay interlayer has strong polarity, so that the reverse photochromism of spiropyran has been observed when incorporated in the clay interlayer [21,22]. Thus, the zwitterionic merocyanine form becomes predominant in the polar space, and the spiropyran appears by the conversion of the merocyanine under visible light irradiation. The polarity of the clay interlayer can be controlled by modification with a surfactant. The modified clay is called organo-clay or hydrophobic clay. As the polarity of the interlayer is weakened by the modification with the surfactant, the spiropyran shows the normal photochromic behavior in the organo-modified clay [21]. The organo-modified clay has also been utilized to intercalate hydrophobic azobenzenes [23,24] or to control the molecular conformation of the intercalated diarylethenes [19]. In this paper, we report the photo-induced coloration of the 2-hydroxychalcones between the layers of montmorillonite, typical cation exchangeable clay. The photochromic reaction of HC to FV is greatly affected by the polarity of the interlayer space as well as by the acidity, because the FV form prefers the polar and acidic environment. The best result of the photo-induced coloration has been obtained both by modifying the interlayer of the montmorillonite with a surfactant and by adding an acidic compound as a promoter for the conversion of HC to FV.

2. Experimental

2.1. Sample preparation

The 2-hydroxychalcones used in this study were prepared from salicylaldehyde and acetophenone derivatives by base catalyzed aldol condensation [1]. They have a dimethylamino group or a methoxy group on the B-ring in their structure, exhibiting magenta or yellow in the colored form, respectively. The colored FV forms are denoted as FVM (magenta) and FVY (yellow), respectively, while their precursor HC forms are denoted as HCM and HCY, although HC forms are colorless.

As a montmorillonite, Kunipia F (KF) supplied from Kunimine Industry was used in this study. Its cation exchange capacity (CEC) is 1.19 meq/g. To modify the interlayer space with a surfactant, 0.2 g of KF was stirred for 2 h with 2 cm^3 of an aqueous solution containing given amount of dodecyltrimethylammonium chloride (DTAC). The amount of DTAC was determined as *x*% *vs.* CEC. For example, for the amount corresponding to 200% *vs.* CEC, 0.47 mmol of DTAC was mixed with 0.2 g of KF. Following to the above step, an aqueous solution containing *y* mmol of benzenesulfonic acid (BSA) was added to the mixture of KF and DTAC (*y* could be zero). After 24 h, the mixture was filtered, and the sediment obtained is denoted as KF(*x*–*y*) where *x* and *y* represents the amount of DTAC and BSA, respectively.

The KF(*x*–*y*) was then mixed with a 5 cm^3 of 1 mmol/dm^3 HCM or HCY ethanolic solution and maintained for 24 h in the dark. After filtration and drying in the air at room temperature, the powder sample was obtained, which is denoted as HCM/KF(*x*–*y*) or HCY/KF(*x*–*y*).

2.2. Characterization and measurements

In order to investigate the property of the photo-induced coloration reaction, the HCM/KF(*x*–*y*) sample was packed in a polyethylene bag and irradiated with a 150 W xenon lamp (Ushio Denki UXL-150D). The irradiated light was not monochromated. However, the colored form FVM is not influenced by the visible light irradiation, and the short-wavelength UV will be cut-off by the polyethylene bag. Therefore, the light required for the photoreaction was taken out without causing the unexpected reaction. The HCY/KF(*x*–*y*) sample was maintained in a glass cell and irradiated with a 27 W black light (Toshiba FPL27BLB, peak wavelength 360 nm). The irradiated samples were just employed for measurements of diffuse reflectance UV–vis spectra as they were. The diffuse reflectance spectra were collected with JASCO V-550 spectrophotometer equipped with ISV-469 integration sphere attachment.

XRD patterns were measured with Rigaku MiniFlex X-ray diffractometer (Cu Kα, step angle and scan speed 0.05° and 2°/min, 15 mA, 30 kV).

3. Results and discussion

3.1. Organo-modification of the clay

Fig. 1 illustrates the XRD patterns of the KF samples before and after modification with the surfactant (DTAC). The d_{001} reflection peak of KF shifted from $2\theta = 7.5–4.9°$ by the modification with the surfactant, indicating the expansion of the interlayer distance. From the Bragg's law, the interlayer distance of the KF(200–0) sample was calculated to be 0.83 nm (subtracting the thickness of the clay sheet, 0.96 nm). As the length of the DTAC molecule was about 1.85 nm, it was concluded that the surfactant molecules formed bilayers between the clay layers with the alkyl chains almost parallel to the silicate sheet (tilt angle 13°), or that the surfactant formed a

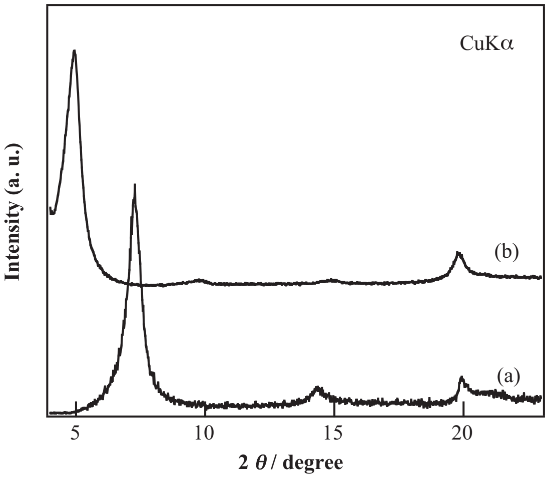

Fig. 1. XRD patterns of (a) unmodified KF and (b) KF(200–0) samples.

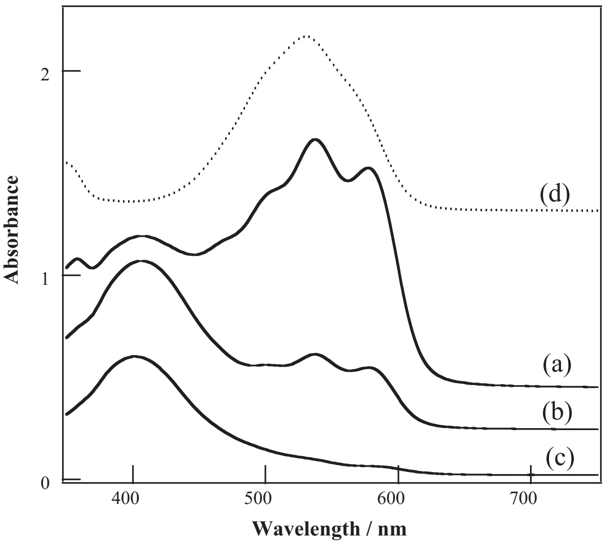

Fig. 2. Diffuse reflectance UV–vis spectra of (a) HCM/KF(25–0), (b) HCM/KF(38–0) and (c) HCM/KF(50–0). The spectrum of aqueous FVM solution was shown by the dotted line (d) for comparison.

single layer with their alkyl chains interdigitated with the tilt angle 27°, as proposed in the previous report [25]. Therefore, it was confirmed that the interlayer space of KF was modified by the organic surfactant molecules.

3.2. *Influence of the amount of surfactant on HCM/KF*

The HCM molecule was incorporated in the interlayer of KF modified with various amount of DTAC. Fig. 2 shows the diffuse reflectance UV–vis spectra of HCM/KF(25–0), HCM/KF(38–0) and HCM/KF(50–0), together with the spectrum of aqueous FVM solution. In the spectrum of HCM/KF(50–0), a single peak was observed at 400 nm. Since the HCM solution shows absorption at the same wavelength, the peak was assigned to the HCM. Therefore, it was concluded that HCM was incorporated in KF(50–0). Since HCM prefers hydrophobic environment, HCM would be mixed in the surfactant phase to be intercalated in the clay layers. In HCM/KF(38–0) two other peaks appeared at 536 nm and 576 nm in addition to the one at 400 nm. In HCM/KF(25–0), the peak at 400 nm was weakened whereas those at 536 nm and 576 nm grew together with the appearance of a shoulder peak at 500 nm. The absorption peaks at around 530 nm were assigned to FVM, because the FVM solution shows the absorption at 535 nm. Thus, FVM form was superior to HCM in HCM/KF(25–0), whereas HCM was a predominant species in HCM/KF(50–0). Since FVM is a cationic form and stabilized in a polar environment, this result implies that the polarity of the interlayer space urges the conversion of HCM to FVM even without irradiation. The conversion of 2-hydroxychalcone to flavylium without irradiation has also been observed in the adsorption of the 2-hydroxychalcone into the polar cavity of zeolite L [26].

The peak at 576 nm was tentatively assigned to the FVM molecule influenced electrostatically by the negative charge of the clay sheet, since the cationic dye molecules are known to show bathochromic shift by such an electrostatic interaction [27–29]. The absorption shift of the flavylium by the effect of the negative charge in the micelle system has been reported [30–32]. However, it is also possible to explain the bathochromic shift by the change in the structure of the dye molecule. If the two phenyl rings of the FVM become planar by the structural restriction in the clay interlayer, the red shift of the absorption will be induced [33]. On the other hand, the blue shift of the peak suggested the formation of an aggregate. Because a large amount of HCM was converted to FVM in HCM/KF(25–0), the concentration of FVM in the clay interlayer became enough to form the aggregate. The aggregation of FVM has also been suggested in case that FVM is condensed by the adsorption into the supercage of zeolite Y [34].

3.3. *Photo-induced coloration of HCM/KF*

The photochemical conversion of HCM to FVM was examined in HCM/KF(25–0), HCM/KF(38–0) and HCM/KF(50–0). The spectral changes during irradiation of the samples are shown in Fig. 3. In HCM/KF(25–0), the increase in the absorption at around 500 nm was not so distinct during irradiation, because most of HCM had already been converted to FVM prior to irradiation. The formation of FVM during irradiation of HCM/KF(38–0) was observed to some extent, but the degree of coloration was insufficient. The peak at 468 nm, which was assigned to the H-aggregate of FVM by analogy to other flavylium derivatives [35,36], was stronger than in HCM/KF(25–0), suggesting that the aggregation of FVM was urged under the nonpolar environment with a large amount of the surfactant. On the contrary, irradiation of HCM/KF(50–0) scarcely caused the clear conversion of HCM to FVM, and the coloration of the sample was very weak. Because the absorption at 400 nm decreased during irradiation, HCM was evidently consumed by a photoreaction. As shown in Scheme 1, irradiation of HCM converts HCM to *cis*-2-hydroxychalcone. Since the blue shift of the absorption assigned to the *cis*-form [37,38] was not observed in Fig. 3c, it is certain that the *cis*-form will subsequently be converted to the hemiacetal, which does not show any absorption peak in the region

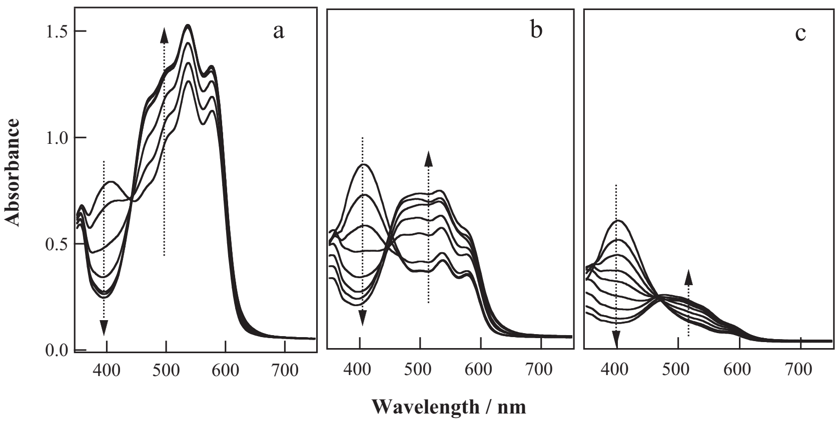

Fig. 3. Spectral changes of (a) HCM/KF(25–0), (b) HCM/KF(38–0) and (c) HCM/KF(50–0) under irradiation with the light from the 150 W Xe lamp. Irradiation period was 120 min for (a), 230 min for (b) and 180 min for (c).

above 350 nm. However, the acid catalyzed dehydration process of the hemiacetal to form FVM did not occur, because FVM prefers less hydrophobic circumstance. Thus, the formation of FVM was hard to occur under highly hydrophobic environment.

3.4. *Effect of the addition of an acidic compound*

As shown in the previous section, modification of the clay interlayer by a large amount of the surfactant was preferable to introduce HCM between the layers, but undesirable for the photo-induced conversion of HCM to FVM. In addition, it has been reported that stronger acidic condition is required to stabilize the flavylium in micellar matrices [30–32,39]. Therefore, the addition of an acidic compound is expected to help convert HCM to FVM under irradiation. Based on this idea, the clay interlayer was perfectly modified by the surfactant, and BSA (benzenesulfonic acid) was added to the modified clay. Since HCM was introduced in the clay layer and the photochemical conversion from HCM to FVM was hindered in the HCM/KF(50–0) sample (Fig. 3c), it is certain that saturated amount of the surfactant helps the incorporation of HCM but obstructs the photochemical conversion. Therefore, the benzenesulfonic acid was expected to work as a promoter of the photochemical conversion in the HCM/KF(200–*x*) samples. Fig. 4 illustrates the spectral changes during irradiation of (a) HCM/KF(200–0.1) and (b) HCM/KF(200–0.4). Before irradiation, the absorption at around 500 nm was unapparent, indicating that most of the introduced HCM was not converted to FVM but stayed as the original HCM form. Irradiation of HCM/KF(200–0.1) caused the decrease in the absorption at 400 nm, however, only a little growth of the FV absorption was observed, indicating that most of the HCM was converted to the colorless hemiacetal form. By comparing Fig. 4a with Fig. 3c, we can conclude that small amount of BSA was insufficient to convert the hemiacetal to the FV form. Irradiation of HCM/KF(200–0.4) resulted in distinct formation of FVM with the growth of an absorption at 470 nm together with shoulder peaks at 536 and 596 nm. The sufficient amount of BSA assisted the conversion to the FV form. Since the amount of the surfactant in the interlayer space was large, the dominant species was the H-aggregate, as described above. From this, it was concluded that the modification of the clay by the surfactant was required to keep the dye in the HCM form, and that the sufficient addition of acidic compound was needed for the photochemical conversion from HCM to FVM.

Fig. 5 shows the dependency of the proceeding of the coloration reaction during irradiation on the amount of BSA loading. As seen in HCM/KF(200–0.1) and HCM/KF(200–0.2), small amounts of BSA loading brought about only limited effect on the enhancement of the formation of FVM. On the other hand, too much amount of BSA obstructed the distinct color change, as seen in HCM/KF(200–0.5). Since too strong acidic condition urged the conversion of HCM to FVM even without irradiation, the change in the absorption by the increase in FVM during irradiation became indistinct. In addition, the change in the absorption at 400 nm was rather small and the absorption was kept at high value (∼0.5). This makes the absorption change dimmer and the A470/A400 ratio small even after continuous irradiation. We could not clarify the reason why the absorption at 400 nm was kept at high value. The possible concentration of the FV form may be limited in the organo-modified clay interlayer.

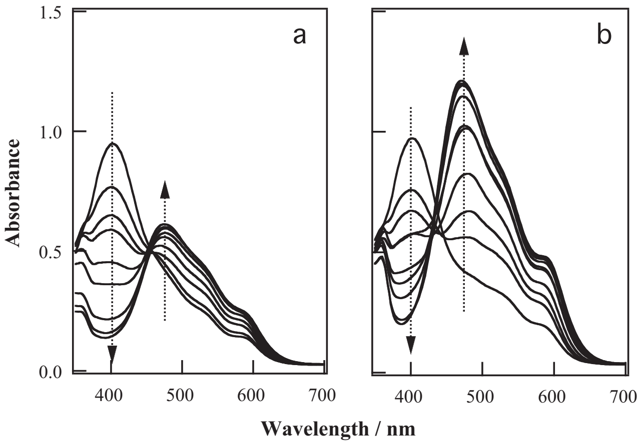

Fig. 4. Spectral changes of (a) HCM/KF(200–0.1) and (b) HCM/KF(200–0.4) containing BSA as an acidic compound. Irradiation time was 170 min for (a) and 100 min for (b).

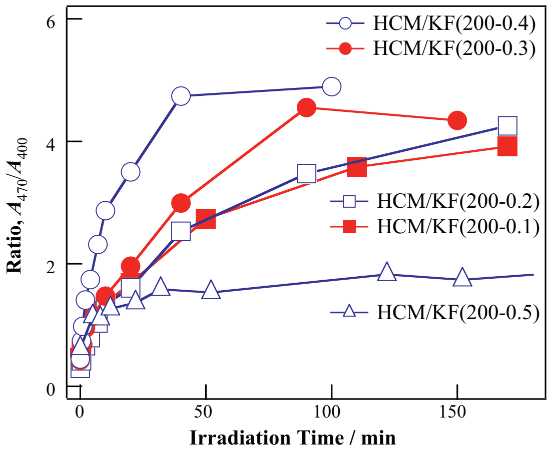

Fig. 5. Relationship between the proceeding of the coloration reaction and the loaded amount of BSA. The ordinate is the ratio of the absorption at 470 nm to that at 400 nm, whereas the abscissa is the irradiation time. The absorption at 470 nm and 400 nm corresponds to those of FVM and HCM, respectively. The introduced amount of BSA was 0.1 mmol for close box, 0.2 mmol for open box, 0.3 mmol for close circle, 0.4 mmol for open circle and 0.5 mmol for triangle symbol.

In any event, excess amount of BSA was not suitable for the photo-induced coloration of the HCM/KF samples. Therefore, the best sample was HCM/KF(200–0.4) showing a dense color and distinct coloration caused by irradiation.

3.5. *Photo-induced coloration of HCY/KF*

The photo-induced coloration was also tested for the HCY/KF sample. Fig. 6 indicates the spectral change of HCY/KF(200–0.4) during continuous irradiation for about 110 min. The peak at 436 nm increased along with the decrease in the absorption at 365 nm. As the peak at 436 nm and 365 nm are assigned to FVY and HCY, respectively [13,40], this result indicates the successful conversion of HCY to FVY in the interlayer space of the organo-modified KF by UV irradiation. The λ_{max} of FVY observed under irradiation of HCY/KF(200–0.4) was identical to that of the FVY solution. This means that there was only weak interaction between the FVY molecule and the negatively charged clay layer, or that the molecular orientation was not restricted so much. It has been reported that no peak shift of the flavylium is observed in a cationic or a neutral micelle system, although bathochromic shift is observed in an anionic micelle [32]. On the other hand, the missing of the spectral shift suggests the absence of the aggregate of FVY. Although the reason is unclear, FVM tend to form aggregate compared to FVY [34].

Fig. 7 illustrates the spectral change of HCY/KF(200–0.4) under 10 s irradiation and subsequent adaptation in the dark for 500 min. Although the absorption of HCY decreased only under the brief irradiation, the growth of the peak at 436 nm proceeded even in the

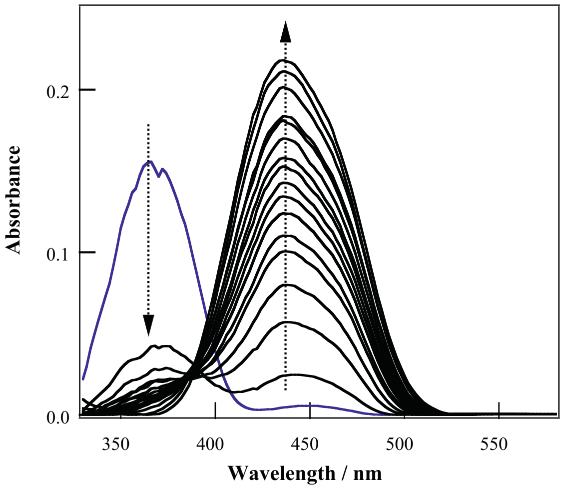

Fig. 6. Spectral changes of HCY/KF(200–0.4) during irradiation for 110 min with the light from the 27 W black light.

dark after the irradiation, indicating the delayed formation of FVY by a thermal reaction following to a photochemical process. There was no isosbestic point in the series of the spectra shown in Fig. 7, suggesting the formation of another stable chemical species other than HCY and FVY through the process. It should be noted that a clear isosbestic point has been observed on the spectral change in the conversion of HCY to FVY in solutions [13,40].

The result shown in Fig. 7 suggests that the photochemical reaction concerning HCY occurred in HCY/KF, otherwise, the coloration process did not proceed rapidly. Therefore, the HCY molecule should be converted to *cis*-form promptly under irradiation of HCY/KF (Scheme 1). It has been reported that the tautomerization reaction of the *cis*-chalcone to the hemiacetal form is a rather fast process, whereas the dehydration process of the hemiacetal to form the flavylium is a slow step, unless the acid concentration is not so high [6]. Considering these, the photochemical conversion of HCY to the *cis*-form and the subsequent tautomerization to the hemiacetal are thought to proceed rapidly under irradiation. However, the formation of FVY by the dehydration of the hemiacetal is delayed, since the acid concentration is not expected to be high. The kinetic barrier may be due to the slow diffusion of the eliminated water molecules in the hydrophobic phase of the surfactant in the clay interlayer. In other words, the coloration rate after irradiation can be controlled by the incorporation into the clay interlayer. The delayed coloration was not found on HCM–FVM. FVM is more stable than FVY since FVM has the electron donating dimethylamino group [41]. Therefore, the conversion of the hemiacetal form to the flavylium form may be smooth in the HCM–FVM system.

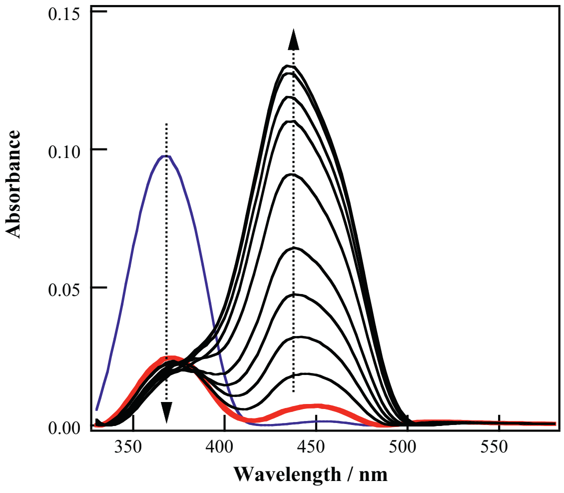

Fig. 7. Spectral change of HCY/KF(200–0.4) during 10 s irradiation and subsequent maintaining in the dark for 500 min. The thick curve illustrates the spectrum just after the irradiation.

Comparing Fig. 6 and Fig. 7, we can see that the formation of FVY was more rapid under continuous irradiation than in a short-time irradiation. Spontaneously, we can notice that the decrease in the absorption assigned to HCY was larger in Fig. 6 than that in Fig. 7. This implies that the consumption of HCY was more active in case of continuous irradiation than in short-time irradiation. Therefore, the equilibrium between HCY and the *cis*-form was more inclined toward right side under continuous irradiation. Consequently, the conversion of the *cis*-form to the hemiacetal and of the hemiacetal to FVY proceeded more rapidly under continuous irradiation.

For summary, the 2-hydroxychalcones were incorporated in the clay interlayer modified with the surfactant. The addition of the acidic compound enabled the photo-induced coloration based on the conversion of the 2-hydroxychalcone to the flavylium. The delayed coloration after irradiation was observed in the present dye/clay photochromic system.

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