Intercalation and Photochromism of Spiropyrans on Clay Interlayers

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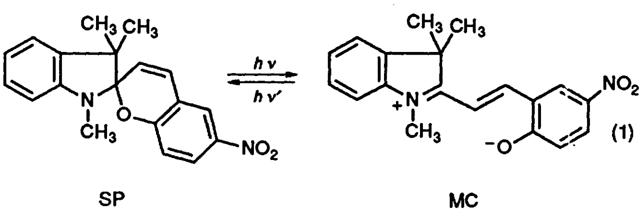
1′,3′,3′-Trimethylspiro[2*H*-1-benzopyran-2,2′-indoline] (abbreviated to H–SP) and its derivatives, 6-nitro (NO_2–SP) and 6-nitro-8-(pyridinium)methyl spiropyrans (Py^+–SP), have been intercalated in the interlayers of Montmorillonite. The intercalation was highly dependent on the substituent groups on the SPs. Charged Py^+–SP was quantitatively adsorbed on the clay as an equilibrium mixture with the corresponding merocyanine (Py^+–MC) in aqueous colloidal solution, the ratio Py^+–SP:Py^+–MC being 35:65 and exhibiting reversed photochromism. In contrast, a preferential adsorption as Py^+–SP was observed for the hydrophobic clay layers coadsorbing cetyltrimethylammonium bromide (CTAB), which displays normal photochromism. The thermal isomerization of Py^+–SP intercalated in aqueous colloidal clay exhibited a linear combination of two components of the first-order reactions, while that of the Py^+–SP–CTAB coadsorbed system satisfied a single first-order kinetics. The two-component kinetics are explicable in terms of the intervention of at least two different kinds of microscopic environment, *e.g.* non-polar and polar phases, in the clay interlayers. We also show that the photochemical decoloration of Py^+–MC was significantly retarded by the intercalation. All of these results are discussed on the basis of the polarity of the intercalation.

Interconversion between spiropyran (SP) and merocyanine (MC) has long been known as a typical example of photochromic behaviour.[1–3] The reversible conversion between SP and MC has drawn much attention as a possible recording medium for information storage and retrieval devices. Their supporting media profoundly influence not only the ease of photochemical coloration and/or decoloration, but also the thermal stability of coloured MC. A number of media have been investigated in which the photochemical and thermal equilibrium of SP and MC may be controlled. Among them are included polymer matrices,[4,5] layer assemblies such as Langmuir–Blodgett (LB) films[6] and micellar systems.[7] Some spiropyrans may aggregate themselves in an ordered form under certain conditions, under which the MC dyes are quite stable thermally.[4p,5] A J-aggregate of MC in LB films exhibits a sharp and intense absorption at 618 nm and is 10^4 times more stable than the usual MC form.[8]



(1)

In this respect, clay minerals would be expected to be useful as media with which to immobilize and align photochromic materials, since they can accommodate organic substances in their interlayers. For example, Montmorillonite clay possesses sodium ions which are exchangeable with organic ions forming molecular aggregates such as mono- or bi-layer films.[9–11] Thus clay interlayers are interesting electrostatic fields serving various types of molecular aggregate.

Of particular interest is the intercalation of photochromic compounds since their film formations are easily accessible. To our knowledge, however, there have been no data reported on the intercalation and photochromic behaviour of 1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indoline](H–SP), a typical photochromic substance, on clay interlayers. The present paper describes the photochromism of Montmorillonite-intercalated H–SP and its 6-nitro (NO_2–SP) and 6-nitro-8-(pyridinium)-methyl derivatives (Py^+–SP). The effect of the intercalation on the rates of thermal coloration or decoloration has been compared with those in other systems such as colloidal SiO_2,[12] cetyltrimethylammonium bromide (CTAB) and sodium dodecylsulphate (SDS) micelles.

Experimental

Apparatus.—UV and visible spectra were recorded on a Shimadzu UV-265 spectrophotometer. Irradiations were performed employing a 150 W xenon lamp equipped with a Hitachi 650-10 monochromator. Clay-intercalated samples were prepared with a Kaijo Denki 200 A homogenizer at ambient temperature. Calculations of rates of isomerization were carried out using an NEC microcomputer, Model PC 9801 VM, with least-squares optimization software. NMR spectra were recorded on a Varian Jemini-200 NMR instrument. All coupling constant values *J* are given in Hz.

Materials.—Montmorillonite (Kunipia F©), a purified natural clay, was a gift from Kunimine Kogyo. The average diameter of the clay powder particles is 0.37 μm, the cation-exchange capacity (CEC) 119 meq 100 g^{-1}. 1′,3′,3′-Trimethylspiro[2*H*-1-benzopyran-2,2′-indoline](H–SP) was prepared by reported methods,[13] m.p. 94.0–95.5 °C (lit.,[13] 96 °C). 6-Nitro-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indoline] (NO_2–SP) was prepared according to reported procedures,[13] m.p. 174.5–175 °C (uncorrected) (lit.,[13] 176–177 °C). 6-Nitro-8-chloromethyl-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indoline] was prepared by reported procedures,[14] m.p. 130.5–132 °C (lit.,[14] 133–134 °C). Its pyridinium salt,[15] (Py^+–SP) was obtained as a yellow powder by treatment with excess amounts of pyridine in refluxing benzene: δ_H(200 MHz; $CDCl_3$; standard Me_4Si) 9.0 (1 H, d, *J* 2), 8.7 (2 H, m), 8.3 (1 H, m), 8.1 (1 H, d, *J* 2), 7.7 (2 H, m), 7.3 (1 H, m), 7.1 (1 H, m), 7.0 (2 H, m), 6.5 (1 H, d, *J* 7), 6.0 (2 H, d, *J* 12), 5.9 (1 H, d, *J* 7), 2.49 (3 H, s, Me), 1.2 (3 H, s, Me) and 1.0 (3 H, s, Me).

Table 1 Intercalation of substituted spiropyrans on clay interlayers[a]

Spiropyran	Percentage intercalation[b]	Major form[c]	Colour
(A) Intercalation in colloidal clay			
H–SP	85	MC	yellow
Protonated H–SP	100	MC	yellow
NO_2–SP	7.6	MC	pale yellow
Protonated NO_2–SP	66	MC	orange
Py^+–SP	94	MC[d]	red
(B) Intercalation in 100% CTAB-modified clay[e]			
H–SP	65	SP	—
NO_2–SP	12	SP	colourless
Py^+–SP[f]	32	SP[g]	pink

[a] Clay colloid was sonicated with an equivalent amount of spiropyran based on CEC in aqueous suspension. Details are noted in the Experimental. [b] The percentage intercalation of SP based on the CEC. [c] The favoured form of SP and MC equilibrated at room temperature in the dark. [d] Ratio of MC and SP is 65:35. [e] 100% means an equivalent amount of CTAB. [f] Colloidal dispersion in decanol. [g] Ratio of SP and MC is 92:8.

Intercalation of Spiropyrans (SP) in the Clay Layers.—(*A*) *SP on aqueous colloidal clay.* Spiropyran (*ca.* 10^{-4} mol dm^{-3}) was sonicated with Montmorillonite colloid (0.2 meq dm^{-3}) in 0–50% aqueous methanolic solution for 1 h at room temperature. When the degrees of intercalation based on the CEC were less than 40%, the resulting SP-intercalated clays were stable and kept dispersed as colloids in water for more than a month. The percentage intercalations were measured by filtering out the clay-intercalated SP on membrane filters of 0.45 μm pore size, affording a transparent film; the amounts of adsorbed SP were determined by UV spectrophotometry.

(*B*) *Protonated SP on aqueous colloidal clay.* An aqueous equimolar solution of HCl and SP (8.0×10^{-4} mol dm^{-3}) was sonicated with the colloidal clay (1.0 meq dm^{-3}) in water for 1 h at room temperature. The percentage intercalations were determined as described above and are summarized in Table 1.

(*C*) *SP on CTAB-modified clay.* An aqueous solution of SP (2×10^{-4} mol dm^{-3}) was sonicated with five equivalents of the clay (5.0 meq dm^{-3}) for 1 h at room temperature. The resulting 20% SP-intercalated clay suspension was successively sonicated with an aqueous solution of 8.0×10^{-4} mol dm^{-3} cetyltrimethylammonium bromide (CTAB) for 1 h, giving rise to white precipitates. These were dried overnight *in vacuo* at room temperature and the resulting white powder was made into a homogeneous colloidal solution in decanol (10 cm^3) by sonication for 1 h followed by overnight magnetic stirring. The degree of adsorption of Py^+–SP was estimated from its absorbance at 340 nm (ε_{max} 9500) of the filtrate separated from the intercalated clay, and that of CTAB was determined by making a complex with Orange II and measuring its absorbance at 485 nm spectrophotometrically.[16]

Adsorption of Py^+–SP *on an Aqueous* SiO_2 *Colloid.*—An aqueous solution of pyridinium spiropyran (Py^+–SP, 5.2×10^{-5} mol dm^{-3}, 50 cm^3) was sonicated with silica colloid (20 wt%, 5 cm^3)* in 5 cm^3 of aqueous alkaline solution (pH 9.5–10.0) for 1 h, affording a clear colloidal solution. The equilibrated ratio Py^+–SP:Py^+–MC was 37:63 at 50 ± 0.5 °C.

Adsorption of Py^+–SP *on Micellar Surfaces.*—The ratios Py^+–SP:Py^+–MC were compared for the cases of anionic and cationic micellar surfaces. The equilibrated ratios of Py^+–SP to Py^+–MC were measured at 50 ± 0.5 °C in aqueous micellar solutions of sodium dodecylsulphate (SDS, 1.0×10^{-2} mol dm^{-3}; 8.1×10^{-3} mol dm^{-3}), the total amount of Py^+–SP and Py^+–MC was $5.2–9.9 \times 10^{-5}$ mol dm^{-3}. The results are summarized in Table 3.

Kinetics of the Thermal Conversion of SP to MC.—The thermal isomerization of SP to MC was monitored by measuring the absorbance of MC (*e.g.* 522 nm in the case of Py^+–MC in MeOH) using a UV-VIS spectrophotometer equipped with a cell holder thermostatted at 20–70 °C with an accuracy of ±0.5 °C. In the case of aqueous clay systems prepared by method (*A*) or (*B*), the rate of isomerization, *i.e.* the coloration, could be expressed by a linear combination of two kinds of first-order reaction [eqn. (1)]. Here, A_t is the absorbance at time *t*, and C_1 and C_2 denote fractions of faster and slower components, respectively. The first-order rate constants, k_1 and k_2, are those of the corresponding isomerizations. Examinations for data fitting were successfully performed by a least-squares method using an NEC microcomputer.

$$A_\infty - A_t = C_1\exp(-k_1t) + C_2\exp(-k_2t) \qquad (1)$$

The isomerization rates for the case of CTAB-modified clay [method (*C*)] resulted in the first-order kinetics of only one component.

Photochemical Conversion of MC to SP.—The photochemical isomerization of MC to SP was carried out by irradiating at 520 ± 10 nm using a 150 W xenon lamp and a monochromator at room temperature. The progress of the reaction was followed by measuring the disappearance of the absorbance of MC (*e.g.* 492 nm in H_2O and 522 nm in methanol). Quantum yields were determined in a 10 mm quartz cell for the photochemical conversion of clay-intercalated MC dispersed in appropriate solvents such as H_2O and decanol. For comparison, the isomerization yields in homogeneous solutions were also determined as listed in Table 4.

Results and Discussion

Intercalation of SP on Clay Interlayers.—Spiropyrans (SP) were shown to be intercalated by sonicating with Montmorillonite in the clay interlayers and the percentage intercalation of the SPs were dependent on the kinds of substituent. Unsubstituted spiropyran (H–SP) was easily intercalated in the clay in the form of merocyanine (MC).

The equilibria between SP and MC were estimated from their absorption spectra. In contrast to the case of H–SP, the nitro derivative (NO_2–SP) was inefficiently intercalated in the clay layer (Table 1).

In order to determine the nature of the intercalation, the effect of protonation was examined. Protonated MC (H–MC, $R^1 = R^2 = H$), which was prepared by treating H–SP with 1 mol dm^{-3} HCl in acetone,[17] was quantitatively intercalated in the clay (Table 1). The effect of protonation was more significant for the case of NO_2–SP, which was quite inefficient under neutral conditions. Thus, it is apparent that the predominant driving force for the intercalation is the electrostatic attraction between the cationic charge of adsorbate and anionic sites on the clay layers. These intercalated photochromic materials exhibited the following characteristics: (i) Protonated MCs shift their absorption maxima hypsochromically by *ca.* 100 nm compared with their neutral forms. (ii) The ring closure of MC to SP is considerably retarded by fixation of the indolenium nitrogen at the anionic sites of clay. (iii) Py^+–SP may be a good adsorbing photochromic substance.

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Table 2 Intercalation of Py^+–SP in the CTAB-modified clay in decanol[a]

Added/mol dm^{-3}		Adsorbed/mol dm^{-3}		Degree of intercalation (%)[b]	
Py^+–SP	CTAB	Py^+–SP	CTAB	Py^+–SP	CTAB
2.4×10^{-5}	22.5×10^{-5}	1.3×10^{-5}	22.1×10^{-5}	5.4 (53)	89 (98)
4.8×10^{-5}	20.0×10^{-5}	2.4×10^{-5}	19.6×10^{-5}	10.3 (51)	79 (98)
24.8×10^{-5}	25.7×10^{-5}	7.2×10^{-5}	25.2×10^{-5}	29 (29)	98 (98)

[a] Amounts of clay are 23.8×10^{-5} mol dm^{-3} based on its CEC. For intercalation conditions see the Experimental. [b] Percentage intercalations based on total amount of clay anionic sites. The figures in parentheses are the percentage intercalations based on added substrates.

Table 3 First-order rate constants for the thermal conversion of Py^+–SP to Py^+–MC at 50 °C[a]

Reaction medium	Percentage intercalation of Py^+–SP	λ_{max} of Py^+–MC/nm	K[b]	Rate constant/ 10^5 s^{-1} [c]		C_1/C_2
				k_1	k_2	
(*a*) Py^+–SP intercalated in clay interlayers						
On clay–H_2O	5	510	26/74	53	5.0	23/77
	10	510	32/68	75	12	45/55
	20	510	35/65	91	19	54/46
On 5% CTAB modified clay–H_2O[d]	10	515	40/60	31	11	61/39
On 10% CTAB modified clay–H_2O[d]	10	515	39/61	36	11	61/39
On 79% CTAB modified clay–decanol[d]	10	540	92/8	4.6		>10
On aqueous colloidal SiO_2[e]		480	37/63	53		>10
(*b*) Py^+–SP in homogeneous and micellar solutions						
Water		492	53/47	13		>10
SDS–H_2O[e]		521	25/75	50		>10
Methanol		522	67/33	16		>10
Acetonitrile		536	66/34	65		>10
Decanol		549	96/4	20		>10
Chloroform		560	90/10	93		>10

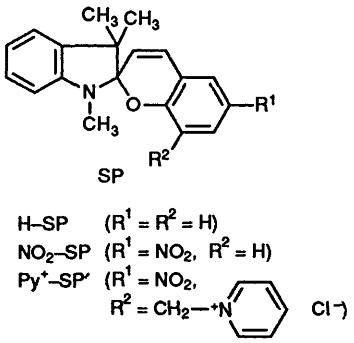
[a] Determined at 50 ± 0.5 °C by means of the absorbance of Py^+–MC at its absorption maximum. [Py^+–SP] = 2.0–6.3 × 10^{-5} mol dm^{-3}; [clay] = 1.25–5.0 × 10^{-4} mol dm^{-3} based on CEC. [b] Thermal equilibrium ratio of SP to MC at 50 ± 0.5 °C. [c] For notations of k_1, k_2, C_1 and C_2 see eqn. (1) and the text. The figures were calculated by dividing the k_{obs} values by the equilibrium ratio of (SP + MC)/MC, *i.e.*, 1 + K. [d] % CTAB means the degree of intercalation of CTAB based on CEC. [e] Snowtex© (Silica 20) available from Nissan Chem. Corp. [f] [SDS] = 1.0 × 10^{-2} mol dm^{-3}.

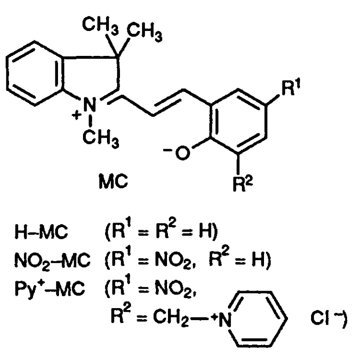
Table 4 Effect of intercalation on the photochemical conversion of Py^+–MC to Py^+–SP[a]

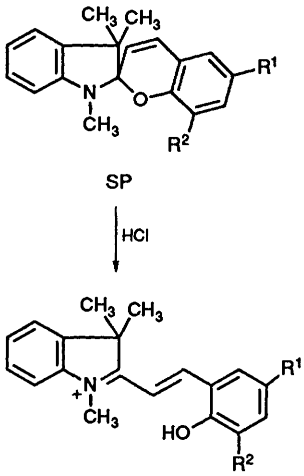
Reaction medium	Percentage intercalation of Py^+–MC	Percentage of Py^+–MC equilibrated thermally	Quantum yield (Φ)
(*a*) Py^+–MC intercalated in clay interlayers			
Clay layers–H_2O	10	68	0.011
	20	65	0.016
	30		0.024
79% CTAB-modified clay–decanol	10	8	0.16
Aqueous colloidal SiO_2[b]	—	63	0.13
(*b*) Py^+–MC in homogeneous and micellar solution			
H_2O	—	47	0.42
SDS–H_2O[c]	—	75	0.48
CH_3OH	—	33	0.34
Decanol	—	4	0.28

[a] Measured at the absorption maximum of Py^+–MC at room temperature. [Py^+–SP] = 2.5 × 10^{-5} mol dm^{-3}; [clay] ≈ 7.5–25 × 10^{-5} mol dm^{-3} based on CEC, see footnote *a* of Table 3 for reaction conditions. [b] Intercalation of CTAB based on CEC. [c] [SDS] = 1.0 × 10^{-2} mol dm^{-3}.

A spiropyran with a pyridinium group (Py^+–SP) is a candidate for the adsorbable photochromic substance. In fact, the intercalation of Py^+–SP was nearly quantitative under neutral conditions in water, giving a red colloidal solution. To obtain a homogeneously dispersed solution of Py^+–MC on clay, the amount of Py^+–MC should be less than 30% intercalation. On addition of Py^+–MC of over 40% intercalation precipitation occurred, and its colour changed from bright red to purple. The coloured colloids consisted of an equilibrium mixture of Py^+–SP and Py^+–MC in a ratio of 35:65 in the dark at 50 ± 0.5 °C and exhibited reverse photochromism. The major forms in the intercalation of H–SP,







(2)

Protonated MC

NO_2–SP and Py^+–SP were always of the MC structure in aqueous colloidal clay and hence all displayed reverse photochromism. It is known that the clay interlayer is quite polar and forms an electric double layer consisting of anionic sites and exchangeable sodium ions. Thermal equilibria between SP and MC are also known to be dependent on solvent polarity; MC becomes the major product with increasing polarity. Thus the reverse photochromism observed can be explained in terms of the polar interlayer of clay.

Intercalation of SP on CTAB-modified Clay Interlayers.—The interlayer surface of the clay may be made hydrophobic by substituting sodium ions with cationic surfactants, *e.g.* CTAB.[18,19] A CTAB-modified clay, including an appropriate amount of CTAB, was prepared as a colloidal solution in decanol and the intercalation of the SPs was examined. Treatment with various ratios of Py^+–SP and CTAB resulted in almost quantitative intercalation of CTAB and 30–50% adsorption of Py^+–SP ions as shown in Table 2. Owing to the much preferred intercalation of CTAB over Py^+–SP, an excess amount of Py^+–SP is to be intercalated as a result of the hydrophobic interaction rather than an electrostatic interaction.

Py^+–SP was shown to be intercalated mainly in the SP form, the ratio of SP and MC being 92:8; the modified system exhibited normal photochromism. Likewise, the 100% CTAB-modified clay accommodated H–SP or NO_2–SP mainly as SP, resulting in normal photochromism (Table 1). It is interesting to note that the major form of the adsorbate and the resulting photochromism could be reversed by changing the polarity of the interlayers. This indicates that the intercalation takes place by means of a hydrophobic interaction as well as electrostatic binding with ionic sites on the clay surface.

Thermal Conversion of Py^+–SP *into* Py^+–MC.—The thermal isomerization of Py^+–SP to Py^+–MC was followed kinetically by monitoring the increase in the absorbance of Py^+–MC, as exemplified in Fig. 1. The absorption maximum of Py^+–MC shifted to longer wavelengths and could be an index of the polarity of its environment. The coloration of Py^+–SP was subject to first-order kinetics in homogeneous and micellar solutions as listed in Table 3(*b*). The rates of isomerization increased significantly in less polar environments with aprotic solvents. When anionic SDS surfactant was added, the isomerization rate of Py^+–SP and the absorbance maximum of Py^+–MC were changed significantly and became close to those in clay interlayers. This suggests that the Py^+–SP ions are solvated in the hydrophobic micellar core of SDS. The cationic CTAB micelle had practically no effect on the isomerization rate although the SP:MC ratio was somewhat altered.

As shown in Fig. 2, the coloration of intercalated Py^+–SP obeyed a linear combination of two kinds of first-order reaction [eqn. (1)]. The two-component kinetics suggest that the clay-intercalated Py^+–SP experiences at least two different kinds of environment. As the percentage intercalation of Py^+–SP increases, the fraction of the C_1 component and the rate constants, k_1 and k_2, increase gradually. By contrast, the thermal isomerization of Py^+–SP on silica colloids followed single first-order kinetics. Py^+–MC on SiO_2 colloids exhibited an absorption maximum at 480 nm, suggesting a rather homogeneous polar environment on the SiO_2 surface. Thus, the observed two-component kinetics for clay interlayers clearly implies that the clay surface provides adsorption circumstances that are more complicated than is the case for SiO_2 colloids.

At this point it is important to comment on the adsorption behaviour of charged organic compounds on the clay interlayers. The electrostatic interaction between charged compounds and charged sites is a major driving force for intercalation.[17a] As a second factor, the organic moiety of the adsorbates causes the formation of molecular aggregates *via* hydrophobic interactions. In fact, recent work performed in our laboratory has shown that stilbazolium ions assemble together, even when the percentage intercalation is as low as 0.1%, suggesting the importance of the hydrophobic interaction of organic adsorbates.[20]

Based on the above information, we present a reasonable explanation for the two kinds of first-order kinetics for the coloration of Py^+–SP on aqueous colloidal clay. That is, the faster component may be due to the less polar molecular aggregates of the Py^+–SP ions. With increasing degree of adsorption, the less polar component (C_1) and the coloration rate (k_1) will increase gradually, as shown in Table 3(*a*). This is because the isomerization of the SPs will be faster in non-polar conditions. On the other hand, the slower component may result from Py^+–SP molecules adsorbed separately, where the adsorption environment is more polar. The observed slower rate is explained well by the solvent effect, as in homogeneous solutions where the polar conditions slow down the isomerization [Table 3(*b*)]. The absorption maxima of the

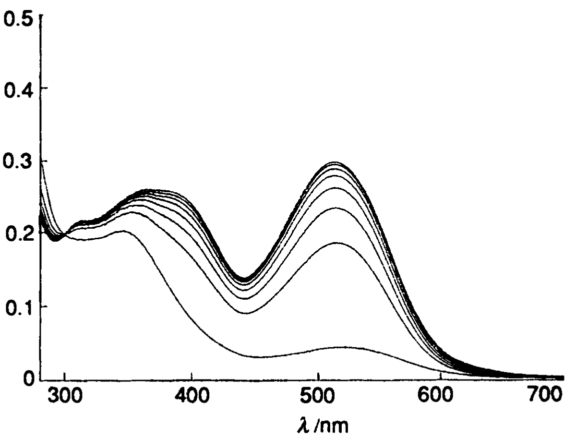


Fig. 1 Thermal isomerization of Py^+–SP to Py^+–MC intercalated in aqueous colloidal clay at 50 °C. The degree of intercalation was 20% and the spectral change with coloration was monitored, at reaction times of 0, 10, 20, 30, 40, 50, 60 and 70 min.

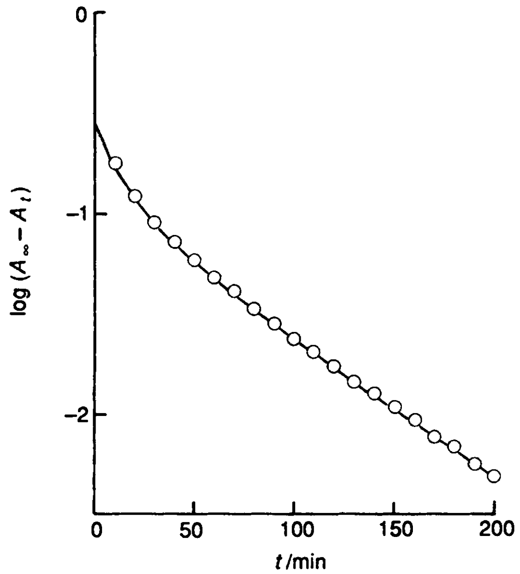


Fig. 2 Thermal coloration of Py^+–SP on aqueous colloidal clay at 50 °C was monitored by absorbance maximum (A_t) or Py^+–MC at 510 nm. Open circles (○) plotted are in accordance with a calculated curve composed of two kinds of first-order kinetics.

merocyanine structures are highly dependent on the solvent polarity; *i.e.* the less-polar solvent shifts the absorption maximum of Py^+–MC from 492 (H_2O) to 560 nm ($CHCl_3$). The absorption maximum of Py^+–MC intercalated in aqueous colloidal clay, however, remains unchanged at 510 nm on altering the degree of intercalation, indicating the intercalation of Py^+–MC ions in rather polar conditions.

In contrast, the adsorption of Py^+–MC on the CTAB-modified clay in decanol is of the non-polar type as reflected in the bathochromically-shifted absorption maximum at 540 nm, and the observation of single-component kinetics suggests a homogeneous adsorption. Notably, the faster component (k_1) altered drastically when the solvent was changed from water to decanol and the slower one (k_2) was not observed in decanol [Table 3(*a*)]. These facts support the assumption that the isomerization is also affected by steric hindrance of the hydrophobic environment.

Photochemical Conversion of Py^+–MC *to* Py^+–SP.—Red Py^+–MC exhibits its absorption maximum at *ca.* 520 nm and isomerizes to the corresponding Py^+–SP by irradiating visible light. Fig. 3 shows the variation of the percentage of the MC component on irradiation of Py^+–SP intercalated on colloidal clay in water, the initial ratio of Py^+–SP and Py^+–MC being 35:65. Fig. 3 is characteristic of reverse photochromism; *i.e.* photo-chemical decoloration and thermal coloration take place. In contrast, the opposite photochromic behaviour was observed for the case of the CTAB-modified clay in decanol, as shown in Fig. 4, which shows normal photochromism; the coloration proceeds photochemically. The interconversion between normal and reverse photochromism is quite interesting.

Quantum yields for the decoloration varied with the reaction media. The data in Table 4 show that the photochemical isomerization of intercalated Py^+–MC is 10–40 times less effective than in the cases without clay. The less effective isomerization may be explained in terms of the electrostatic interaction between the positive charge of Py^+–MC and the

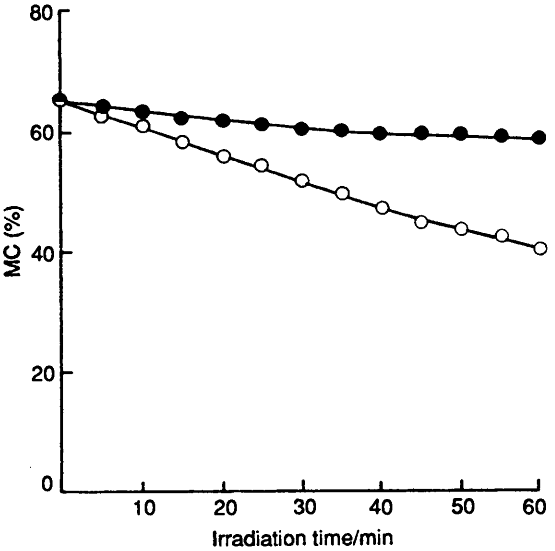


Fig. 3 Photochemical conversion of Py^+–MC to Py^+–SP on irradiation at ⩽300 nm (–●–●–) or in the visible region >400 nm (–○–○–). Percentage intercalation was 20% on aqueous colloidal clay, and Py^+–MC was the major form (*i.e.* 65%).

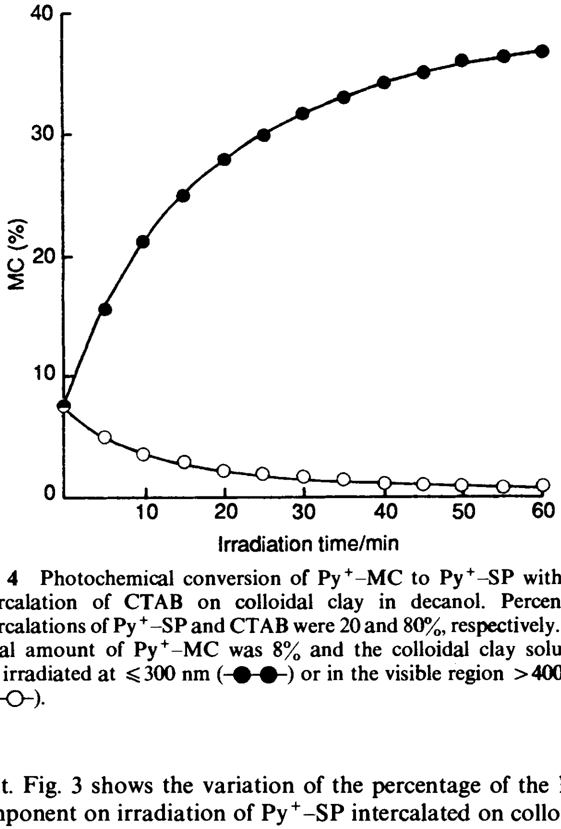


Fig. 4 Photochemical conversion of Py^+–MC to Py^+–SP with co-intercalation of CTAB on colloidal clay in decanol. Percentage intercalations of Py^+–SP and CTAB were 20 and 80%, respectively. The initial amount of Py^+–MC was 8% and the colloidal clay solution was irradiated at ⩽300 nm (–●–●–) or in the visible region >400 nm (–○–○–).

anionic site on the clay. Adsorption on the ionic interlayer causes an increase in the stability of MC.

The efficiencies for the photochemical isomerization of intercalated Py$^+$–MC increased dramatically when CTAB was added. It is apparent that the efficiencies are higher under less-polar conditions and increase with increasing degree of intercalation. All of these facts are explicable on the basis of the polarity of the intercalation. Appreciable amounts of ionic sites remain vacant in the case of low coverage of Py$^+$–MC (*e.g.* $\leqslant 30\%$), which is reflected in the slower isomerization rate owing to the stabilization of Py$^+$–MC by the electrostatic interaction. This is in contrast to the cases of homogeneous and micellar solutions where the quantum yields of the decoloration are quite high (*i.e.* 0.3–0.5) irrespective of the solvent polarity or surfactant [Table 4(*b*)]. Thus, the electrostatic interaction between Py$^+$–MC and anionic sites on the clay interlayers is the main reason why the quantum yields become 40 times lower than those in homogeneous solutions.

Conclusions

6-Nitro-8-(pyridinium)methylspiropyrans (Py$^+$–SP) have been shown to be efficiently intercalated in clay interlayers in aqueous colloidal solutions. The system was characteristic of reverse photochromism, where two-component first-order thermal coloration indicates the presence of two different adsorption environments. When CTAB was co-adsorbed, the resulting Py$^+$–SP–CTAB system was characteristic of normal photochromism, single first-order kinetics being observed. The photochromism of Py$^+$–MC was shown to be considerably retarded by the intercalation. The interconversion between Py$^+$–SP and Py$^+$–MC was discussed on the basis of the polarity change caused by intercalation. Clay intercalation of Py$^+$–SP may prove useful for functional devices on the basis of the ease of preparation of films, its stability and polarity change.

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