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Effect of Alkylammonium Ions on the Photochemical Behaviors of γ-Stilbazolium Aggregates in Clay Interlayers

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Effect of alkylammonium ions (C_n^+) has been studied on the clusterization and photochemical behaviors of γ-stilbazolium (4-(2-phenylvinyl)pyridinium) ion (**1**) adsorbed on clay interlayers. The aggregates of **1** were shown to be dissociated by the coadsorption of C_n^+ with molecular length longer than that of **1**. The major photoreaction was changed from cyclodimerization to *E–Z* isomerization on coadsorbing C_n^+'s longer than **1**. The efficient excimer emission from intercalated **1** was dramatically reduced by coadsorbing alkylammonium ions. The resulting concentration dependence of excimer emission intensity is nicely simulated by a Monte Carlo method for two-dimensional lattice site models.

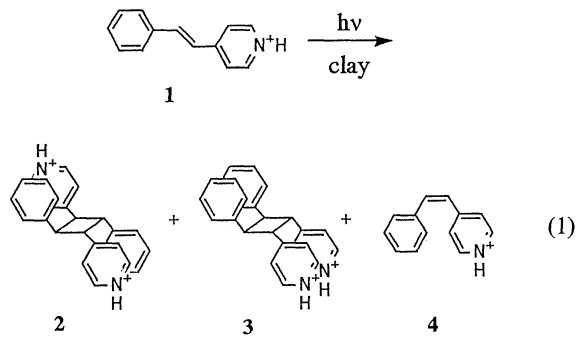
A marked interest has been focused on the photochemistry and photophysics of molecules in heterogeneous systems including micelles, vesicles, and so on.[1,2] On the other hand, only a little has been studied for photochemistry in heterogeneous systems such as silica gel,[3] zeolites,[4] and layered clay minerals.

Smecite clays consist of planar polyanionic sheets and exchangeable sodium ions, providing a stable electrostatic field. An interesting point to be noted is such that the restricted space, i.e., clearance space, in clay layers is variable depending on the size of organic cations to be intercalated.[5] In clay systems, a unique absorption behavior has been reported where different guest molecules are adsorbed separately from each other.[6] It is also reported that the coadsorption of alkylammonium ions induces a significant conformational change of adsorbents.[7]

However, little is known about a possibility, scope, and limitation of photoreaction in clay interlayers. We have been interested in applying the interlayer space of clay as a unique reaction field for spatially controlled photoreactions. We have recently reported that a clay-intercalated stilbazolium ion (**1**) undergoes a selective photodimerization to give *syn* head-to-tail type cyclodimer.[8] It has been also shown that the intercalation is quite efficient and the molecules are relatively immobile.[9] The present paper discloses an interesting effect of alkylammonium ions (C_n^+) on the photochemical behaviors of intercalated aggregates, which are adequately simulated by a Monte Carlo method for a two-dimensional lattice model.

Results and Discussion

In the previous report,[8] the intercalation of γ-stilbazolium (4-(2-phenylvinyl)pyridinium) ion (**1**) on clay interlayers was shown to result in a quite efficient photochemical dimerization affording *syn* head-to-tail (Eq. 1). The selective cyclodimerization was discussed on the basis of antiparallel packing of intercalated molecules.



(1)

Effect of Alkylammonium Ions (C_n^+) on the Photoreaction of Intercalated 1. The effect of alkylammonium ions (C_n^+) on the photochemical behaviors of intercalated **1** was determined in order to examine the formation and dissociation of molecular aggregates in clay interlayers. Irradiations of **1** intercalated on Saponite clay were carried out in the presence of various amounts of C_n^+. The photochemical reaction of **1** was found to be remarkably affected by certain kinds of C_n^+. As shown in Fig. 1, octylammonium ion (C_8^+) heavily retarded the dimerization, while butyl homolog (C_4^+) was practically of no effect. For the case of C_8^+, the *E–Z* isomerization became the predominant photoreaction.

Two possibilities are conceivable as an origin for the inefficient cyclodimerization in the presence of longer chain ammonium ions. One is such that stibazolium ions in the clay layers are substituted by ammonium ions and extracted into the bulk solution, resulting in the efficient *E–Z* photoisomerization. The other one is that coadsorbed C_n^+ ions may cause a significant change in the packing mode of **1** favorable for the isomerization. In order to differentiate the two possibilities, the effect of chain length of ammonium ions on the adsorption of **1** was examined as described in the followings.

Substitution of Intercalated 1 with C_n^+. Adsorption equilibrium and its constant, K_{ad}, for the adsorption of C_n^+ on clay interlayers are expressed as Eqs. 2 and 3, respectively. The K_{ad} values have been shown to increase

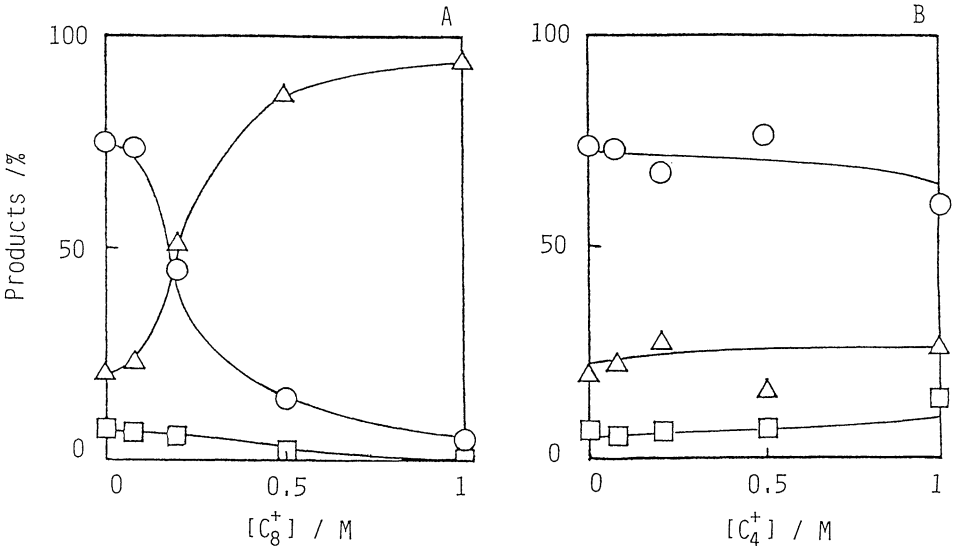


Fig. 1. Effect of alkyl ammonium ions on photoreactivity of pre-intercalated **1** on clay; —○—, *syn* head-to-tail dimer (**2**); —□—, *syn* head-to-head dimer (**3**); —△—, *Z*-**1** (**4**). Intercalated **1**-clay complex (40 mg or 6.8 mM based on CEC; i.e., 100% adsorption) was suspended in 5 ml of aqueous solution of alkylammonium ions; A, octylammonium (C_8^+); B, butylammonium (C_4^+). After stirring overnight, irradiation was carried out for 30 min with a 300 WHg lamp through a Pyrex filter.

Table 1. Substitution of Stilbazolium Ions (**1**) by Alkylammonium Ions (C_n^+) in Clay Interlayer[a]

Alkylammonium ions		K_{ad}[c]	Substituted stilbazolium ions[d]/%
Alkyl group	Molecular length[b]/Å		
—[e]	—	—	1
Butyl (C_4^+)	6.7	0.72	1
Pentyl (C_5^+)	7.9	0.96	2
Hexyl (C_6^+)	9.2	1.99	4
Heptyl (C_7^+)	10.4	3.92	87
Octyl (C_8^+)	11.7	9.2	86
Decyl (C_{10}^+)	14.2	35.7	—

a) In aqueous solution of C_n^+ (0.5 M and 0.6 M HCl, 5 ml) 40 mg of **1**-clay complex was dispersed and stirred overnight. The ratio of $[C_n^+]/[\mathbf{1}]$ was 74. b) Calculated for the all staggered conformers using the following bond lengths: 1.54 Å (C–C), 1.47 Å (C–N), 1.09 Å (C–H), 1.01 Å (N–H). All of the bond angles were assumed to be 109.5°. The molecular length of **1** is 10.4 Å. c) Equilibrium constants of adsorption of C_n^+ on clay.[10] d) Estimated from uv absorption of filtrate through a membrane filter. See experimental section for details. e) No additives.

with increasing chain lengths of C_n^+;[10] e.g., K_{ad}=0.7 for C_4^+ and 9.2 for C_8^+ as listed in Table 1.

$$C_n^+ + Na^+\text{-clay}^- \overset{K_{ad}}{\rightleftharpoons} C_n^+\text{-clay}^- + Na^+ \quad (2)$$

$$K_{ad} = [C_n^+\text{-clay}^-][Na^+]/[C_n^+][Na^+\text{-clay}^-] \quad (3)$$

Stilbazolium ion (**1**) was shown to be effectively intercalated with K_{ad}=ca. 490.[9] Attempted substitution of intercalated **1** by excess amount of C_n^+ added was carried out. As shown in the last column of Table 1, the substitution with C_n^+ where $n \leqslant 6$ was practically negligible, but that with C_7^+ or C_8^+ was quite effective. The expelling effect of C_7^+ and C_8^+ is not explicable in terms of the K_{ad} value of C_n^+ itself, since the increase of one methylene in C_n^+ results in an increase of K_{ad} values only by a factor of two, despite of discontinuous increase of substitution efficiencies at n=6 and 7 (see the third column in Table 1). It is interesting to note that the substitution is most effective when the molecular length of C_n^+ ions is close to that of **1** (i.e., 10.4 Å). The origin of the dramatic effect is unclear at present and remains to be explored. However, the apparent retardation of photodimerization by adding octylammonium ion, as shown in Fig. 1, is mainly due to the effective substitution of **1** by C_8^+.

Effect of C_n^+ on Aggregation Mode of 1. Effect of alkylammonium ions on the photoreaction of intercalated **1** was studied and the results are summarized in Table 2. Hereafter, the amounts of C_n^+ ions were adjusted not to exceed the clay CEC in order to assure the coadsorption of **1** and C_n^+ on clay interlayers. The cyclodimer formation was decreased and the *E*–Z isomerization became predominant by increasing chain length in C_n^+. These features are more apparent in Fig. 2, which demonstrates an alteration of photoproduct distributions by changing the chain lengths. Notable here is that the critical length of C_n^+ is again comparable

Table 2. Effect of Coadsorbed Alkylammonium Ions on the Photoreaction of **1**

$C_n^{+a)}$	Conversion/%	Products/%		
		2	**3**	**4**
—	47	60	14	26
C_4^+	50	58	4	38
C_6^+	56	58	4	38
C_8^+	50	45	4	51
C_{10}^+	61	36	3	61
C_{12}^+	63	44	3	53
C_{14}^+	65	45	4	51

a) Mixed solutions of **1** (0.16 mM, 4% adsorption), C_n^+ (3.2 mM, 80% adsorption), and Saponite clay (4 mM, vs. CEC) were stirred for two hours and irradiated.

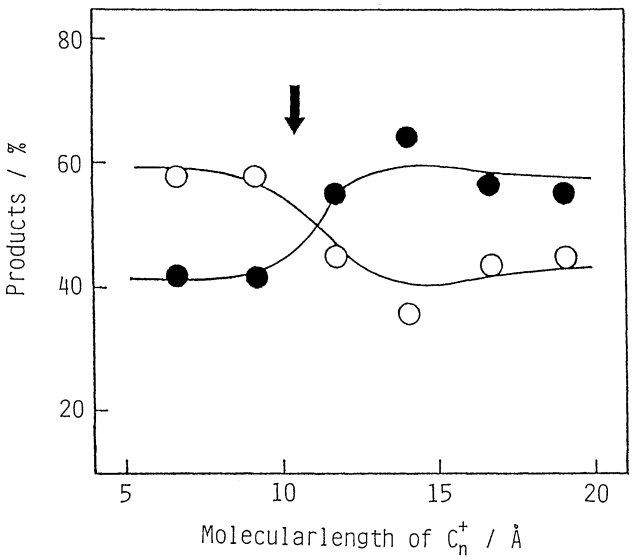


Fig. 2. Effect of molecular lengths of C_n^+ on the photoreaction of intercalated **1**; —○—, cyclodimer (**2**+**3**); —●—, *Z*-**1** (**4**). Suspended solution of **1** (0.16 mM; 4% adsorption) and C_n^+ (3.2 mM; 80% adsorption) intercalated on clay (4 mM) were irradiated by a 300 WHg lamp through a Pyrex filter. The bold arrow represents the molecular length of **1**.

to that of **1** (10.4 Å) as shown by an arrow in Fig. 2.

It is known that the anionic sites of Saponite clay interlayers are scattered on every five angstroms as an average distance.[8,12] The stereochemistry of cyclodimers and emissions from **1** suggested the intercalation of **1** in an alternative antiparallel fashion.[8] The present effect of alkylammonium ions suggests that clusters of **1** are homogenized by the C_n^+ ions of molecular length similar to that of **1** to yield isolated stilbazolium ions responsible for *E*–*Z* isomerization. This fact could be interpreted by a phase separation affected by molecular size, shape and the polar functional groups as known in the case of micelles, microemulsions[11] and clay interlayers.[6] It is tentatively proposed that the present photodimerization is significantly affected by the degree of homogenization of **1** and C_n^+. The addition of

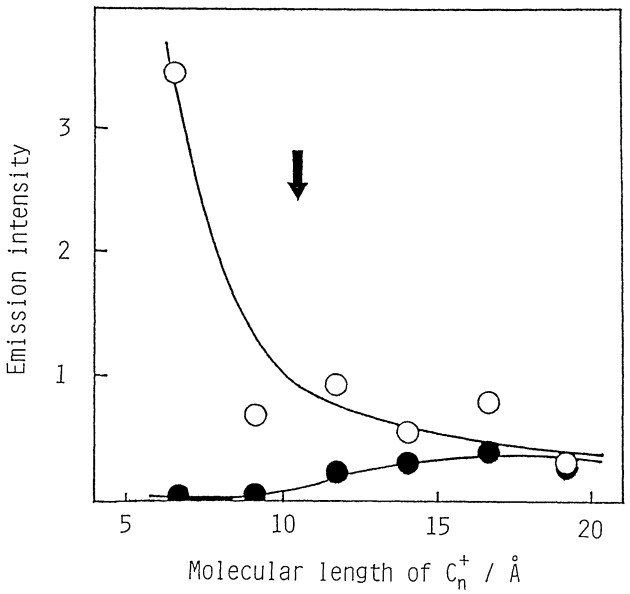


Fig. 3. Effect of molecular lengths of C_n^+ on the emission of **1** intercalated on clay; (a) —○—, excimer fluorescence monitored at 495 nm; (b) —●—, monomer fluorescence monitored at 423 nm. Colloidal suspensions of **1** (5 μM; 5% adsorption) and C_n^+ (95 μM, 95% adsorption) intercalated on clay (100 μM) were excited at 330 nm under Ar. The bold arrow represents the molecular length of **1**.

octylammonium ion would decompose a cluster of **1** by homogenized coadsorption.

Effect of C_n^+ on Monomer and Excimer Fluorescence of 1. In order to get a further insight in the molecular aggregates of **1**, the effect of alkylammonium ions was examined from the monomer and excimer fluorescence of intercalated **1**. Fig. 3 shows the effect of chain lengths of C_n^+ on the fluorescences from **1** in clay layers. The excimer fluorescence was efficiently inhibited by C_n^+'s with longer chain length, and the monomer fluorescence increased with the increasing length. These facts indicate that C_n^+ ions higher than octylammonium ion effectively dissociate the molecular aggregates of **1**. The resulting relative intensity of monomer and excimer fluorescence may be a probe for the aggregation and dissociation of adsorbents.

As shown in Fig. 4, the excimer fluorescence from intercalated **1** is nearly constant in a wide range of 0.1 to 20% adsorption, which indicates an efficient cluster formation or a heterogeneous adsorption of stilbazolium ions.[8] Then, it is interesting to examine the effect of alkylammonium ions on the concentration dependence of fluorescences from **1**. The results with C_8^+ are quite interesting as shown in Fig. 4B. That is, the excimer fluorescence was effectively reduced by coadsorption of C_8^+ and was practically negligible in case of the adsorption of **1** below 5%. This fact suggests that the molecular cluster of **1** was dissociated by C_8^+ and that the two adsorbents of **1** and C_8^+ were homogeneously

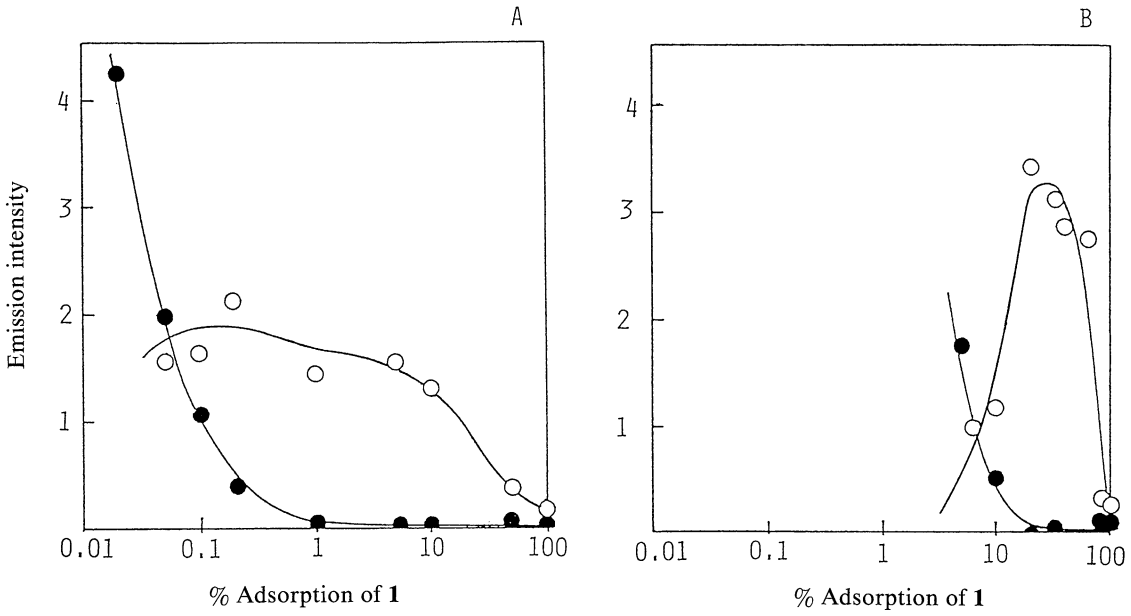


Fig. 4. Effect of C_8^+ on the fraction dependence of fluorescence intensity from **1**; (a) —○—, excimer fluorescence monitored at 495 nm; (b) —●—, monomer fluorescence monitored at 423 nm on the excitation at 330 nm. A: Colloidal suspension of **1** (5 μM and 6 μM of aqueous HCl) intercalated on clay.[8] B: Colloidal suspension of **1** (5 μM and 6 μM aqueous HCl) intercalated on clay, where the remaining sodium ions were completely exchanged by C_8^+.

adsorbed on the clay interlayer.

Simulation of Intercalation on Two-Dimensional Lattice. The effective cluster formation even with 0.1% adsorption of **1** and its dissociation by coadsorbed C_8^+ may be understood more quantitatively by the following simulation behavior for intercalation. It is established that cationic species are adsorbed electrostatically on anionic sites of clay interlayers. The adsorbed species may scramble among any available sites on clay layers. Thus, the adsorbed species aggregate with guest molecules to form clusters depending on their strength of interaction.

A Monte Carlo simulation can treat a mutual interaction of adsorbent on homogeneously dispersed sites. Put n particles of adsorbent (S_1) on a flat surface with a two-dimensional lattice, assuming that the S_1 particles are free to change their adsorbing sites but confined within the lattice. In this model, S_1 can associate with S_n to form an aggregate S_{n+1} with an equilibrium constant K_n, as expressed in case of micelles, in Eqs. 4—6.[2] Here, S_2, S_3, and S_n denote dimer, trimer, and n-mer of S_1, respectively.

$$S_1 + S_1 \rightleftharpoons^{K_1} S_2 \tag{4}$$

$$S_1 + S_2 \rightleftharpoons^{K_2} S_3 \tag{5}$$

$$S_1 + S_n \rightleftharpoons^{K_n} S_{n+1} \tag{6}$$

For the simplicity, K_1, K_2, and K_n could be assumed to be equal to K as the case of the association of surfactant molecules, where the total concentration of S_1 is put

$$[S_1] + 2[S_2] + 3[S_3] + \cdots + n[S_n] + \cdots = 1 \tag{7}$$

unity as Eq. 7. Here, $[S_1]$, $[S_2]$, ···, and $[S_n]$ indicate the fractions of S_1, S_2, ···, and S_n, respectively.

When the two-dimensional lattice possesses a large number of sites, the fractions of n-mers with $n \geqslant 4$ are negligibly small, and Eq. 7 is reduced to Eq. 8.

$$[S_1] + 2[S_2] + 3[S_3] = 1 \tag{8}$$

The fractions of $[S_1]$, $[S_2]$, and $[S_3]$ are calculated as a function of K on the basis of Eqs. 4—6, according to Eq. 9 (See experimental section for details). For example, $[S_1]:[S_2]:[S_3]=1.0:0:0$, $0.56:0.16:0.04$, and $0.42:0.18:0.07$ when $K=0$, 0.5, and 1.0, respectively.

When the number of lattice sites is not of large excess, a more complicated treatment is needed. Suppose that n particles of S_1 are scattered over the two-dimensional lattice. The extent of attractive interaction between the particles could be estimated by means of a probability for an added S_1 particle to be settled on a site without neighboring S_1 particles; the details are described in Experimental section.

In case of 10% intercalation, typical distribution patterns are shown with $K=0$, 0.5, 2, and 20 in Figs. 5A—D. As apparent from these Figures, adsorbent clusters appear and grow with increasing K values. Fig. 6 shows simulation curves for a relationship between %-adsorp-

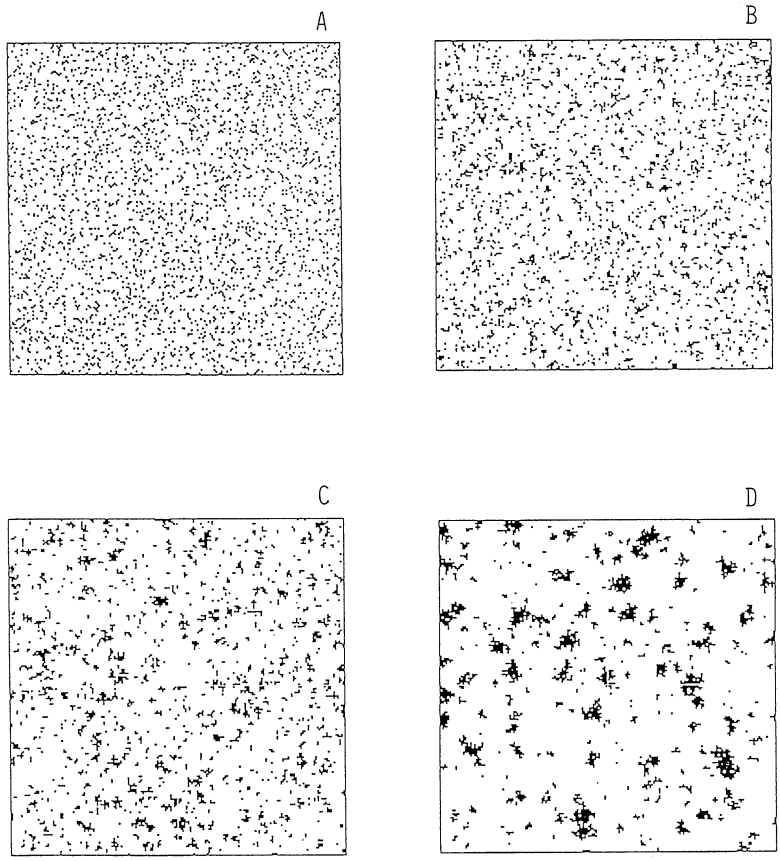


Fig. 5. Adsorption model of S_n on two-dimensional lattice as simulated by a Monte Carlo method; (A) K=0; (B) K=0.5; (C) K=2; (D) K=20. See text for details.

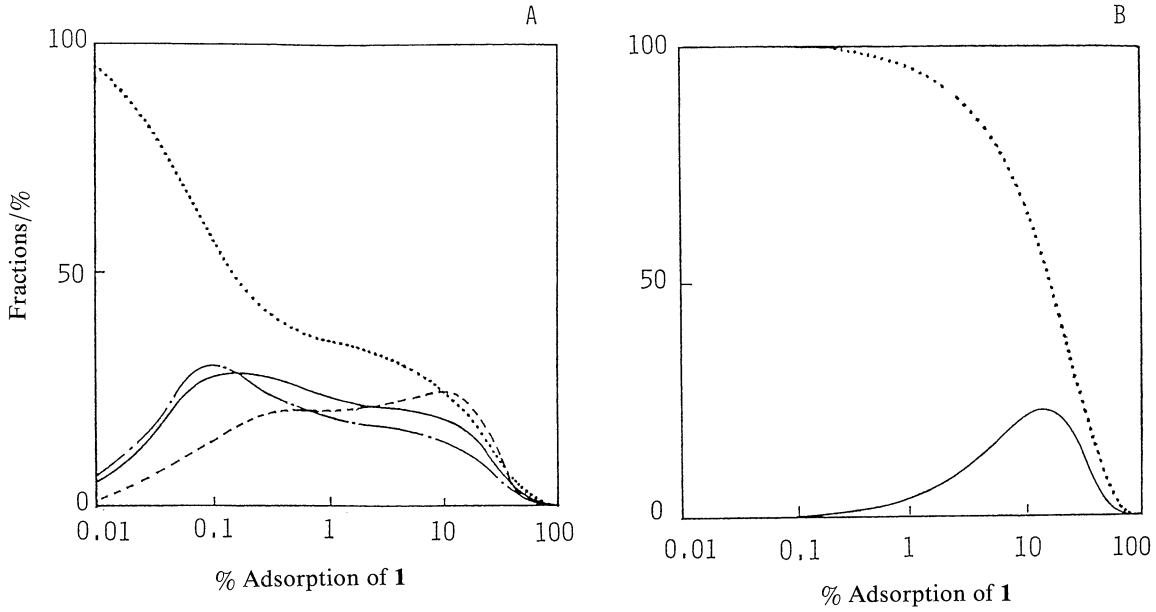


Fig. 6. Computer simulation of fractions of monomer and dimeric aggregates depending on the %-adsorption. A: [S_2] with K=0.1 (----), K=0.5 (—), and K=1.0 (—·—). [S_1] with K=0.5 (·····). B: [S_2] (—) and [S_1] (·····) with K=0.

tion and fractions of S_1 and S_2 in case of K=0 and 0.5. The resulting profiles of S_1 and S_2 fractions in Fig. 6A are quite comparable with the observed monomer and excimer fluorescence intensities in Fig. 4A. The adequate simulation with K=0.5 was confirmed by comparing with the S_2 fraction curves in case of K=0.1 and 1 in Fig. 6A. The coincidence between the two Figures implies a moderate interaction between stilbazolium ions, i.e., K=0.5.

As shown in Fig. 6B, profiles of $[S_1]$ and $[S_2]$ against %-adsorption with K=0 are very close to the features of Fig. 4B for the relative intensities of the monomer and excimer emissions of **1**, where C_8^+ is coadsorbed with **1**. This definitely suggests that specific interaction between the stilbazolium ions is canceled by the coadsorption of C_8^+.

Conclusion. The efficient formation of clusters of stilbazolium ions in clay interlayer is retarded or inhibited by adding alkylammonium ions, C_n^+, with comparable chain length. This is evidenced by an effect of C_n^+ upon the photochemical cyclodimerization and fluorescence intensities. The formation of dimer or cluster of adsorbent is adequately simulated by a Monte Carlo method for a two-dimensional lattice site model.

Experimental

Emission spectra were measured using a Hitachi 650-10S spectrophotometer. Product analyses were carried out with a JASCO UVIDEC-100-III HPLC instrument. Fractions were monitored at 250 nm using a Sil–NH_2 column (30 cm) and the mixed solvent of hexane, ethanol, and 25% aqueous ammonium hydroxide (450 : 50 : 1, v/v) as an eluent flowed at 1 cm^3 min^{-1}.

Materials. A synthetic Saponite clay, Sumecton SA (>110 mesh), was kindly gifted by Kunimine Ind. Co.; the cation-exchange capacity (CEC) is 99.68 mequiv/100 g. Synthesis of stilbazolium (**1**) and the identification of products, *syn* head-to-tail (**2**) and head-to-head (**3**) dimers, and *Z*-stilbazolium ion (**4**), were carried out as reported previously.[8,13] Alkylamines of extra pure grade were used as received from Tokyo Kasei Co.

Irradiations. The irradiation of **1** intercalated on clay layers in the presence of akylammonium ion (C_n^+) was carried out according to following two procedures.

I) Suspended System: The **1**-adsorbed sample were prepared by stirring for 2 h the mixed solutions of **1** (5 mM and 6 mM HCl aq, 100 ml) (1 M=1 mol dm^{-3}) and Saponite clay (10 mM aq, 50 ml). The resulting pale yellow precipitates were filtered out using a membrane filter (Advantech, pore size: 0.45 μm), dried overnight in vacuo, and were ground up with a mortar. From the absorbance of the filtrate, the %-adsorption of **1** on the clay was easily determined. Forty milligrams of the powdered clay-intercalated **1** were dispersed in 5 ml of alkylamine solution (0—1 M and 1.2 equivalents of HCl aq) and were stirred overnight. The irradiation was carried out with a 300 W high-pressure mercury lamp through a Pyrex filter for 30 minutes under Ar. The resulting reaction mixtures were added to concd HCl (10 ml), kept overnight, neutralized with NaOH aq, extracted by CH_2Cl_2, and analyzer by HPLC.

II) Colloidal System: The aqueous solution of **1** (2 mM and 2.4 mM HCl aq, 2 ml) was added to the mixture of aqueous clay (10 mM, 10 ml) and an alkylamine (40 mM and 48 mM HCl aq, 2 ml); the mixed solution was made 25 ml by volume by adding water. After the similar irradiation for 30 min, the products were analyzed as described above.

Emission Spectra. Aqueous solutions of **1** (50 μM and 60 μM HCl aq, 1 ml) and the clay (1000 μM, 1 ml) and/or alkylamines (950 μM, 1 ml) were mixed, made 10 ml by adding water, and stirred overnight. The mixed solution was taken in 1 cm cell, purged with Ar for five minutes. The emission spectra of intercalated **1** were measured by exciting at 330 nm and monitoring at 423 and 495 nm for the monomer and excimer emissions, respectively.

Simulation of Adsorption Modes on Clay Layers. The aggregation modes of **1** on clay layers were simulated on the basis of algorithm noted in the text using a Monte Carlo method. The random numbers for the method were generated using the subroutine of BASIC language program for a NEC PC-9801 microcomputer.

In order to estimate an extent of the attractive interaction between the particles, the Monte Carlo simulation was carried out under the following restrictions. A probability for an added S_1 particle to be settled on a site without neighboring S_1 particles is adjusted so as to be coincident with the fraction, $[S_1]$, obtained from Eq. 9 derived from Eq. 8, when K is fixed on 0 to 20. If not, the S_1 particle is again

$$[S_1] + 2K[S_1]^2 + 3K[S_1]^3 = 1 \quad (9)$$

resettled, until it is adsorbed as an isolated one, with maximum limit of 20 times retrials. This treatment means that the $[S_1]$ is equal to that in the presence of large number of sites.

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