

SOLID-STATE INTERCALATION OF NAPHTHALENE AND ANTHRACENE INTO ALKYLAMMONIUM-MONTMORILLONITES

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Abstract— Intercalation of naphthalene and anthracene into alkyltrimethylammonium ($C_nH_{2n+1}(CH_3)_3N^+$; $n = 8, 12, 14, 16,$ and 18)-montmorillonites was carried out by novel solid-solid reactions at room temperature. Octyltrimethylammonium(C8)-montmorillonite did not form an intercalation compound with either naphthalene or anthracene. Naphthalene was intercalated into both dodecyltrimethylammonium(C12)- and octadecyltrimethylammonium(C18)-montmorillonites to give intercalation compounds. On the other hand, the solid-solid reaction between dodecyltrimethylammonium(C12)- or tetradecyltrimethylammonium(C14)-montmorillonite and anthracene gave only partly intercalated compounds while hexadecyltrimethylammonium(C16)- and octadecyltrimethylammonium(C18)-montmorillonites gave single phase intercalation compounds. The hydrophobic interactions between alkylammonium-montmorillonites and the aromatic compounds are thought to be the driving force for the solid-state intercalation. The extent of the increase in the basal spacing may also be involved in the different reactivity.

Key Words— Alkylammonium-montmorillonites, Anthracene, Intercalation, Naphthalene, Solid-state intercalation.

INTRODUCTION

Montmorillonite-organic intercalation compounds have widely been investigated and the mechanisms of clay-organic interactions have been reported (Theng, 1974). Cation exchange of interlayer exchangeable cations, adsorption of polar molecules through ion-dipole interactions, hydrogen bonding, and protonation are suggested intercalation mechanisms. If a clay mineral has metal cations in the cation exchange sites, its surface is hydrophilic and is often not a good adsorbent for poorly water-soluble organic species which cannot compete with highly polar water for adsorption on the clay mineral surface. However, when the interlayer metal cations are replaced by organoammonium cations, the surfaces of the clays are greatly modified to become strongly organophilic. Various organoammonium exchanged montmorillonites have been synthesized, and the properties and applications have been investigated as so-called “organophilic clays” which swell in organic solvents to form a thixotropic gel (Jordan, 1950; Jones, 1983). These organoammonium-clays have been studied as a chromatographic stationary phase (Bondarenko *et al.*, 1982), shape selective adsorbates (Barrer, 1978), sorbents for organic contaminants dissolved in water (Lee *et al.*, 1989, 1990; Boyd *et al.*, 1988a, 1988b; Jaynes *et al.*, 1991), catalysts (Cornelis and Laszlo, 1982), rheology controlling agents in a wide variety of solvent systems (Jones, 1983), and so on. The modifications have provided new ways to utilize swelling clay minerals in practice.

Recently, we have succeeded in solid-state intercalation of organoammonium cations by cation exchange mechanism into montmorillonites (Ogawa *et al.*,

1990a), and acrylamide (Ogawa *et al.*, 1989), n-alkylamine (Ogawa *et al.*, 1990b) and 2,2'-bipyridine (Ogawa *et al.*, 1991) by adsorption. Nevertheless, little is known about the factors controlling the solid-solid reactions. Moreover, the solid-solid reactions have advantages such as the ease of operation compared to conventional solution methods and the possibility to prepare compounds not accessible from solutions. Therefore, further study on the solid-state formation of intercalation compounds is of great importance from both theoretical and practical viewpoints.

In this study, we investigated solid-solid reactions between organophilic montmorillonites and poorly water soluble organic compounds to examine whether the hydrophobic interactions can be a driving force for the solid-state intercalation. Naphthalene and anthracene were selected as the guest species because these aromatic compounds are stable and no intercalation compounds of them have been reported.

EXPERIMENTAL METHODS

Materials

Na-montmorillonite (Kunipia F, supplied from Kunimine Industries Co.) obtained from Aterazawa mine (Yamagata, Japan) was used as the starting material. The cation exchange capacity was 119 meq/100 g clay and the chemical composition was the same as described in a previous report (Sugahara *et al.*, 1984). Homoionic ($C_nH_{2n+1}(CH_3)_3N^+$; $n = 8, 12, 14, 16,$ and 18) montmorillonites were prepared by a conventional ion exchange method using aqueous solutions of appropriate organoammonium chlorides. The amounts of added organoammonium salts were just equal to the

Table 1. The basal spacings and the amounts of the intercalated alkyltrimethylammonium cations of the alkylammonium-montmorillonites.

Host $C_nH_{2n+1}N(CH_3)_3^+$ - montmoril- lonites	Abbreviation	d(001) (nm)	$\Delta d(001)$ (nm)	Amount of adsorbed guest (meq./ 100 g clay)
n = 8	OTMA-	1.40	0.44	88
n = 12	DTMA-	1.79	0.83	102
n = 14	TDTMA-	1.90	0.94	112
n = 16	HDTMA-	2.08	1.12	113
n = 18	ODTMA-	2.27	1.31	120

cation exchange capacity (119 meq/100 g clay) of the clay, because organic salts may be adsorbed by the clay in excess of the cation exchange capacity. After the ion exchange, the products were washed with deionized water repeatedly until a negative $AgNO_3$ test was obtained.

Naphthalene was obtained from Kanto Chemical Co. as extra pure grade. Anthracene was obtained from WAKO Pure Chem. Ind. Co. These reagents were used without further purification.

Intercalation of naphthalene and anthracene into alkylammonium-montmorillonites by solid-solid reactions

The solid-solid reactions between organoammonium-montmorillonites and naphthalene or anthracene were carried out according to the method described in a previous report (Ogawa *et al.*, 1989). The mixture of an organoammonium-montmorillonite and naphthalene or anthracene was ground with a mortar and pestle at room temperature for 10 min. The weight ratio of the mixture was varied from 10:1 to 1:2 for host : guest. Since neither component is hygroscopic, the reactions were carried out in the atmosphere under ambient conditions.

Characterization

X-ray powder diffraction was performed on a Rigaku RADII-A diffractometer using Mn filtered $FeK\alpha$ radiation. Infrared spectra of KBr disks were recorded on a Perkin Elmer FT-1640 Fourier-transform spectrophotometer. DTA curves were recorded on a Shimadzu DT-20B instrument at the heating rate of $10^\circ C/min$ using $\alpha-Al_2O_3$ as a standard material. The amounts of adsorbed alkylammonium cations were determined by thermogravimetric analysis performed on a Shimadzu TGA-40 instrument at the heating rate of $10^\circ C/min$.

RESULTS AND DISCUSSION

Preparation of alkylammonium-montmorillonites

Table 1 shows the basal spacings and the amounts of the adsorbed organoammonium cations of the organophilic montmorillonites prepared in this study.

Judging from the observed basal spacings and the thickness of the alkyl-chain, intercalated alkylammonium ions were lying flat as a monomolecular layer, bimolecular layer, and *pseudo*-trimolecular layer for octyltrimethylammonium ($C_8H_{17}(CH_3)_3N^+$; OTMA)-, dodecyltrimethylammonium ($C_{12}H_{25}(CH_3)_3N^+$; DTMA)-, and octadecyltrimethylammonium ($C_{18}H_{37}(CH_3)_3N^+$; ODTMA)-montmorillonites, respectively. These arrangements are consistent with those reported by Lagaly (1981) for n-alkylammonium ions in the interlayer space of smectites. Tetradecyltrimethylammonium ($C_{14}H_{29}(CH_3)_3N^+$; TDTMA)- and hexadecyltrimethylammonium ($C_{16}H_{33}(CH_3)_3N^+$; HDTMA)-montmorillonites showed intermediate values between bimolecular and *pseudo*-trimolecular layers.

Intercalation of naphthalene into alkylammonium-montmorillonites by solid-solid reactions

Although no evidence for intercalation of naphthalene into OTMA-montmorillonite was obtained, DTMA- and ODTMA-montmorillonites formed intercalation compounds by a solid-solid reaction. With the increase in the alkyl-chain length of the alkyltrimethylammonium ions, the alkylammonium-montmorillonites contain greater amounts of alkylammonium ions in their interlayer spaces (Table 1). Therefore, the hydrophilic interlayer surface of montmorillonite was covered by the alkyl-chains more effectively with the increase in the alkyl-chain length to cause increased organophilicity of the interlayer space. The reactivities of alkylammonium-montmorillonites with naphthalene depend on the extent of the organophilic nature of the interlayer space, suggesting that the hydrophobic interactions played a major role for the solid-solid reactions.

The solid-solid reaction between DTMA-montmorillonite and naphthalene caused the d(001) diffraction peak of the DTMA-montmorillonite to shift to a lower 2θ region. The variation in the XRD patterns with the change in the ratio of the host : guest is shown in Figure 1. In the XRD pattern of the product from the mixture at the weight ratio of 10:1 (DTMA-montmorillonite : naphthalene), a new broad peak with a basal spacing of 3.0 nm ($3.7^\circ 2\theta$) was observed together with the d(001) diffraction peak at 1.8 nm ($6.2^\circ 2\theta$). The basal spacing of 1.8 nm is due to the original DTMA-montmorillonite. When the weight ratio of DTMA-montmorillonite : naphthalene was 4:1, the d(001) peak due to unreacted DTMA-montmorillonite disappeared and the diffraction peak showing the basal spacing of 3.0 nm intensified. The infrared spectrum of the product obtained from the mixture of DTMA-montmorillonite and naphthalene at the weight ratio of 4:1 is shown in Figure 2 together with that of DTMA-montmorillonite. In the spectrum, the absorption band due to C-H out-of-plane bending vibration of naphthalene ap-

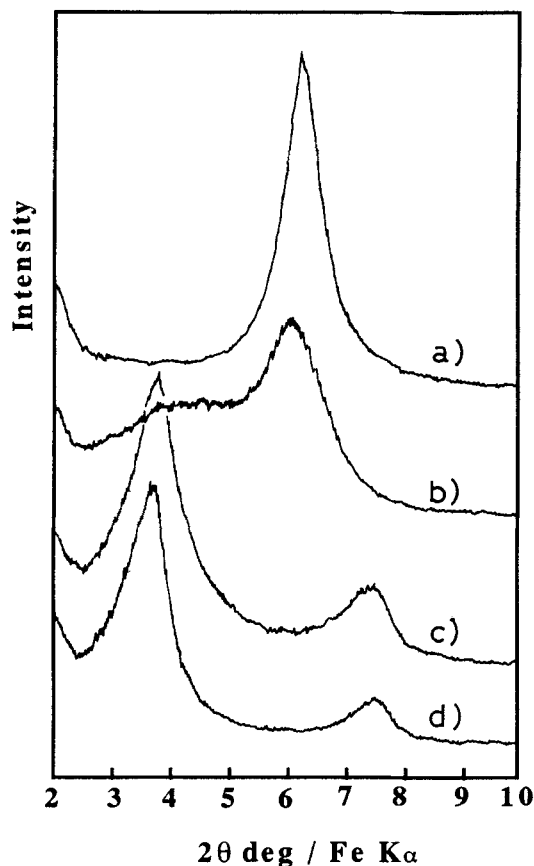


Figure 1. X-ray powder diffraction patterns of (a) DTMA-montmorillonite, (b-d) DTMA-montmorillonite-naphthalene intercalation compounds prepared by solid-solid reactions from the mixtures of DTMA-montmorillonite and naphthalene at the weight ratios of (b) 10:1, (c) 4:1, and (d) 1:2.

peared at 791 cm^{-1} , while the band was observed at 781 cm^{-1} for naphthalene in KBr. It is supposed to reflect the change in the surrounding of each naphthalene molecule, though the precise origin of this shift of the absorption band is not known at present. These observations indicated that naphthalene was intercalated into the DTMA-montmorillonite by the solid-solid reactions at room temperature to give an intercalation compound with the basal spacing of 3.0 nm. An identical intercalation compound with the basal spacing of 3.0 nm was obtained by a solid-solid reaction under a dry air atmosphere, indicating that there is no possible role of atmosphere for the solid-state intercalation.

In order to check the possibility of intercalation of naphthalene from vapor phase, both components were placed together in a vessel in separate containers and the vessel was stored at ambient temperature. Although naphthalene was intercalated into the interlayer space of DTMA-montmorillonite by the treatment from va-

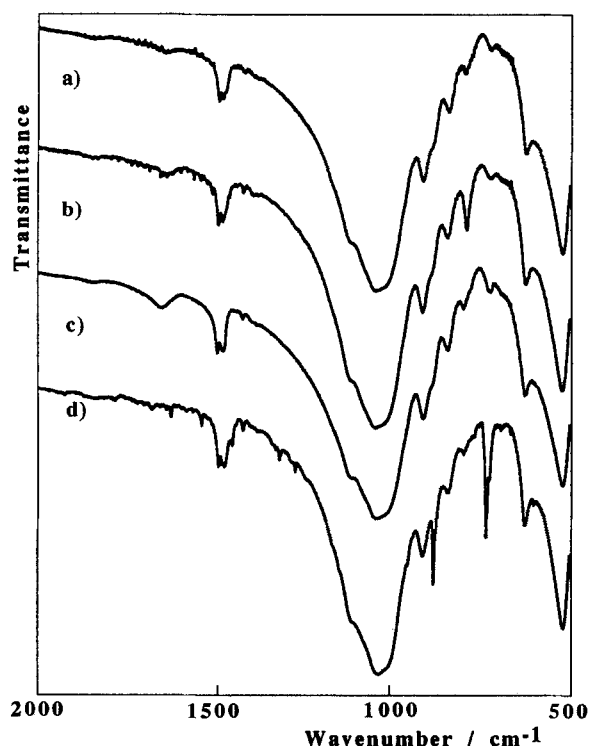


Figure 2. Infrared spectra of (a) DTMA-montmorillonite, (b) DTMA-montmorillonite naphthalene intercalation compound prepared from the mixture of DTMA-montmorillonite and naphthalene at the weight ratio of 4:1, (c) ODTMA-montmorillonite, and (d) ODTMA-montmorillonite anthracene intercalation compound prepared from the mixture of ODTMA-montmorillonite and anthracene at the weight ratio of 4:1.

por phase, the reaction took an extremely long time (more than a week at room temperature) compared with the solid-solid reaction (minutes). Therefore, the intercalation can be concluded to proceed mainly by the solid-solid reaction mechanism, though reaction from vapor phase may be involved. In our previous studies on the intercalation of polar molecules into montmorillonites by solid-solid reactions (Ogawa *et al.*, 1989, 1990a, 1991), we have found that the reactions were completed within a few minutes. Toda *et al.* (1987) mentioned that some organic host-guest complexes formed faster in the solid-state than in solutions. Since the solid-solid reactions are conducted with high concentration, it is possible that the reactions proceed very fast. It seems that naphthalene molecules have a high mobility comparable to that in the liquid state even in the solid state.

With the increase in the amount of naphthalene relative to DTMA-montmorillonite, the $d(001)$ peak of 3.0 nm became sharper (Figure 1). The XRD patterns of the intercalation compounds prepared from the mixtures of DTMA-montmorillonite and naphthalene at the weight ratios of 2:1, 1:1, and 1:2 gave well-

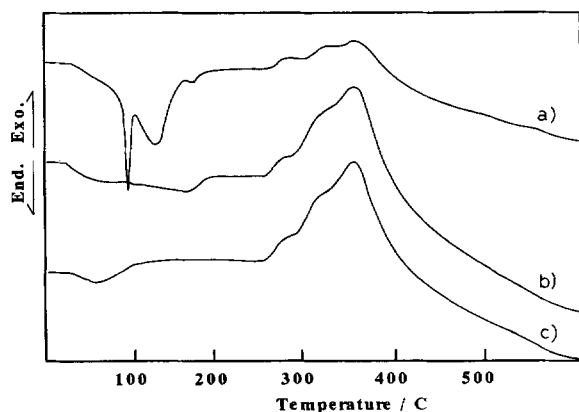


Figure 3. DTA curves of (a, B) DTMA-montmorillonite naphthalene intercalation compounds prepared from the mixture of DTMA-montmorillonite and naphthalene at the weight ratio of (a) 1:2 and (b) 4:1, and (c) DTMA-montmorillonite.

resolved XRD peaks with a basal spacing of 3.0 nm. A diffraction peak due to naphthalene was observed at $2\theta = 15.3^\circ$, $d = 0.73$ nm (not shown in Figure 1) and the intensities became stronger with the increase in the relative amount of naphthalene. In the DTA curves of the products obtained at the weight ratios of 2:1, 1:1, and 1:2, two sharp endothermic peaks due to melting and vaporization of naphthalene appeared at 80° and 100°C (Figure 3a) and the peaks were intensified with the increase in the amounts of naphthalene relative to DTMA-montmorillonite. When the weight ratio of DTMA-montmorillonite : naphthalene was 4:1 or 10:1, no evidence of the existence of excess naphthalene was obtained. Similar phenomena have been observed in the study on the formation of montmorillonite-acrylamide (Ogawa *et al.*, 1989), *n*-alkylamine (Ogawa *et al.*, 1990a), and 2,2'-bipyridine (Ogawa *et al.*, 1991) intercalation compounds by solid-solid reactions. Judging from the above results, the intercalated naphthalene molecules arranged in a certain orientation in the interlayer space, though the arrangement cannot be determined at present.

In the DTA curve of the DTMA-montmorillonite naphthalene intercalation compound (obtained from the mixture at the weight ratio of 4:1), a broad endothermic peak appeared around 90° – 180°C (Figure 3b). The TG curves of the products showed a weight loss around 100°C , suggesting intercalated naphthalene was desorbed. Recently, immobilization of pesticides in smectites for controlled release has been reported (Choudary *et al.*, 1989). The thermal desorption behavior of naphthalene observed in this study suggests that the complexation of organophilic clays and organic compounds can be a novel way for controlled release.

In order to determine the amount of intercalated species, the DTMA-montmorillonite naphthalene intercalation compound prepared from the mixture at

the weight ratio of 2:1 for host : guest was washed with organic solvents (methanol or *n*-hexane). However, the washing resulted in the decrease in basal spacing due to desorption of the intercalated naphthalene. Although the extent of the desorption depended on the kind and amount of solvents, there were no appropriate solvents to remove excess of naphthalene without affecting the basal spacing. The interlayer space of the DTMA-montmorillonite is apparently so organophilic that the organic solvents penetrate into the interlayer space to replace the intercalated naphthalene. Therefore, the amount of the intercalated species cannot be determined. Judging from the change in the XRD patterns [the change in the shape of $d(001)$ diffraction peaks and appearance of diffraction peaks due to an excess of naphthalene crystal] with the weight ratio of the guest to the host, 1 g of the DTMA-montmorillonite can accommodate at least 0.25 g of naphthalene in the interlayer space.

The solid-solid reactions between ODTMA-montmorillonite and naphthalene showed similar results. The basal spacing of the ODTMA-montmorillonite naphthalene intercalation compound was 3.5 nm. The expansion of the interlayer space by the intercalation of naphthalene was 1.3 nm, being close to that for the DTMA-montmorillonite naphthalene intercalation compound. Since the basal spacings of the original organophilic montmorillonites were different (1.8 and 2.3 nm for DTMA- and ODTMA-montmorillonite, respectively), the similarity in the expansion of the basal spacings means the intercalated naphthalene was sandwiched by alkyl-chains of the organoammonium cations and closely packed in the interlayer space.

Intercalation of anthracene into alkylammonium-montmorillonites by solid-solid reactions

Figure 4 shows the XRD patterns of the reaction products between the alkylammonium-montmorillonites and anthracene. Anthracene was not intercalated into OTMA-montmorillonite by the solid-solid reaction compound with a well-resolved XRD pattern, the reactions with anthracene did not give a similar result. In the XRD pattern of the product obtained by a solid-solid reaction between DTMA-montmorillonite and anthracene (at the weight ratio of 1:2), a broad diffraction peak, with a basal spacing of 3.4 nm, appeared along with the $d(001)$ peak with a basal spacing of 1.8 nm, corresponding to the unreacted DTMA-montmorillonite (Figure 4a). In the XRD pattern, the diffraction peaks due to excess anthracene were also observed (the most intense one was observed at $2\theta = 12^\circ$, $d = 0.93$ nm), meaning that there was more than enough to satisfy the requirements of intercalation. Similar change in the XRD pattern was observed for TDTMA-montmorillonite by a solid-solid reaction with anthracene (Figure 4b). The increase in the alkyl-chain length

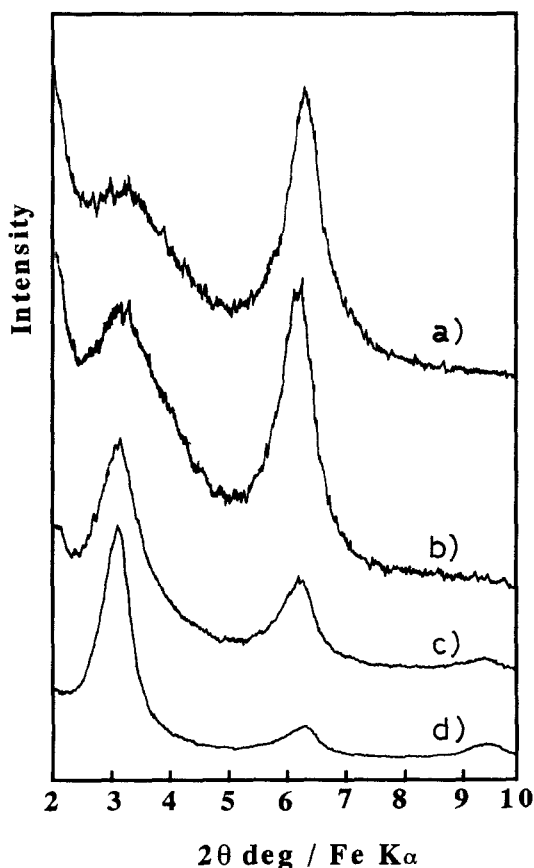


Figure 4. X-ray powder diffraction patterns of the products obtained by the reactions between (a) DTMA-, (b) TDTMA-, (c) HDTMA-, and (d) ODTMA-montmorillonites and anthracene.

of the interlayer organoammonium ions increased the relative intensity of the $d(001)$ diffraction peak of the anthracene intercalated part to that of the original host materials (Figure 4). In the XRD pattern of the reaction product between HDTMA-montmorillonite and anthracene (Figure 4c), the diffraction peak due to original HDTMA-montmorillonite was not clearly detected and the basal spacing became 3.5 nm. The ODTMA-montmorillonite-anthracene intercalation compound gave a sharper single phase X-ray powder diffraction pattern showing the basal spacing of 3.6 nm (Figure 4d). The infrared spectrum of the product obtained by the solid-solid reaction between ODTMA-montmorillonite and anthracene is shown in Figure 2. The absorption bands due to C-H out-of-plane deformation vibrations of anthracene appeared at 884 and 736 cm^{-1} , while they are normally observed at 884 and 726 cm^{-1} for anthracene in KBr. This shift of the absorption band indicates the intercalation of anthracene. As was the case for the reactions between alkylammonium-montmorillonites and naphthalene, the difference in the reactivities with anthracene was thought to result from the variable hy-

drophobicity of the interlayer spaces of the alkylammonium-montmorillonites. Because of the bulkiness and more hydrophobic nature of anthracene compared to those of naphthalene, the intercalation of anthracene is thought to require more hydrophobic host material. The larger basal spacings of alkylammonium-montmorillonites with longer alkyl-chain length may also be involved in the different reactivity.

The XRD patterns of the ODTMA-montmorillonite-anthracene intercalation compounds varied with the change in the host : guest ratio of the mixture. When the weight ratio of ODTMA-montmorillonite : anthracene was 10:1, the $d(001)$ diffraction peak split into two; one shows the basal spacing of ca 3.5 nm and the other shows that of ca 2.3 nm. The former value is thought to be due to the intercalation compound and the other is due to unreacted ODTMA-montmorillonite. With the increase in the relative amount of anthracene, the $d(001)$ peak due to unreacted ODTMA-montmorillonite disappeared and the $d(001)$ peak with the basal spacing of ca 3.6 nm was intensified. The basal spacings of the products were constant when the ratios of host : guest were 1:1 and 1:2, indicating that the amount of anthracene to be intercalated into the ODTMA-montmorillonite was limited. Therefore, we can conclude that the intercalated anthracene has a certain arrangement in the interlayer space.

CONCLUSION

Naphthalene and anthracene were intercalated into alkylammonium-montmorillonites by solid-solid reactions at room temperature. These reactions were complete within 10 min, showing that the mobility of the organic species was very high, even in the solid state. The alkyl-chain length of alkylammonium ions affected the reactivity, showing that the hydrophobic interactions between alkylammonium-montmorillonites and aromatic compounds are the driving force for the solid-state intercalation.

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