



FT-IR Spectroscopic Investigation of Adsorption of Pyrimidine on Sepiolite and Montmorillonite from Anatolia*

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Abstract

The adsorption of pyrimidine (PM) on natural montmorillonite and sepiolite from Turkey was investigated by FT-IR spectroscopy. The intercalation of PM within montmorillonite has been shown by X-ray diffraction to increase the interlayer spacing. The spectroscopic results indicate that PM molecules adsorbed on sepiolite are coordinated to Lewis acidic centers or surface hydroxyls by H-bonding interaction through one of the pyrimidine ring nitrogen lone pairs. Moreover, some of the adsorbed PM molecules may enter the interior channels of the sepiolite structure and replace zeolitic water. The intercalated PM molecules within montmorillonite are coordinated to exchangeable cations directly or indirectly through water bridges.

Introduction

Clays are found naturally in the environment. They have adsorptive and catalytic properties. The clays that are of primary catalytic interest are those known as sepiolite and montmorillonite [1]. Sepiolite is a hydrated magnesium silicate. It has a fibrous structure consisting of talc-like chains (ribbons) parallel to the fibre axis. It is structurally formed by an alteration of blocks and tunnels that grow up in the fibre direction (c-axis). Each structural block is constructed by two tetrahedral silica sheets enclosing a central magnesia sheet in a similar way that occurs in other 2:1 silicates such as talc, although in sepiolite there are discontinuities of the silica sheet that give rise to those structural tunnels [2, 3]. Montmorillonite is an expanding layer of silicate mineral; composed of aluminosilicate layers stacked one above the other. Each layer has a small net negative charge because of isomorphous substitution of ions in the framework. The charge is compensated by interlayer hydrated cations, which are known as exchangeable cations. It is well known that montmorillonite can accommodate various types of compounds in its interlayer space to give an intercalation type of inclusion compounds [4–9].

Inclusion of organic compounds into layered inorganic solids has attracted considerable attention from both fundamental and practical viewpoints. Ordered inorganic-organic assemblies with unique microstructures controlled by host-guest and guest-guest interactions have been constructed in

these reactions [1, 10–12]. Ammonia and pyridine have been widely used as probe molecules to determine the type of adsorbing sites [10–12]. However, due to their strong basicity, they adsorb strongly, and therefore, unspecifically even on the weakest acid sites [10]. Diazines are less basic than pyridines, and are more appropriate for selective detection of strong acid sites [10]. The objective of this study is to investigate the sorption properties of pyrimidine by clays using IR spectrometry. In our previous studies on the adsorption of organics on clay surfaces, the sorption properties of bipyridine [7–8], amino pyridine [13–15] and biquinoline [16] were reported. In the present work, the sorption behavior of PM onto natural sepiolite and montmorillonite from Anatolia has been investigated using FT-IR Spectrometry.

Experimental

The natural montmorillonite and sepiolite samples used were from Cankiri and Mihalliccik-Eskisehir regions of Anatolia (Turkey), respectively. The samples were first identified by X-ray diffraction, differential thermal and IR spectroscopic analyses. The chemical compositions of starting sepiolite and montmorillonite are as follows: Sepiolite; 58.0% SiO₂, 25.5% MgO, 0.5% Al₂O₃, 0.5% K₂O, 0.5% CaO, 0.05% TiO₂, 0.05% Na₂O, 0.01% P₂O₅, 0.01% MnO, 0.05% (FeO + Fe₂O₃), 14.5% loss on ignition, montmorillonite; 58.3% SiO₂, 2.5% MgO, 16.0% Al₂O₃, 1.1% K₂O, 3.5% CaO, 0.6% TiO₂, 2.1% Na₂O, 0.1% P₂O₅, 3.0% (FeO + Fe₂O₃), 13.1% loss on ignition. The IR spectrum of natural montmorillonite indicated a moderate Fe³⁺ content (885 cm⁻¹) with the presence of detectable quartz (697 cm⁻¹) and silica phase (797 cm⁻¹) impurities.

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The clays were ground to approximately 200-mesh size powder. PM used was reagent grade (Fluka) and was used as received. PM treated clays were prepared by immersing air-dried clays in liquid PM in sealed bottles at room temperature for 24 hours. The products were then filtered and then kept in a desiccator to dry. The clays were found to be not altered in colour after being treated with PM. The FT-IR spectra of self supporting films ($\sim 2 \text{ mg cm}^{-2}$), oriented films supported onto CaF_2 window or KBr discs of samples were recorded on a Jasco 300E FT-IR spectrometer.

Results and discussion

The XRD pattern of natural and pyrimidine treated montmorillonite were recorded and the basal spacing of 12.2 Å and 14.8 Å were observed, respectively. The expansion in the basal spacing of the montmorillonite due to intercalation of PM was calculated as $\Delta d = d - 9.6 \text{ Å}$ [9], where d is the basal spacing of the PM treated clay and 9.6 Å is the thickness of a 2:1 clay layer. Δd is found to be 5.2 Å. This observation suggests that PM molecules intercalate into the interlayers of montmorillonite with a monolayer arrangement.

Recently FT-IR spectra of pyrimidine-water complexes in Ar matrices were investigated by Destexhe *et al.* [17] and the experimental results, supported by theoretical calculations, of the predicted frequency shifts of the pyrimidine modes induced by the formation of the H-bonding were reported. In order to characterise the species formed upon sorption, we carefully investigated the vibrational wavenumbers of PM treated clays in comparison to those of liquid PM, H-bonded PM [17] and PM complexes [18]. The vibrational bands of sorbed PM molecule by sepiolite and montmorillonite were tabulated in Table 1, along with those of liquid PM and $\text{Cd}(\text{PM})_2\text{Cd}(\text{CN})_4$ complex [18]. The wavenumber shifts of the PM modes, due to the formation of the H-bond [17], were also included in Table 1 for comparison.

The FT-IR spectra of PM treated and untreated montmorillonite are illustrated in Figure 1. The 1350–1750 cm^{-1} region of the IR spectra of PM treated montmorillonite and liquid PM is given in Figure 2. The FT-IR spectra of PM treated sepiolite are given in Figures 3–5. The band component analysis is found to be very useful in order to pick up the overlapping bands, in particularly the PM modes under strong absorption bands of the clay framework.

IR spectroscopic studies of adsorption of pyridine and pyridine derivatives by clays and zeolites indicate that certain modes of the aromatic molecule are very sensitive to the type of adsorbing site [5–8, 10, 13–16], particularly the ring modes around 1400–1600 cm^{-1} and the ring breathing mode are the most sensitive to the changes in π -bond order. They increase in value upon coordination of the lone pair on nitrogen atom to Lewis acidic sites or to exchangeable cations, both due to the coupling with M–N(py) bond vibrations and due to alterations of ring force field. This is what we observed in the vibrational spectra of PM treated

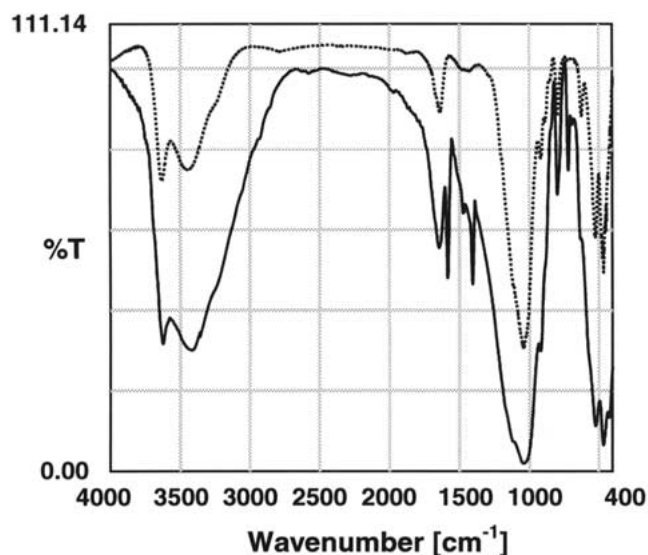


Figure 1. FT-IR spectra of pyrimidine treated montmorillonite (solid line) together with starting montmorillonite (dotted line).

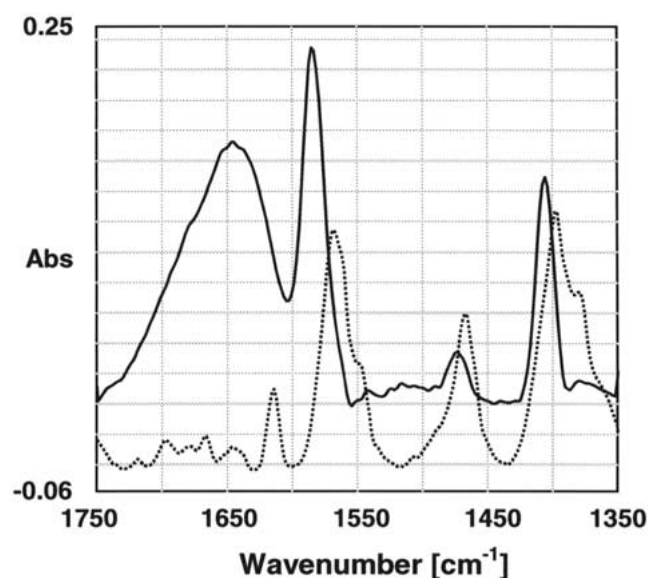


Figure 2. 1350–1750 cm^{-1} region of the FT-IR spectra of pyrimidine treated montmorillonite (solid line) and liquid pyrimidine (dotted line).

clays. A glance at Table 1 clearly shows the presence of upward shifts in comparison to those of liquid PM, on certain vibrational modes of adsorbed and intercalated PM, which are marked in bold. Similar shifts were also predicted upon formation of H-bonding through one of the pyrimidine ring nitrogen [17]. The ring-breathing mode of PM is observed at 991 cm^{-1} in the IR spectrum of liquid PM. It is unfortunately obscured by the host vibrational modes of the clay structure, [$\nu(\text{Si-O})$], in the IR spectra of clays; however by band component analysis of the 1300–800 cm^{-1} region of the IR spectra of PM treated and untreated clays indicated the presence of ca. 1010 cm^{-1} band in the IR spectra of PM treated clays which was not present in those of untreated clays $\{\Delta(\nu_{\text{ads}} - \nu_{\text{liq}}) = 19 \text{ cm}^{-1}\}$. This mode was observed around 1007–1020 cm^{-1} in the IR spectra of $\text{M}(\text{PM})_2\text{M}'(\text{CN})_4$ complexes $\{\Delta(\nu_{\text{complex}} - \nu_{\text{liq}}) = 16\text{--}29 \text{ cm}^{-1}$, where the coordination to the transition metals

Table 1. Vibrational wavenumbers of adsorbed and intercalated pyrimidine^a

Assignment [17]	Pyrimidine		Pyrimidine on		Cd-pyrimidine complex [18]
	[17] ^b	This Study ^c	Sepiolite	Montmorillonite	
$\nu(\text{CH})$	3058	3076 s	3068 vw	3068 vw	3075 m
$\nu(\text{CH})$	3053	3049 vs	3051w	3049 vw	3065 m
$\nu(\text{CH})$	3042	3022 s	3030 vw	–	3030 sh
$\nu(\text{CH})$	3019	3002 s	3018 w	3020 vw	3024 w
ν_{ring}	1571 (+6)^d	1568 vs	1584 vs	1583 vs	1589 vs
ν_{ring}	1567	1560 sh	1571 vw	1570 w	1564 s
$\delta(\text{CH})$	1465	1468 s	1473 w	1473 w	1466 s
$\delta(\text{CH}) + \nu_{\text{ring}}$	1400 (+4)	1398 vs	1404 s	1404 vs	1406 vs
$\delta(\text{CH})$	1362	1380 sh	1363 vw	1367 w	1365 sp 1358 vw
$\delta(\text{CH})$	1223 (+3)	1225 s	1230 w	1229 vw	1227 m
Ring breath.	990 (+6)	991 s	1010^e m	1009^e m	1020 m
γ_{CH}	804 (+3)	792 m	808 w	812 w	806 s
γ_{ring}	719	719 vs	717 m	717 m	706 vs
δ_{ring}	678 (+4)	679 m	684 w	682 vw	685 m
δ_{ring}	621 (+4)	623 s	635 vw	634 vw	638 vs
γ_{ring}	414	420 vw	422 m	423 m	418 vw

^aThe vibrational modes of adsorbed pyrimidine which show upward frequency shifts are marked in bold. ^bPyrimidine in Ar matrix, taken from [17]. ^cLiquid pyrimidine. ^dThe shifts of the vibrational wavenumbers of pyrimidine due to hydrogen bonding effect are given in parenthesis, taken from [17]. ^eObtained from band component analysis.

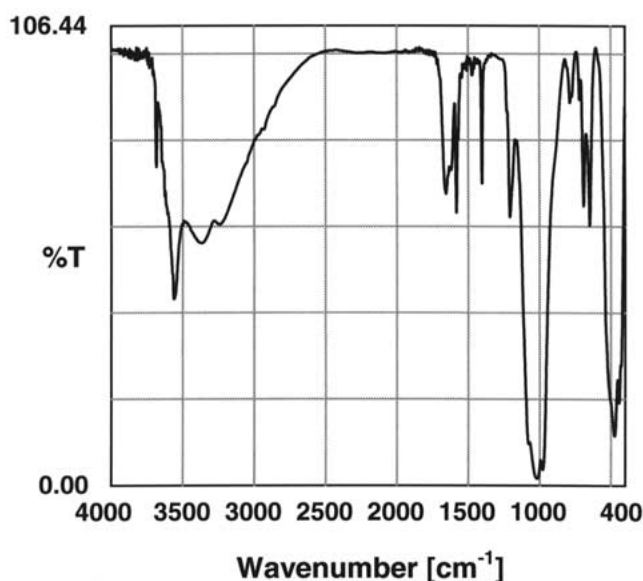
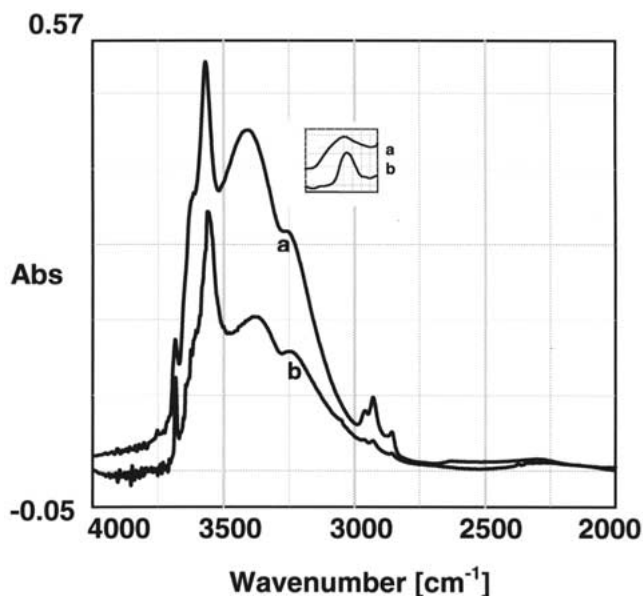


Figure 3. FT-IR spectra of pyrimidine treated sepiolite.

(M=Mn, Co, Zn, Ni, Cu or Cd) occurs through one of the nitrogen of pyrimidine ring, as monodentate ligand [18].

The coordination sensitive ring stretching modes of PM are observed ca. 1584 cm^{-1} and 1404 cm^{-1} as very strong bands in the IR spectra of PM treated clays, whereas the corresponding modes are observed at 1568 cm^{-1} and 1398 cm^{-1} , respectively in the IR spectrum of liquid PM $\{\Delta(\nu_{\text{ads}} - \nu_{\text{liq}}) = 16 \text{ cm}^{-1}$ and 6 cm^{-1} , respectively. Analogous shifts were observed in the $M(\text{PM})_2M'(\text{CN})_4$ complexes and explained by coupling with metal-ligand vibrational frequencies [18]. The comparison of the vibrational values of PM treated clays to those of liquid PM, H-bonded PM in Ar

Figure 4. 2000–4000 cm^{-1} region of the FT-IR spectra of natural sepiolite (a) and pyrimidine treated sepiolite (b). The 3670–3707 cm^{-1} regions of both samples is shown comparatively in the small frame given above.

matrix [17] and $\text{Cd}(\text{PM})_2\text{Cd}(\text{CN})_4$ complex [18] indicated that adsorbed pyrimidine molecules are coordinated through one of the ring nitrogen lone pairs. In the case of sepiolite, the most probably binding sites are surface hydroxyls and Lewis acidic centers [7, 8, 14–16]. On the other hand the perturbation observed on the zeolitic and bound water vibrations of sepiolite (see Figure 4) indicates that some of the adsorbed PM molecules enter the interior channels and replace zeolitic water molecules. In Table 2, the OH group vibrational wavenumbers of natural and PM treated

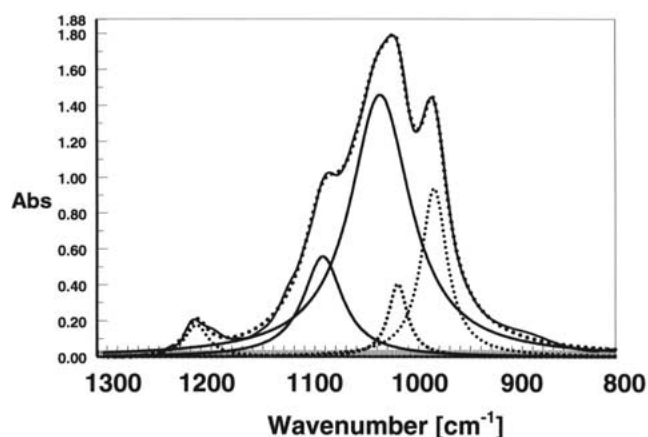


Figure 5. Band component analysis of the 800–1300 cm^{-1} region of the IR absorption spectrum of pyrimidine treated sepiolite.

sepiolite, as obtained band component analysis, are given. The vibrational wavenumbers of the OH group vibrations of the starting sepiolite are found to be in agreement with those reported absorption bands of sepiolite as obtained band component analysis [19]. We observed downward frequency shift in the $\nu(\text{OH})$ vibrations of bound and zeolitic water and decrease in the intensity of the zeolitic water. The frequency shifts may indicate the formation of new H-bonds between bound/zeolitic water and PM molecules whereas weakening in intensity of the $\nu(\text{OH})$ vibrations of the zeolitic water is the indication that PM molecules replace part of the zeolitic water. In the case of adsorption of pyridine by sepiolite, it is known that pyridine molecules penetrate into the channels by replacing part of the zeolitic or bound water and form hydrogen bonds with the rest of zeolitic and/or bound water molecules [20]. Analogous to the adsorption of pyridine onto sepiolite, we also propose that part of the adsorbed PM molecules onto sepiolite penetrate into the channels by replacing some of the zeolitic water and form hydrogen bonds with the bound or zeolitic water molecules.

Thus, the spectroscopic results indicate that the PM molecules adsorbed on sepiolite are coordinated to Lewis acidic sites and/or surface hydroxyls by H-bonding interaction through ring nitrogen lone pairs. Moreover, some of the adsorbed PM molecules may enter the interior channels of the sepiolite structure by replacing zeolitic water and involving H bonding interaction with the zeolitic/bound water molecules. The PM molecules intercalated in the layers of montmorillonite are coordinated to exchangeable cations directly or indirectly through water bridges.

Conclusions

The IR spectroscopic investigation by using band component analysis is found to be very informative in shedding light on the nature of the surface species formed on clays. The intercalation of PM within montmorillonite has been shown by X-ray diffraction to increase the interlayer spacing. IR spectroscopy indicates that sorbed PM molecules by montmorillonite are coordinated to exchangeable cations directly

Table 2. OH group vibrations of natural and pyrimidine treated sepiolite in the IR spectra, as obtained from band component analysis

Assignment [21]	Natural sepiolite	Pyrimidine treated sepiolite
$\nu(\text{OH})$ Mg_3OH	3689 w 3682 vw	3683 ms
$\nu(\text{OH})$ dioctahedral system	3627 s	3619 s
$\nu(\text{OH})$ coordinated water	3569 vs	3557 vs 3465 s
$\nu(\text{OH})$ zeolitic water	3417 vs br 3226s br	3370 s br 3219 m br
$\nu(\text{H}_2\text{O})$	1712vw 1660 s 1625 m –	– 1666 m 1648 m 1616 m
OH deformations	978 m	975 m
OH deformations	785 m	785 m
OH deformations	766 m	769 m
OH translation	690 m	690 m
OH translation	646 m	646 m

or indirectly through water bridges. PM molecules adsorbed on sepiolite are coordinated to Lewis acidic sites and/or surface hydroxyls by H-bonding interaction through pyridine ring nitrogen lone pairs. Moreover, some of the adsorbed PM molecules may enter the interior of the sepiolite structure and replace zeolitic water.

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