

FT-IR and FT-Raman spectroscopic studies of adsorption of isoniazid by montmorillonite and saponite

Sevim Akyuz*, Tanil Akyuz

Department of Physics, Science and Letters Faculty, Istanbul Kultur University, Atakoy Yerleskesi, 34156 Istanbul, Turkey

ARTICLE INFO

Article history:

Received 19 July 2007

Received in revised form 20 December 2007

Accepted 29 February 2008

Available online 18 March 2008

Keywords:

Adsorption

Clay minerals

IR and Raman spectroscopy

Isoniazid

Montmorillonite

Saponite

ABSTRACT

The adsorption of isoniazid on natural montmorillonite and saponite from Anatolia was investigated by FT-IR and FT-Raman spectroscopy. The intercalation of isoniazid within these clays has been shown by X-ray diffraction to increase the interlayer spacing. Vibrational spectroscopy indicates that isoniazid molecules, intercalated into the layers of montmorillonite or saponite, are coordinated to exchangeable cations directly or indirectly through water bridges. It is concluded that the endocyclic nitrogen is mainly involved in the coordination. The carbonyl group oxygen, however, may be involved in a weak H-bonding interaction with water molecules.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Isoniazid (abbreviated as INH) is the most widely used drug in the treatment of tuberculosis. It also seems to be effective in the treatment of extrapulmonary illnesses such as meningitis and genito-urinary infections [1,2].

In recent years smectite clays with intercalated organic molecules have attracted great research interest, since they exhibit novel physical and chemical properties [3,4]. Montmorillonite and saponite are a smectite group of clays that have a layered structure. Each layer has a small net negative charge due to the isomorphous substitution of anions in the framework. The charge is compensated by interlayer hydrated cations, which are known as exchangeable cations. It is well known that a wide variety of organic molecules can intercalate between the interlayer regions of expandable clays [5], and clays have recently been investigated as drug carriers [2,6].

In this study, the adsorption of INH on natural montmorillonite and saponite from Anatolia was investigated by FT-IR and FT-Raman spectroscopy. The aim of this study was to investigate the sorption properties of INH by clays. Since INH has pharmacological activity, we hope to contribute to the explanation of the host–guest interaction through the study of the vibrational spectra of the pure

and adsorbed species, and hence contribute to the use of clays as drug carriers.

2. Experimental

The natural montmorillonite and saponite samples used were from the Cankiri and Mihaliccik-Eskisehir regions of Anatolia (Turkey), respectively. The chemical compositions of the montmorillonite and saponite are as follows (in wt.%): Montmorillonite; SiO₂ (58.3), Al₂O₃ (16.0), CaO (3.5), $\sum(\text{FeO} + \text{Fe}_2\text{O}_3)$ (3.0), MgO (2.5), K₂O (1.1), Na₂O (2.1), TiO₂ (0.6), P₂O₅ (0.1), loss on ignition (13.1). Saponite; SiO₂ (57.9), Al₂O₃ (15.4), CaO (2.2), $\sum(\text{FeO} + \text{Fe}_2\text{O}_3)$ (6.3), MgO (8.0), K₂O (1.5), Na₂O (0.1), TiO₂ (0.5), P₂O₅ (0.1), MnO (0.1), loss on ignition (8.0).

The clays were ground to an approximately 200-mesh size powder. Solid INH was reagent grade (Sigma) and was used as received. Isoniazid treated clays were prepared by immersing the clays in an aqueous solution of the organic molecule in sealed bottles at room temperature for 2 days, after which the clay organic suspension was centrifuged at 7000 × g for 10 min. The IR spectra (400–4000 cm⁻¹) of self-supporting films, prepared according to [7], oriented films supported on a CaF₂ window, or KBr discs of samples, were recorded on a Jasco 300E FT-IR spectrometer (2 cm⁻¹ resolution) based on averaging 200 samples and 16 background scans. In order to reduce the water content, the KBr discs containing samples were heated overnight at 150 °C [7]. The FT-Raman spectra of the powdered samples were recorded on a

* Corresponding author.

E-mail addresses: sakyuz@istanbul.edu.tr, s.akyuz@iku.edu.tr (S. Akyuz).

DigiLab FTS 7000 FT-Raman instrument using 1064 nm excitation from a Nd:YAG laser. The laser power was 100 mW and the detector was a liquid nitrogen cooled Ge detector. 500 scans were accumulated with a resolution 4 cm^{-1} .

The XRD patterns of the natural and isoniazid treated clays were obtained on a Rigaku D/Max-2200/PC diffractometer using Cu K α radiation.

3. Results and discussion

The molecular model of isoniazid is given in Fig. 1. Treatment of natural montmorillonite and saponite with isoniazid resulted in an increase in the basal spacing indicating formation of intercalates. The basal spacing of isoniazid treated montmorillonite and saponite are 15.1 and 15.4 Å, respectively, compared with the value of 12.0 Å (montmorillonite) or 12.5 (saponite) for the basal

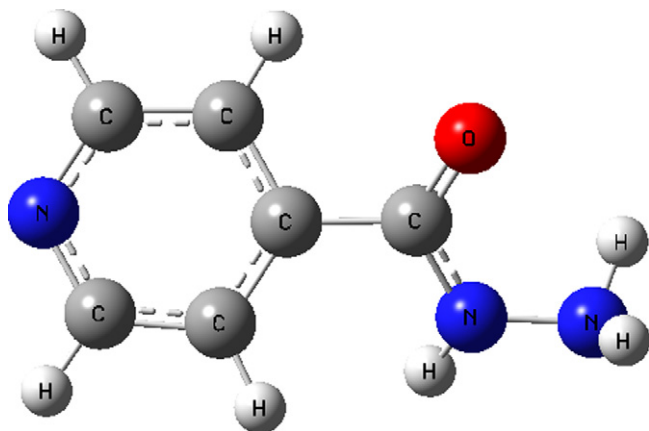


Fig. 1. The structural model of isoniazid.

Table 1
Vibrational wavenumbers (cm^{-1}) of sorbed INH onto clays together with those of solid INH^a

Assignment	Solid INH		INH on clays ^b	
	IR	Ra	Mont.	Saponite
ν_8 , ν (CO)	1666	1669	1676	1674
ν_9 , δ (NH ₂)	1634	1642	1644	1645
ν_{10} , ν_{ring}	1602	1602	1604	1606
ν_{11} , ν_{ring}	1556	1552	1554	1557
ν_{12} , δ (CH)	1491	1494	1505	1507
ν_{13}	1459		1457	1457
ν_{14} , δ (CH)	1412	1411	1414	1416
ν_{15} , δ (CH)	1334	1332	1339	1340
ν_{16} , NH ₂ rock	1322	1322	1322	1322
ν_{20}	1190	1187	1180	–
ν_{21} , δ (CH)	1141	1131	1154R 1147R	1155R 1149R
ν_{22} , ν_{ring}	1098	1095	1119R 1111R	1120R 1113R
ν_{23} , ν_{ring}	1061	1056	1076R 1068R	1073R
ν_{24} , ν_{rings} , ring breath	995	1002	1009R	1011R
ν_{26} , γ (CH)	964	965	980R	981R
ν_{27} , ν (NN)	942		969R	970R
ν_{28} , γ (CH)	887	888	886	886
ν_{30} , γ (CH)	845	848	845	844
ν_{31} , γ (CH) + τ_{ring}	746	757	754	753
ν_{33} , δ (ring)	672	682	690	688

^a Coordination sensitive modes are marked bold.

^b All wavenumbers are obtained from IR spectra except where indicated. R: Raman values.

spacing of the untreated air-dried clays. These observations suggest that INH molecules intercalate into the interlayers of clays with a monolayer arrangement [5]. The observed vibrational bands of sorbed isoniazid are tabulated in Table 1, along with those of solid isoniazid [8].

In the 2700–2600 cm^{-1} region of the IR spectra of the INH-treated clays we did not observe any band which could be attributed to the N⁺H stretching vibration [9], indicating that cationic surface species were not generated on the clays.

It is well known that the adsorption of an organic molecule on a clay surface, or formation of intercalates, gives rise to changes in the vibrational spectra of the interacting species. In order to determine the interaction mechanism of adsorbed isoniazid molecules by clays, the vibrational wavenumbers of adsorbed molecules are carefully investigated by taking into account the coordination effects through the endocyclic and exocyclic nitrogen atoms and through the >C=O group.

When coordination occurs through the oxygen of the carbonyl group, a negative shift is expected in the ν (C=O) mode of the coordinated molecule with respect to the free ligand. In the INH treated clays, however, the ν (C=O) mode is observed at a higher wavenumber than in the solid. It is worth mentioning that in solid INH, the amino group hydrogens and the >C=O group are expected to be involved in H-bonding interactions [10]. All our attempts to dissolve INH in an apolar solvent failed and the gas phase vibrational spectrum of INH was not available in the literature. However, when the C=O stretching wavenumber of INH in the IR spectra of INH treated clays (1676–1674 cm^{-1}) is compared with that of the gas phase spectrum of 2-pyridinecarboxamide (1736–1724 cm^{-1}) [11], one may conclude that the carbonyl group oxygen of the sorbed INH involves a H-bonding interaction, but this interaction is weaker than the interaction in the solid phase of INH itself.

Earlier IR spectroscopic studies of the adsorption of pyridine and pyridine derivatives by clays indicated that certain vibrational modes of the aromatic molecules, particularly the ring modes around 1600–1400 cm^{-1} and the ring breathing mode around 1000 cm^{-1} , are very sensitive to the adsorbing sites [12–14]; they

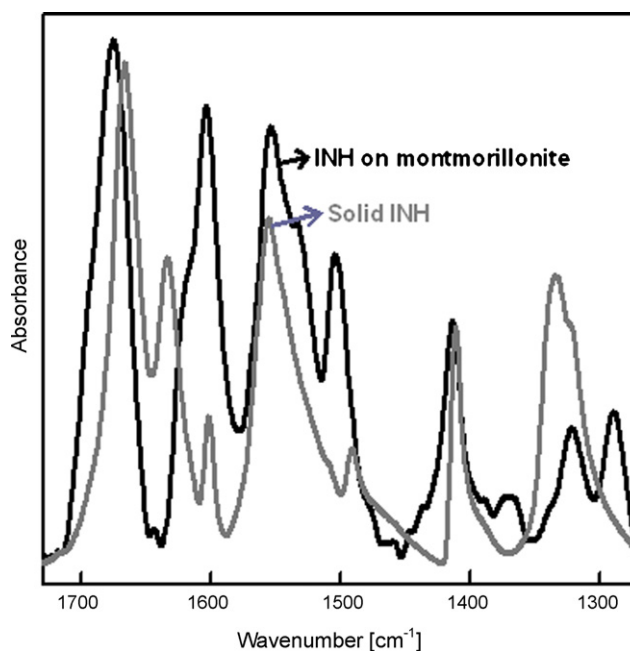


Fig. 2. The 1725–1275 cm^{-1} region of the FT-IR spectra of isoniazid treated montmorillonite film on a CaF₂ window, after subtraction of the untreated montmorillonite bands (black) and isoniazid as KBr disk (grey).

Download English Version:

<https://daneshyari.com/en/article/1249719>

Download Persian Version:

<https://daneshyari.com/article/1249719>

[Daneshyari.com](https://daneshyari.com)