



Investigation of Adsorption of 5-Bromouracil from Aqueous Solutions to Montmorillonite and Its Interaction with Clay Framework: A FT-IR Spectroscopic Study

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Adsorption of 5-bromouracil molecules onto montmorillonite was studied by FT-IR spectrometry. 5-Bromouracil, a thymine antagonist, is used to treat inflammatory tissues. The intercalation of 5-bromouracil within montmorillonite has been shown by X-ray diffraction to increase the interlayer spacing. The results indicate that sorbed 5-bromouracil molecules on montmorillonite are coordinated to exchangeable cations indirectly through water bridges.

Key Words: Adsorption, 5-Bromouracil, Clays, Infrared spectroscopy, Montmorillonite.

INTRODUCTION

5-Bromouracil (5-bromo-2,4(1*H*,3*H*)-pyrimidinedione) (5-BrU) is a brominated derivative of uracil that acts as an antimetabolite or base analog. Substitution of thymine with 5-bromouracil in DNA is known to change interaction between DNA and proteins, thereby inducing various biological phenomena¹. The principal biological importance of 5-bromouracil is that it is one of the well-known uncommon nucleotide bases and has the ability to coordinate with metals or to bind to tissues *via* metals, which interface with the growth of cancer cells². Moreover, 5-bromouracil is used to treat inflammatory tissues^{3,4}.

Montmorillonite is an expandable type of clays that has 2:1 layered structure. The layers are composed of two tetrahedral sheets sandwiching a central octahedral sheet. Each layer has a small net negative charge due to 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 wide variety of organic molecules can intercalate between the interlayer regions of expandable clays⁵⁻⁸. Clay-organic composites have been recognized as one of the most promising material as drug delivering systems⁹⁻¹¹. In previous studies we have investigated adsorption of 2,2-bipyridine¹², 2-aminopyridine¹³ and 5-fluorouracil onto clays¹⁴. In continuation of our studies on clay-organic complexes, in this study the adsorption of 5-bromouracil by natural montmorillonite from Anatolia has been investigated using FT-IR spectrometry. The aim of this study is to investigate the interaction of 5-bromouracil with montmorillonite.

EXPERIMENTAL

The natural montmorillonite sample used was obtained from the Cankiri region of Anatolia (Turkey). The chemical composition of the montmorillonite is as follows; SiO₂ (58.3), Al₂O₃ (16.0), CaO (3.5), S(FeO + Fe₂O₃) (3.0), MgO (2.5), K₂O (1.1), Na₂O (2.1), TiO₂ (0.6), P₂O₅ (0.1), loss on ignition (13.1). The clay sample was ground to fine powder of < 0.5 μm particle size and was analyzed by X-ray diffraction, differential thermal and IR spectroscopic techniques for purity. 5-Bromouracil (solid state) was reagent grade (Aldrich Chemicals) and used as received. 5-Bromouracil treated clay was prepared by immersing the clay in aqueous solution of 5-bromouracil in sealed bottle at room temperature for 2 days, after then clay organic suspension was washed and centrifuged at 7000 g for 10 min. The chemical analysis indicated that the amount of 5-bromouracil adsorbed onto montmorillonite is 0.92 mmol/g.

The IR spectra (4000-400 cm⁻¹) of self-supporting film, prepared according to Madejova¹⁵, oriented film supported onto a CaF₂ window or KBr discs of sample were recorded on a Jasco 300E FT-IR spectrometer (2 cm⁻¹ resolution) based on averaging 200 sample and 16 background scans.

The XRD patterns of the natural and 5-bromouracil treated clays were obtained on a Rigaku D/Max-2200/PC diffractometer using CuK_α radiation.

RESULTS AND DISCUSSION

Treatment of natural montmorillonite with 5-bromouracil resulted in an increase in the basal spacing indicating formation of intercalate. The basal spacing of 5-bromouracil treated

montmorillonite is 15.2 Å. The result, compared with the value of 12.0 Å for the basal spacing of untreated air-dried clay, indicates that 5-bromouracil molecules intercalate into the interlayers of montmorillonite with a monolayer arrangement. Present result is in agreement with that of 5-fluorouracil treated montmorillonite (14.8 Å)¹⁴.

The molecular model of 5-bromouracil is given in Fig 1. The FT-IR spectrum of 5-bromouracil treated montmorillonite in comparison to those of starting montmorillonite and solid 5-bromouracil is given in Fig. 2. Fig 3 represents the 1880-1280 cm⁻¹ region of the IR spectrum of 5-bromouracil treated montmorillonite, after subtracting the vibrational bands of the natural clay, in comparison to that of solid 5-bromouracil. 5-Bromouracil exists in three tautomeric forms; keto (Fig. 1), enol and ion forms. As seen in Figs. 2 and 3, we observed strong C=O stretching bands in the 5-bromouracil treated montmorillonite, indicating that adsorbed 5-bromouracil molecules are in the keto form as like as in the solid phase. In solid 5-bromouracil, the oxygen atoms are expected to involve in strong hydrogen bonding interactions, therefore we compared the 5-bromouracil vibrational wavenumbers adsorbed on clays, to those of 5-bromouracil in an argon matrix^{16,17}. The C=O stretching wavenumbers of 5-bromouracil adsorbed on montmorillonite are found to be lower than those in Ar matrix (1729 and 1761 cm⁻¹). But one component of the C=O stretching wavenumber is found to be higher than the corresponding one of the solid phase, the other component is found to be slightly lower. The result indicates that the adsorbed 5-bromouracil oxygens involve H-bonding interaction but H-bonding strength might be less than that of in solid case (Fig. 3).

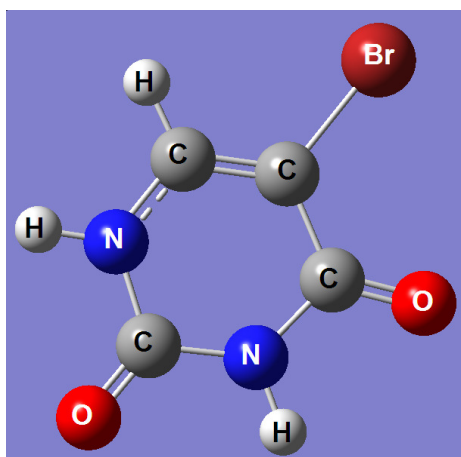


Fig 1. Molecular model of 5-bromouracil

In our previous study the coordination sensitive vibrational bands of 5-fluorouracil were investigated by DFT calculations and it was found that particularly the two ring stretching vibrations around 1500-1400 cm⁻¹ and C-X stretching mode altered in wavenumber upon coordination to Al(OH)₃ through one of the oxygen atoms (C=O). As seen in Fig. 3 we also observed shifts on adsorbed 5-bromouracil vibrations in comparison to those of solid 5-bromouracil, on the coordination sensitive modes of 5-bromouracil. In order to analyze clearly the adsorbed 5-bromouracil modes under water bands of the

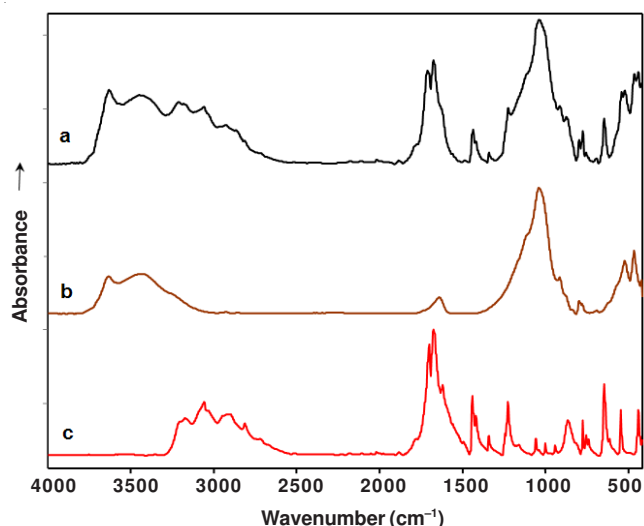


Fig. 2. FT-IR spectra of 5-bromouracil treated montmorillonite (a), untreated montmorillonite (b) and solid 5-bromouracil, recorded as KBr disc

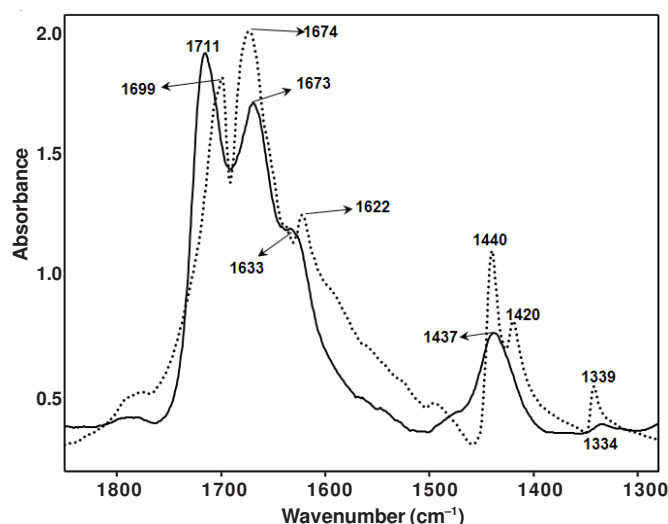


Fig. 3. 1880-1280 cm⁻¹ region of the IR spectra of 5-bromouracil treated montmorillonite, after subtracting the vibrational bands of the natural clay (solid line) and solid 5-bromouracil (dotted line)

clay framework, we performed band component analysis. Band component analysis is a mathematical process, that results in several solutions. But if the analysis is performed by using the second derivative of the original curve, as the guide, the most reliable solution can be achieved. The band component analysis together with the second derivative profile of the 1800-1300 cm⁻¹ region of the IR spectrum of the 5-bromouracil treated montmorillonite is given in Fig. 4. As seen in Fig. 4, all the Gaussian band components correspond to one of the second derivative minimum of the original curve. The band component analysis of the IR spectrum of water bending region of the untreated montmorillonite is given in Fig. 5. The band component analysis is found to be useful in order to pick up the overlapping bands. Comparison of Figs. 4 and 5 indicates that OH bending bands of the clay framework of 5-bromouracil treated montmorillonite are altered. In the IR spectrum of 5-bromouracil treated montmorillonite (Fig. 4), the 1789, 1711 and 1677 cm⁻¹ band components are attributable to C=O

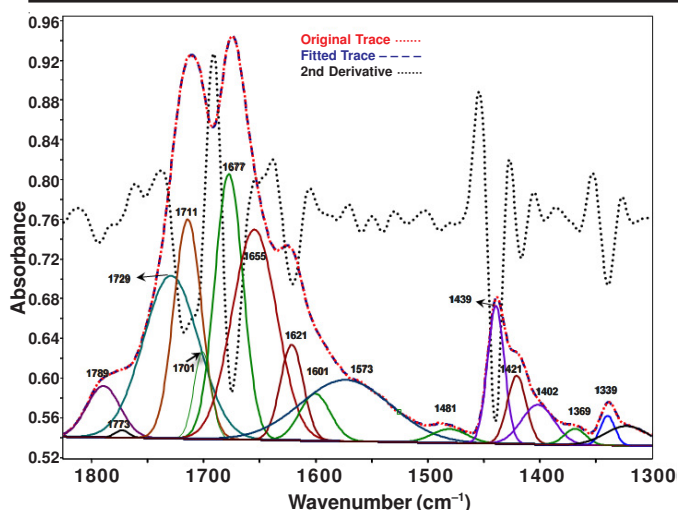


Fig. 4. Band component analysis and the second derivative profile of the 1800-1300 cm^{-1} region of the IR spectrum of 5-bromouracil treated montmorillonite

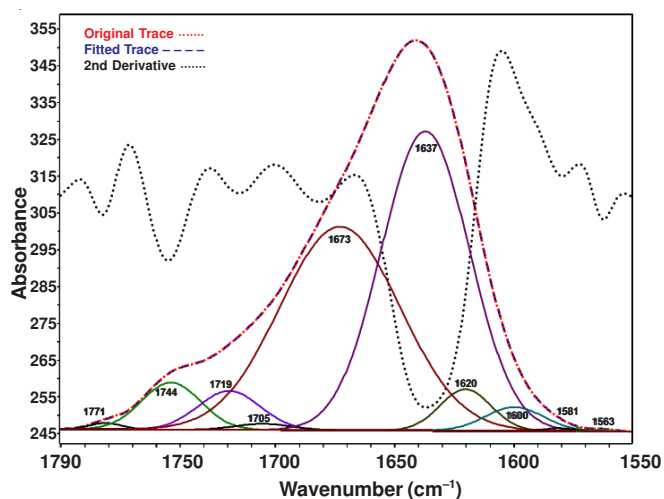


Fig. 5. Band component analysis and the second derivative profile of the 1790-1550 cm^{-1} region of the IR spectrum of untreated montmorillonite

stretching vibration of adsorbed 5-bromouracil. The 1773, 1729 and 1701 cm^{-1} bands are assigned to strongly H-bonded water molecules of the clay framework. These bands were observed at 1771, 1719 and 1705 cm^{-1} , respectively, in the IR spectrum of untreated clay. Adsorption of 5-bromouracil is also affected the OH stretching bands of the clay framework. The 3800-2600 cm^{-1} region of the IR spectrum of 5-bromouracil treated clay is given in Fig. 6, in comparison with that of untreated clay. The OH stretching band of water, weakly H-bonded surface oxygens⁵ (type I water) of the silicate layers of the montmorillonite, was observed at 3634 cm^{-1} in the IR spectrum of untreated clay. After treatment with 5-bromouracil this band is observed at 3627 cm^{-1} (Fig. 5), which indicates the alteration in hydrogen bonding interactions of water weakly H-bonded surface oxygens. On the other hand OH stretching band of the inter molecularly H-bonded water⁵ (type II water) also showed a decrease in frequency and an increase in bandwidth, indicating the formation of H-bonds between water and 5-bromouracil molecules. The spectroscopic results indicate that intercalated 5-bromouracil

molecules involve H-bonding interaction through one of the oxygen atoms as monodentate ligand to the water molecules in the clay framework.

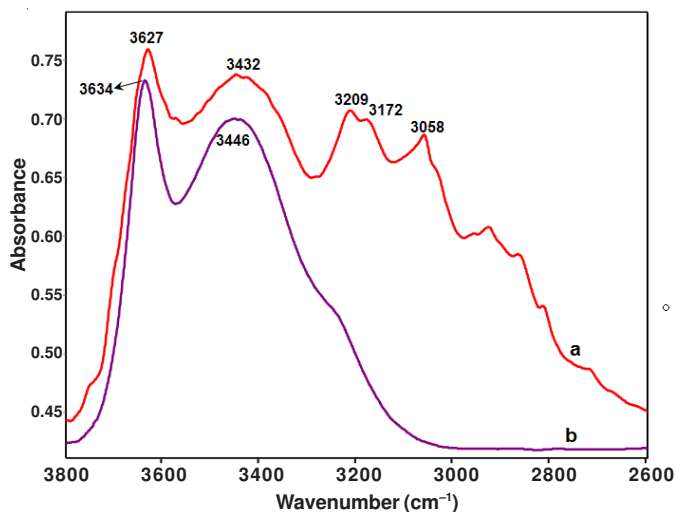


Fig. 6 3800-2600 cm^{-1} region of 5-bromouracil treated montmorillonite (a) and untreated montmorillonite (b)

Conclusion

The comparison of the IR spectra of the adsorbed and intercalated 5-bromouracil to that of free 5-bromouracil offered data on the nature and characteristics of the formed clay-organic complexes. Band component analysis, in comparison with the second derivative profile of the IR spectrum is found to be very informative to shed light on the overlapping bands. The intercalation of 5-bromouracil within montmorillonite has been shown by X-ray diffraction to increase the interlayer spacing. IR spectroscopy indicates that sorbed 5-bromouracil molecules on montmorillonite are coordinated to exchangeable cations indirectly through water bridges.

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