Asian Journal of Chemistry Vol. 20, No. 5 (2008), 3767-3773

Adsorption and Interaction of 2-Aminopyridine with Loughlinite (Na-Sepiolite) from Anatolia

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FT-IR spectroscopy has been used to characterize adsorption and interaction of 2-aminopyridine by loughlinite, which belongs to palygorskite-sepiolite group of phyllosilicates class of clay minerals. The spectroscopic results indicate generation of 2-aminopyridinium cations. Cationic and neutral surface species adsorbed on loughlinite are coordinated to Bronsted acidic sites and surface hydroxyls (by H-bonding interaction through pyridine ring nitrogen lone pairs), respectively. It must be noted that the adsorption of 2-aminopyridine affected the hydroxyl group vibrations of loughlinite.

Key Words: Adsorption, Aminopyridine, Clay minerals, IR spectroscopy, Loughlinite, Sepiolite.

INTRODUCTION

Loughlinite belongs to palygorskite-sepiolite group of phyllosilicates class of clay minerals[1,2] which has fibrous nature. It is also known as natural Na-sepiolite. Loughlinite is virtually identical in appearance to sepiolite both in a hand specimen and microscopically, however, field observations and mineralogical determinations indicate that loughlinite and sepiolite are formed authentically and independently in different physico-chemical environments rather than being the product of transformation of one to the other[2]. The structures of this group of clay minerals consist of talc-like chains (ribbons) parallel to the fibre axis and are formed by an alteration of blocks and channels that grow up in the fibre direction (c-axis). Each structural block is build up of two tetrahedral silica sheets enclosing a central octahedral magnesia sheet in a similar way that occurs in other 2:1 silicates such as talc, but in palygorskite-sepiolite group of clay minerals there are discontinuities and inversions of the silica sheet that give rise to those structural channels[3-5] that may be filled by water or organic molecules. The chemical formula of loughlinite[1] is $Na_2Mg_3Si_6O_{16}\cdot 8H_2O$ and that of sepiolite[3] is $Mg_4Si_6O_{15}(OH)_2\cdot 6H_2O$. Loughlinite and sepiolite are identified by d (110) reflections at 12.9 and 12.3 Å, respectively[2].

The middle to Upper Miocene volcano-sedimentary units in the Mihalliccik-Eskisehir area of Anatolia consist mainly of altered tuff and claystone[2]. Sepiolite and loughlinite are dominant in the claystone of this area[2]. In this study natural loughlinite obtained from this area was used.

Pyridine derivatives are widely used as analytical reagents, dyes, drugs, pesticides and alkaloids. On the other hand 2-aminopyridine-tagged oligosaccharides have been widely used for sensitive qualitative and quantitative analysis by high-performance liquid chromatography with fluorescence detection[6]. 2-Aminopyridine is used in the preparation of cytidine analogs[7]. In addition to these applications, 2-aminopyridine is also immensely used as a reagent in analytical chemistry, thus it is distributed in nature, to a wide extend. For that reason, all the knowledge about the reactivity of organic substances on soils and clay minerals can help in the prevention of some cases of contamination. In our previous studies, adsorption behaviour of nicotinamide, pyrazinamide, pyrimidine and 4-aminopyrimidine on loughlinite were investigated[8-10]. In this study, adsorption and interaction of 2-aminopyridine on loughlinite have been studied by using IR spectrometry.

EXPERIMENTAL

Loughlinite sample used was from Mihaliccik, Eskisehir Province, Central Anatolia Region of Turkey. The coordinates of sampling station are: 39°54'51"N, 31°29'43"E. It is green clay stone. The clay ground to a fine powder of < 0.5 μm particle size was analyzed by X-ray diffraction, differential thermal analysis and IR spectroscopy for purity and dried in a desiccator to remove adsorbed water before analysis. The results indicate that loughlinite is associated with analcime (*ca.* 6 %) and Al_2O_3 (*ca.* 2 %) and has detectable calcite impurity (IR; 1435 cm^{-1}). The chemical composition of loughlinite is as follows: 55.0 % SiO_2; 12.5 % MgO; 7.0 % Na_2O; 6.5 % Al_2O_3; 2.8 % $\Sigma(FeO + Fe_2O_3)$; 1.1 % K_2O; 1.0 % CaO; 0.3 % TiO_2; 0.1 % P_2O_5; 0.05 % MnO; 14.0 % loss on ignition. 2-Aminopyridine was reagent grade (Merck) and was used as received. 2-Aminopyridine treated loughlinite was prepared by immersing clay in either aqueous solution of the organic molecule in sealed bottle at room temperature for 2 d or by solid-solid reactions between clay and the organic molecule, analogous to that described by Ogawa *et al.*[11] and Khaorapapong *et al.*[12]. In the former case clay organic suspension was centrifuged at 7000 g for 10 min. The clay was found to be not altered in colour after being treated with 2-aminopyridine. The IR spectra (4000-400 cm^{-1}) of self-supporting films, prepared according to[13], oriented films supported onto a CaF_2 window or KBr discs of samples were recorded on a Jasco 300E FT-IR spectrometer (2 cm^{-1} resolution) based on averaging 200 sample and 30 background scans.

RESULTS AND DISCUSSION

Neutral 2-aminopyridine and 2-aminopyridine monocation molecules are potentially tautomeric. But it is firmly established that the former exists predominantly in the aminopyridine, not in the imine form (produced by a proton transfer from the NH_2 group to the ring nitrogen) and the predominant 2-aminopyridine monocation is that in which proton has added to the ring rather than the exocyclic nitrogen atom[14,15].

It is well known that the adsorption of the organic molecule onto clay surface gives rise to the changes in the IR spectra of the interacting species. In order to determine the interaction mechanism of adsorbed 2-aminopyridine onto loughlinite, the vibrational wavenumbers of adsorbed molecule are carefully investigated by taking into account the protonation effects and the coordination effects. FT-IR spectrum of 2-aminopyridine treated loughlinite is given in Fig. 1 in comparison to those of solid 2-aminopyridine and natural loughlinite. Fig. 2 represents 1700-1250 cm^{-1} region of the IR spectrum of 2-aminopyridine treated loughlinite in comparison with the IR spectra of solid 2-aminopyridine. The vibrational bands of adsorbed 2-aminopyridine are assigned in comparison to those of the free molecule[14], 2-aminopyridine complexes[16] and the IR spectra of species adsorbed on montmorillonite[17], depending on pH. There are clear differences in the IR spectra of neutral 2-aminopyridine molecule and its protonated form. For instance 2-aminopyridinium cation has a major band at 1664 cm^{-1} which is attributed to N^+H_2 scissoring mode[14] whereas, the corresponding NH_2 scissoring mode is observed at 1630 and 1611 cm^{-1} in the IR spectra of solid 2-aminopyridine and that of in CCl_4 solution, respectively[18]. Band component analysis

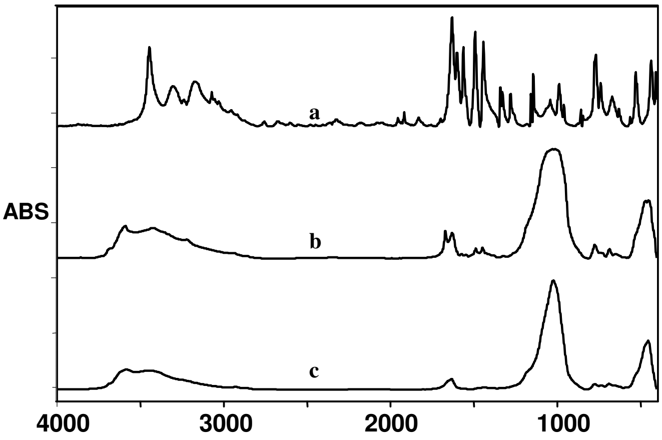

Fig. 1. FT-IR spectra of solid 2-aminopyridine (a), 2-aminopyridine treated loughlinite (b) and starting loughlinite (c)

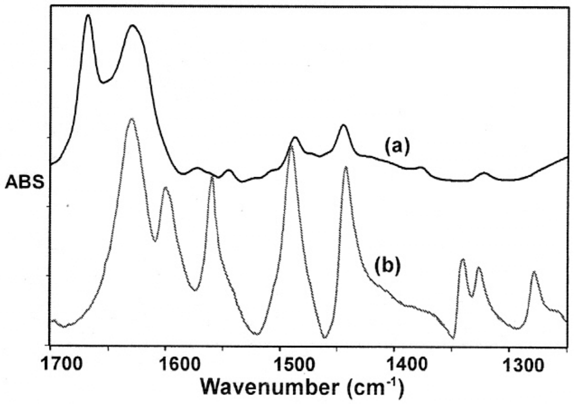

Fig. 2. 1700-1250 cm^{-1} region of the FT-IR spectra of 2-aminopyridine treated loughlinite (a) and solid 2-aminopyridine (b)

of the 1700-1600 cm^{-1} region of the IR spectra of 2-aminopyridine treated loughlinite is given in Figs. 3 and 4. The vibrational bands observed at 1669 (δN^+H_2), 1619 ($C=N^+$ *str.*) 1546, 1473, 1377 cm^{-1} are correspond closely to the vibrational modes of 2-aminopyridinium cation[14,17]. Similar bands were also observed 2-aminopyridine treated montmorillonite at low pH and explained as a result of formation of 2-aminopridinium ions[17]. In the IR spectrum of 2-aminopyridine treated loughlinite the vibrational bands observed at 1605 (ν_4 ring *str.*) 1571 (ν_{13}, ring *str.*), 1487 (ν_5 ring *str.*), 1445 (ν_{14}, ring *str.*), 1340 (ν_{15}, ring *str.*), 1324 ($C-NH_2$ *str.*) are correspond closely to coordinated 2-aminopyridine through ring nitrogen[16].

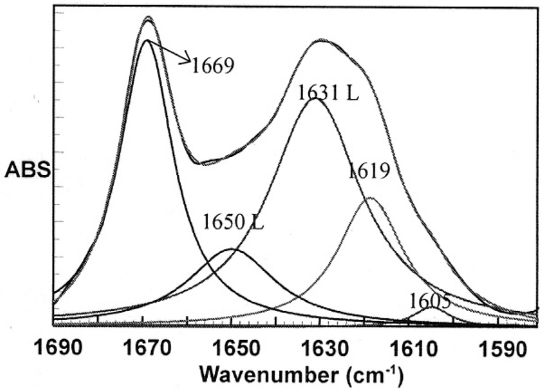

Fig. 3. Band component analysis of the 1690-1600 cm^{-1} region of the FT-IR spectrum of 2-aminopyridine treated loughlinite. Water deformation bands of loughlinite are marked as L, the others are due to sorbed 2-aminopyridine

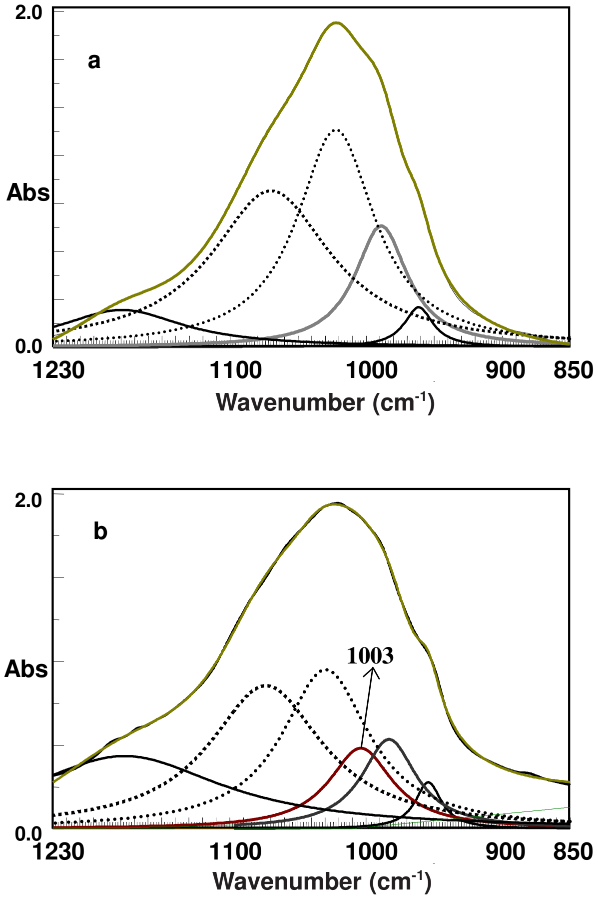

Fig. 4. Band component analyses of the Si-O stretching region of the FT-IR spectra of starting loughlinite (a) and 2-aminopyridine treated loughlinite. Ring breathing mode of 2-aminopyridine at 1003 cm^{-1} is marked

In recent study[19], the adsorption of 2-chloropyridine on oxide surfaces were investigated and the vibrational wavenumber shifts that accompany the different types of interaction of the aromatic molecule with surface sites were calculated. It was shown that the ring stretching vibrations around 1600-1400 cm^{-1} and the ring breathing mode increase in wavenumber upon H bond formation or adsorption at Lewis acid sites[19]. The ν_4, ring stretching mode of 2-aminopyridine was observed at 1599 cm^{-1} in the IR spectrum of solid 2-aminopyridine, but at 1605 cm^{-1} in that of 2-aminopyridine treated loughlinite $\{\Delta(\nu_{ads.} - \nu_{solid}) = 6\ cm^{-1}\}$. This mode was observed around 1607-1605 cm^{-1} in the IR spectra of M(2-aminopyridine)$_2$Ni(CN)$_4$ complexes, where the coordination to the transition metal occurs through the ring nitrogen[16].

The ring-breathing mode of 2-aminopyridine is observed at 986 cm^{-1} in the IR spectrum of solid 2-aminopyridine. It is unfortunately obscured by the host vibrational modes of the clay structure, [ν(Si-O)], in the IR spectra of clays. However, by analysis of the 1230-850 cm^{-1} region of the IR spectra of 2-aminopyridine treated and untreated loughlinite indicated the presence of *ca.* 1003 cm^{-1} band in the IR spectra of 2-aminopyridine treated loughlinite which was not present in those of untreated loughlinite $\{\Delta(\nu_{ads} - \nu_{solid}) = 19\ cm^{-1}\}$. This mode was observed around 1004-1002 cm^{-1} in the IR spectra of M(2-aminopyridine)$_2$Ni(CN)$_4$ complexes, where the coordination to the transition metal occurs through the ring nitrogen[16]. The most probable binding sites of loughlinite, as analogous to sepiolite[3], are expected to be surface hydroxyls and Lewis acidic centers. It is well known that the broken Si-O-Si bonds of the terminal silica tetrahedra on the external surfaces compensate their residual charge by accepting a proton or hydroxyl group and form Si-OH groups[3,19,20]. If adsorbed organic molecule interacts with surface silanol groups of loughlinite, the Si-OH stretching band must be altered. The Si-OH stretching vibration is found to be slightly increased in intensity and decreased in value after adsorption of 2-aminopyridine on loughlinite (Fig. 5). Thus, the spectroscopic results indicate that 2-aminopyridine molecules adsorbed on loughlinite are mostly coordinated to Bronsted acidic centers and some of the adsorbed molecules coordinate to surface hydroxyl by H-bonding interaction through the ring nitrogen.

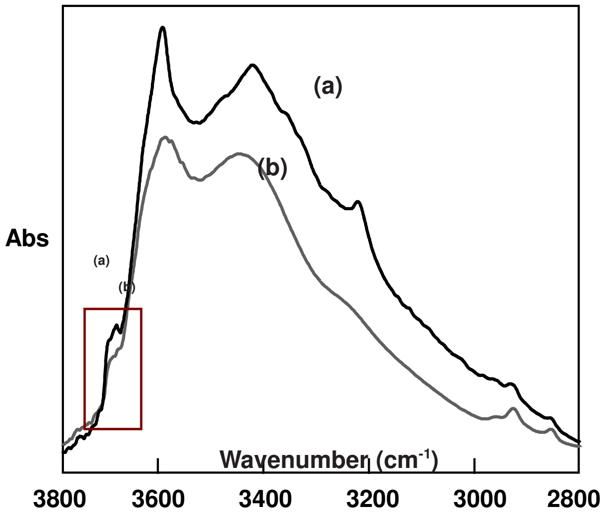

Fig. 5. 3800-2800 cm^{-1} region of the FT-IR spectra of 2-aminopyridine treated loughlinite (a) and starting loughlinite (b). OH stretching (Si-OH) band of the loughlinite due to surface silanol groups is marked

Conclusion

The interpretation of the IR spectral changes of the clays and adsorbents provides information on the nature and characteristics of the formed clay-organic complexes. IR spectroscopy indicates that the sorbed 2-aminopyridine molecules by loughlinite are coordinated to Bronsted acidic centers and 2-aminopridinium cationic surface species are generated. Some of the adsorbed molecules are coordinated to surface hydroxyls by H-bonding interaction through pyridine ring nitrogen lone pairs.

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(*Received*: 20 September 2007; *Accepted*: 6 February 2008) AJC-6310