

## SPECTROSCOPIC INVESTIGATIONS OF 1,4-DIOXANE ADSORBED ON BENTONITE FROM ANATOLIA

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### ABSTRACT

The adsorption of 1,4-dioxane on a natural bentonite sample from Ünye region of Turkey has been examined using infrared and solid state magic angle spinning nuclear magnetic resonance spectroscopic techniques. It was observed that adsorption on bentonite is due to hydrogen bonding between the waters of interlayer and either hydrogen atoms of  $-CH_2$  or oxygen atom of  $-CH_2OCH_2$  groups of 1,4-dioxane. No noticeable interactions, however, are observed at the Al-(Mg)-OH edges by FT-IR (Fourier Transform Infrared) and CP/MAS NMR (Cross Polarization/Magic Angle Spinning Nuclear Magnetic Resonance) techniques.

**Keywords:** Bentonite, <sup>29</sup>Si, <sup>13</sup>C, CP/MAS NMR

### 1. INTRODUCTION

Bentonite, mainly composed of montmorillonite, with a slightly negative charged layered structure is the most common clay of the dioctahedral smectites group [1-3]. The main component in bentonite is smectite which is a 2:1 layer clay mineral formed by one Al octahedral (O) sheet placed between two Si tetrahedral (T) sheets. Bentonites and smectite have a variety range of applications in ceramics, paint, nuclear waste, food, rubber, perfume and plastic [4-6]. 1,4-dioxane molecule is extensively used as a solvent and as a stabilizer in chlorinated organic solvents [7-8]. However, the exposure to large amounts of 1,4-dioxane can cause deaths due to hepatic and renal failures both in acute and subacute phases [9-10].

The interpret of the hydrogen bonded structures is difficult since the hydrogen bonding influences dynamics of the molecules and, hence it leads to a broadened vibrational bands or peaks. The purposes of the present study are to investigate possible hydrogen bonding interactions between 1,4-dioxane and natural bentonite from Ünye/Turkey and, to understand the interaction mechanism of the adsorbed 1,4-dioxane molecule using FT-IR, <sup>29</sup>Si MAS and <sup>13</sup>C CP/MAS NMR spectroscopic methods. The findings of this research are herein reported.

### 2. MATERIALS AND METHODS

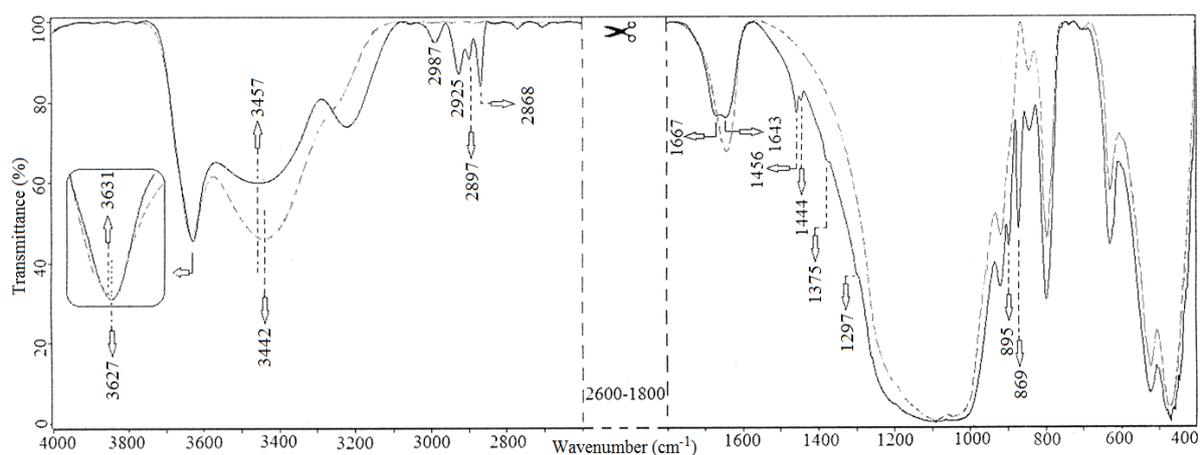
1,4-dioxane (99.8%) was obtained from Sigma Aldrich at reagent grade and used without further purification. Natural bentonite samples were obtained from Nuriye deposits of Ünye region of Turkey. The samples were crushed, ground and sieved to pass through a  $< 90 \mu m$  sieve. Some of us previously reported FT-IR and MAS NMR (<sup>27</sup>Al, <sup>29</sup>Si) of this bentonite [11]. The mixture was prepared according to following conditions; 5.0 ml 1,4-dioxane and 1.0 g bentonite was mixed together in a sealed bottle at room temperature and kept for three days. The obtained product was filtered and left in a desiccator for three days.

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FT-IR spectra of the bentonite samples were recorded (4000-400)  $\text{cm}^{-1}$  with Bruker Optics IFS66v/s FTIR spectrometer at a resolution of 2  $\text{cm}^{-1}$  using KBr pellet technique. All solid state NMR experiments were done at room temperature and were performed by high power hydrogen decoupling. Zirconium oxide rotor with a 4 mm diameter was used to acquire the MAS NMR spectra of  $^{29}\text{Si}$  and  $^{13}\text{C}$ . The operating frequencies were 59.63 MHz and 75.47 MHz for  $^{29}\text{Si}$  and  $^{13}\text{C}$ , respectively. For  $^{29}\text{Si}$  MAS and  $^{13}\text{C}$  CP/MAS NMR, the spinning rate was kept at 7 and 8 kHz, and the data collection was carried out under MAS technique with a delay between  $90^\circ$  pulses (5 s) and 3000 numbers of scans and under CP/MAS technique by the pulse sequence used a repetition time of 2.0 s for 90.000 numbers of scans, respectively. Chemical shifts were assigned in ppm from external TMS and glycine correspondingly.

### 3. RESULTS AND DISCUSSION

FT-IR spectra together with vibrational wavenumbers for 1,4-dioxane treated and untreated bentonite samples are given in Figure 1. The absorption band at  $3627\text{ cm}^{-1}$  is due to stretching vibrations of structural OH groups of bentonites (Al-Al-OH coupled by Al-Mg-OH stretching vibrations). For the untreated sample, it was found as  $3631\text{ cm}^{-1}$  and previously reported as  $3630\text{ cm}^{-1}$  [11]. All results suggest that the guest 1,4-dioxane has hardly reach the OH groups of Al-Al-OH and Al-Mg-OH structures. In the literature, it is commonly accepted that hydrogen bonding of water and dioxane couple cause a shift particularly in the stretching mode of water to the high frequency region which is due to the reduction of the association of the water molecules [12-14].

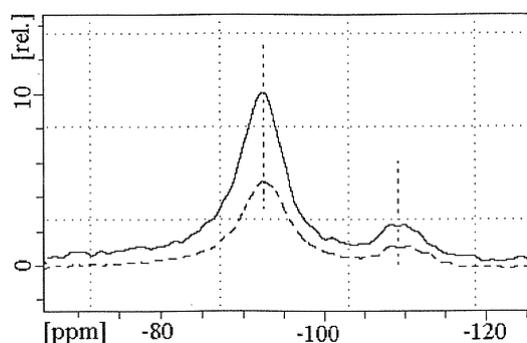


**Figure 1.** FT-IR spectra of 1,4-dioxane treated and untreated (dotted lines) bentonite samples

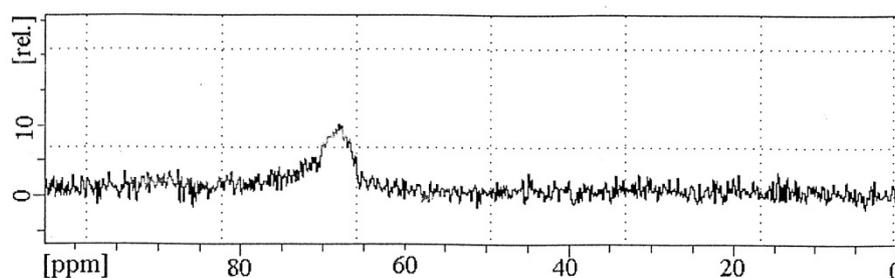
Stretching bands of water appeared at  $3457\text{ cm}^{-1}$  which is shifted  $15\text{ cm}^{-1}$  high frequency region relative to untreated bentonite sample. However, this change cannot be totally attributed to 1,4-dioxane molecule. It is hard to keep to amount of water constant during 1,4-dioxane intercalation in the bentonite sample. The amount of water changes the position of the OH stretching band changes since the number of possible hydrogen bonding increases. This eases the OH bond strength and leads to a red shift in the IR spectrum [15].  $\text{CH}_2$  stretching vibrations appeared at 2987, 2925, 2897 and  $2868\text{ cm}^{-1}$ . Those values were previously reported as 2961, 2917, 2891 and  $2855\text{ cm}^{-1}$  for liquid 1,4-dioxane by Ramsay [16]. It can be seen that the  $\text{CH}_2$  stretching vibrations show an upward shift in this study relative to liquid p-dioxane. Bands at 1667 and  $1643\text{ cm}^{-1}$  are due to bending vibrations of water molecules. The bending mode of water for untreated bentonite sample appears around at  $1640\text{ cm}^{-1}$  [11]. The splitting or  $27\text{ cm}^{-1}$  upward shift of this band is a clear evidence of an interaction between water molecules of untreated bentonite sample and the guest molecule 1,4-dioxane. 1456 and  $1444\text{ cm}^{-1}$  are deformation bands of 1,4-dioxane and it was previously reported as  $1451\text{ cm}^{-1}$  [16]. Vibrations observed at 1375 and  $1297\text{ cm}^{-1}$  are possibly due to O-C-H bending modes of 1,4-dioxane which are in

compliance with previously reported data 1366 and 1290  $\text{cm}^{-1}$  [17]. As can be seen that the bending vibration bands shift to higher wavenumbers which implies that the CH groups of 1,4-dioxane are under the effect of attractive force of water molecules similar to the case reported by Mizuno et al. [18]. Bands at 895 and 869  $\text{cm}^{-1}$  are arising from the  $\text{CH}_2$  rocking and ring stretching of 1,4-dioxane those of which reported as 887 and 874  $\text{cm}^{-1}$  before [19]. It is hard to comment about the 1200-1000  $\text{cm}^{-1}$  region since this region was obscured by large Si-O stretching vibrations of the untreated bentonite sample.

$^{29}\text{Si}$  MAS and  $^{13}\text{C}$  CP MAS NMR spectra for 1,4-dioxane treated bentonite samples are given in Figures 2-3. Resonance frequencies of  $^{29}\text{Si}$  MAS NMR spectrum of 1,4-dioxane treated sample shows no change which indicates no interaction around Si edges of tetrahedral structure (also  $\text{SiO}_2$  impurity) and 1,4-dioxane as supported by FT-IR results.  $^{13}\text{C}$  NMR of 1,4-dioxane gives a singlet at 66.5 ppm [20]. Liquid to solid chemical shifts ( $\Delta = \delta_{\text{solution}} - \delta_{\text{solid}}$ ) reflect intermolecular and intramolecular interactions [21]. In the present study,  $^{13}\text{C}$  CP/MAS of 1,4-dioxane intercalated bentonite sample gave a broad singlet spanned through almost 5.0 ppm at around 68.0 ppm. The broad singlet indicates that the chemical environment of intercalated 1,4-dioxane is different than its solution form or intramolecular rotation is inhibited as expected due to possible hydrogen bonding.



**Figure 2.**  $^{29}\text{Si}$  MAS NMR spectra of 1,4-dioxane treated and untreated (dotted lines) bentonite samples



**Figure 3.**  $^{13}\text{C}$  CP/MAS NMR spectrum of 1,4-dioxane treated bentonite sample

#### 4. CONCLUSION

In the current work, the nature of interaction mechanism of 1,4-dioxane and clay sample from Ünye region of Turkey has been investigated by FT-IR,  $^{29}\text{Si}$  MAS and  $^{13}\text{C}$  CP/MAS NMR techniques. In conclusion, the following results can be summarized:

- i. The comparison of FT-IR spectra of the treated and untreated bentonite samples offered data on the nature and characteristics of the formed clay-dioxane complexes.

ii. There is no evidence of interaction between dioxane and surface hydroxyls of bentonite sample. The absorption band of Al-Al-OH coupled by Al-Mg-OH stretching vibrations show very weak changes ( $4\text{ cm}^{-1}$ ) and  $^{29}\text{Si}$  NMR values show no change.

iii. Some of the adsorbed 1,4-dioxane molecules may involve hydrogen bonding interaction through oxygen and  $\text{CH}_2$  groups of 1,4-dioxane with water molecules present in the clay structure which is supported by FT-IR spectrum.

iv. Mobility of 1,4-dioxane is restricted within the bentonite structure because there is a difference in the resonance frequency of carbon atoms of free 1,4-dioxane and 1,4-dioxane-clay system. Moreover, carbon resonance peak broadens due to this inhibition and possibly 1,4-dioxane prefers more than one possible orientation through hydrogen bonding.

v. The CP/MAS NMR and FT-IR techniques are very useful complementary methods for examining the host guest interactions for clay samples.

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