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Nature of organic fluid–montmorillonite interactions: An FTIR spectroscopic study

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ABSTRACT

The changes in the H–O–H stretching vibration in the interlayer water and Si–O stretching vibration of a Na-montmorillonite (MMT) structure in the FTIR (Fourier transform infrared) spectra provide insight into the effect of fluids of different dielectric constants on the clay structure. Mechanisms by which the different fluids of varying polarities enter into the clay interlayer and the rates at which these molecules interact with the clay structure and the interlayer water are studied at the molecular level using six different fluids with dielectric constants ranging from 110 to 2.4. The shift in H–O–H bending vibrations of interlayer water and changes in the Si–O vibration bands of MMT occur almost immediately after mixing with the solvent regardless of the polarity of the solvent. However, the extent and the rate of changes in H–O–H bending and Si–O stretching are dependent on the polarity of the solvent. Results show a very good correlation between the polarity of the solvent and the shift in H–O–H bending of interlayer water, and also between the polarity of the fluids and the $d_{(001)}$ spacing of the MMT–solvent samples. Low polar fluids such as methanol tend to make weak electrostatic interactions with clay surface oxygen and interlayer-water molecules, which result in an increase in interlayer spacing. Although, the alteration of the Si–O structure due to high polar molecules such as formamide is a continuous process, the influence of nonpolar fluids such as TCE (trichloroethylene) on the Si–O structure is almost instantaneous, which may result in high hydraulic conductivity in the clay.

1. Introduction

Due to its unique swelling capacity and low hydraulic conductivity, montmorillonite has been used in geosynthetic clay liners (GCL) for many years. The usefulness of bentonite clays in civil engineering and environmental applications such as sealant and liners in dams and landfills can be attributed to their small particle size, high surface area, high swelling capacity, and most importantly, low hydraulic conductivity. Although, the composition of landfill leachate may vary from landfill to landfill depending on waste composition, the age of the landfill, and the technology that has been used in building the landfill, it has been seen that many municipal landfill leachates contain many organic compounds that are toxic, carcinogenic, or otherwise hazardous in nature [1]. Studies have shown that leachates tend to increase the hydraulic conductivity of GCL (geosynthetic clay liner), in which smectite-type clay is the main constituent, by many fold compared to the hydraulic conductivity of water [2–6]. Therefore, understanding the influence of organic fluids on the clay structure at the molecular and nanoscale level is essential in designing effective clay liner systems and for accurate prediction of macroscale behavior of swelling clays.

The effect of organic fluids and landfill leachates on clay has been studied extensively both theoretically and experimentally in the past [7–11]. Dios-Cancela et al. have studied the formation of montmorillonite samples with different ligands such as acetone and acetonitrile, using characterization techniques such as X-ray diffraction (XRD), infrared spectroscopy, and ab initio quantum mechanical methods and found out that the clay cation–ligand interaction is ion–dipole electrostatic in nature and these samples are formed by the direct interaction of the oxygen or nitrogen atom of ligand and the interlayer cation [12]. Molecular dynamics studies on clay–water interactions have shown the quantitative relationship between swelling of interlayers of clays with hydration [13–15]. XRD study shows the the extent of interlayer expansion of Ca-montmorillonite with polar organic molecules depends on the magnitude of the dipole moment and the dielectric constant of the immersion liquid [16]. However, clays that are modified by ions such as ammonium become organophilic and thus expand the clay interlayer spacing on interacting with organic molecules [17]. There is, however, little information available, on the molecular level interaction between organic molecules of a range of polarities, with smectite-type clay minerals. Mechanisms, by which the different fluids of varying polarities enter into the clay interlayer, and the rates at which these molecules interact with the clay structure, and the interlayer water, are still unknown. The objective of this work is to carry out a systematic study on the effect of the dielectric properties of the organic molecules on

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Na-montmorillonite interlayers at the molecular and nanoscale level using FTIR and X-ray diffraction techniques. We have used six organic liquids with dielectric constants ranging from 2.4 to 110 to study the interaction with the Na-montmorillonite interlayer. Some of the organic entities such as trichloroethylene (TCE) are very toxic [18] in nature and some of them such as acetone and toluene are the key organic constituents of municipal solid waste leachates [6].

Infrared spectroscopy is a powerful method for monitoring and analyzing clay–fluid interactions. Study of the characteristic IR bands, such as Si–O stretching, O–H stretching of structural O–H group, O–H stretching and H–O–H bending of interlayer water, in clay, and characteristic IR vibration bands such as C=O and C–C–O stretching bands in solvents, is utilized in understanding the clay–fluid interactions at the molecular level [19–23]. Hertl and Hair have compared the adsorption heats of 23 compounds that are adsorbed to surface hydroxyl groups with the O–H stretching bands of hydroxyl groups of silica at 3750 cm^{-1}[24]. The interaction of organic molecules with the hydroxyl groups on silica gel has been investigated by Elkington and Curthoys using IR spectroscopy, and they have observed shifts in the structural hydroxyl stretching vibration band on interacting with different organic compounds [25]. It is seen that the adsorption of acetylacetone to layer silicates takes place through carbonyl oxygen [22]. Significant modification of the spectrum of the clay mineral is observed when the clay interacts with water [21,26–28]. Studies have shown that the interaction of the polar molecules with clay water molecules is one of the key factors in the process of entry of the crude oil into the clay interlayer [29]. In our prior work, we have studied the effect of swelling of clay on the molecular clay–water interaction [30] and molecular hydraulic properties of the Na-montmorillonite interlayer [31] using FTIR and XRD techniques. Interactions of clays with organic moieties have also been investigated using near IR spectroscopy [32]. Also, we have used FTIR extensively to investigate the role of various functional groups of several modifiers in organomodified clays on Si–O and O–H vibrations of the clay structure [33–36]. In this study, we describe the mechanisms, by which organic moieties, which exhibit a range of polarity from high polarity to nonpolarity, enter into the clay interlayer and the rates at which these molecules interact with the clay structure and the interlayer water, by evaluating the Si–O stretching vibration of clay sheets and H–O–H bending vibrations of interlayer water as well as some characteristic bands, such as C–O and C=O stretching, of the organics. Two FTIR techniques, reflectance and transmission, were employed. In reflectance FTIR technique, the polarized IR beam was used. Relevant band assignments of MMT and organic solvents that were used in this study are shown in Table 1. Molecular structures and the dielectric constants of the organics used are shown in Table 2.

Table 1
Band assignments of Na-montmorillonite (MMT) and organic solvents used in this study.

Wavenumber range (cm^{-1})	Band assignment
1398	C–H in-plane bending of formamide [45]
1323	C–N stretching and N–H wagging of formamide [45]
1049	C–H out-of-plane bending of formamide [45]
1620	H–O–H bending of structural water of MMT
950–1100	C–O stretching of methanol [45,46]
1740	C=O stretching of gas phase acetone
1721	C=O stretching of liquid phase acetone
1228	C–C backbone stretching of liquid acetone
1350–1375	C–H bending of acetone [51,53]
1560	C=C stretching Of TCE [54,55]
1590	C=C stretching Of TCE [54,55]
1605	C–C stretching of toluene [56]

It is a well-known phenomenon that the swelling is caused by an increase in the interlayer spacing of smectite-type clay. In addition, swelling results in the breakdown of clay particles [37]. XRD analysis is one of the classical techniques that can be used to measure the $d_{(001)}$ spacing of clays accurately. Increase in the $d_{(001)}$ spacing of montmorillonite has been observed when the clay is modified with different organic modifiers [35–42]. Wang et al. have shown that the exfoliated clay reduces its interlayer distance after acetone was added to the clay suspension possibly due to removal of water from the interlayer space [43]. In this work, changes in interlayer distance of MMT with different solvents with different dielectric constants are studied using XRD analysis.

2. Materials and methodology

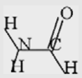
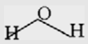
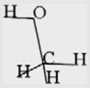
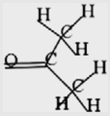
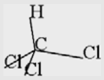
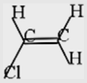
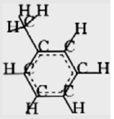
2.1. Materials

Na-montmorillonite (SWy-2) was obtained from the clay minerals repository at the University of Missouri, Columbia, Missouri. The cationic exchange capacity of the clay is about 76.4 meq/100 g. The SWy-2 montmorillonite has the chemical formula $NaSi_{16}$ $(A_{l6}FeMg)O_{20}(OH)_4$ [44]. In order to have a consistent water content in all clay samples, finely ground Na-montmorillonite (MMT) that was passed through a No. 325 sieve (45 μm mesh), was dried at 50 °C for 24 h prior to each sample preparation. Further, 90–100% purity formamide, 99.9% purity acetone, 99.7% purity toluene, and 99.9% purity trichloroethylene were obtained from Mallinckrodt Baker, Inc. (NJ), 99.9% purity chloroform was obtained from EMD Chemicals Inc. (NJ), and 99.9% purity methanol was obtained from Alfa Aesar (MA). For the preparation of MMT–water paste for XRD experiments deionized water was used.

2.2. Spectroscopic technique

MMT–organic solvent samples were prepared by gently compressing a very thin layer of MMT on the gold-coated metal substrate with a glass slide and adding solvent on the sample surface, so that the concentration of solvent to clay is about 200 wt%. For transmission experiments, samples were prepared by gently compressing a thin layer of clay against a silicon window with a glass slide and adding solvent on the clay surface so that the clay to solvent concentration is same as in reflectance experiments.

Table 2
Molecular structures and the dielectric constant values of the solvents that are used in this study.

Fluid type	Formamide	Water	Methanol	Acetone	Chloroform	TCE	Toluene
Structure							
Dielectric constant	110	80	33	20	4.8	3.4	2.4