WETTABILITY CONTRASTS IN KAOLINITE AND ILLITE CLAYS: CHARACTERIZATION BY INFRARED AND X-RAY ABSORPTION SPECTROSCOPIES

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Abstract—A reservoir rock is a porous geological formation in contact with 2 liquids, brine and oil. An improved knowledge of rock wettability is of primary importance to estimate the amount of crude oil in underground resources. The petroleum industries have observed that wettability contrasts in sedimentary reservoir rocks are largely correlated to the presence of clays, illite and/or kaolinite in the rocks' intergranular space.

More precisely, the grain surfaces of illite show a preference for brine. Kaolinite preferentially adsorbs oil, which imparts its hydrophobic characteristics to the mineral surface. Using X-ray absorption spectroscopy (XAS) and Fourier transform infrared (FTIR) spectroscopy, we studied the adsorption process of asphaltenes in the presence of water at the microscopic level. We demonstrate experimentally that the wettability contrasts observed in kaolinite and illite are related to structural differences between these 2 clays, and we show the role of the grain surface hydroxyls. With clay materials, the purity of the samples is the most important limitation of the quantitative use of extended X-ray absorption fine structure (EXAFS).

Key Words—Adsorption, Clay, EXAFS, Illite, Infrared, Kaolinite, Wettability, XANES.

INTRODUCTION

The petroleum crisis led to a significant research effort in the development of new methods for oil recovery from fields. On the average, 5 to 25% of the total oil in place in an underground reservoir can be recovered by natural depletion, whereas 10 to 20% more oil may be extracted by water flooding or gas injection. The remaining fraction, the target of the new methods, is mainly associated with petroleum components adsorbed onto rocks. In this context, understanding the rock wettability mechanism is of primary importance in estimating the amount of crude oil in underground resources (Cuiec 1991). Wettability controls the localization and displacement of fluids at the level of the rock pores (Yariv 1992). It can be defined as the preference for a solid surface to be wetted by a fluid in presence of other immiscible fluids: in this case, brine and oil. Initially, underground reservoir rocks were believed to be a preferentially water-wet medium. On the average, 5 to 30% of the total oil in place in a water-wet medium can be recovered by natural depletion. Nutting has shown that some reservoir rocks are oil-wet (Nutting 1934). In this case, it is more difficult to recover the trapped oil. Statistical studies have shown that reservoirs that are preferentially oil-wet or of intermediate wettability, spontaneously imbibing both water and oil, are far more numerous that initially believed (Cuiec 1991).

Cryo-scanning electron microscopy studies (Fassi-Fihri 1991) on sandstone reservoir rocks of intermediate wettability have displayed heterogeneous wettability at pore scale, associated with the nature of the minerals of the pore network. Fluid trapping has been shown to be largely correlated to the presence of clays in the intergranular space. Clays found in the oil fields are mainly illites and kaolinites (Czarnecka and Gillott 1980). It is now well established (Fassi-Fihri 1991; Jerauld and Rathmell 1994) that, in oil-saturated sandstones, kaolinites are preferentially wetted by oil while illites and other minerals are essentially wetted by water. Numerous studies have been performed at the macroscopic level to characterize the thermodynamic parameters of the clay surface related to the adsorption process (Van Oss 1992, 1993; Yan and Masliyah 1994). They showed that the process affects only the surface of the grains. The adsorption onto clay particles does not involve chemical reactions, and it is therefore regarded as a physisorption process. More precisely, the wettability properties are believed to be related to the presence of asphaltenes, which are one part of the heavy components of crude oil (Clementz 1976).

However, few characterizations of the adsorption phenomenon at the microscopic level and from the clay side have been reported. The aim of this work was to identify the physicochemical factors responsible for the hydrophilic-hydrophobic character of illite and kaolinite in reservoir rocks; more precisely, to determine whether the wettability contrasts of clays have intrinsic causes, inherent to their crystalline structures and chemical compositions. The structures of the kaolinite and the illite phases are largely described in Ledoux and White (1964) and Yariv (1992). So, as the

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grain surfaces of illite and kaolinite are different, we sought to know whether these differences were sufficient to explain the behavior of clays toward oil in the presence of water.

Hydroxyl groups are largely present at the surface of the kaolinite where the surface of the octahedral sheet, which forms 1 of the 2 basal planes, is formed by hydroxyl groups bonded to Al. The TOT structure of the illite indicates that OH groups are not present on the basal plane surfaces. The OH are present at the broken edges of the grains (Ledoux and White 1964) for illite and kaolinite. Infrared spectroscopy has been extensively used to investigate intercalation of polar organic compounds in phyllosilicates' interlayer spacing. More precisely, hydroxyl stretching vibrations have been shown to be very sensitive to the presence of guest species in the interlayer region (Barrios et al. 1977; Raupach et al. 1987; Sugahara et al. 1988, 1990; Heller-Kallai et al. 1991; Tunney and Detellier 1994). To characterize the sensitivity of the OH grain surface to the adsorption process, we studied the hydroxyl stretching vibration region of illite and kaolinite (3550 to 3750 cm^{-1}) by FTIR.

An XAS investigation was undertaken to follow the adsorption process at the local scale. The advantage of this technique is that it is element-selective and sensitive to the local environment up to 4.5 Å of the chosen absorbing atom. Henderson (1995) showed that numerous earth scientists have taken full advantage of its unique properties. Chisholm-Brause, Hayes et al. (1990) and Chisholm-Brause, O'Day et al. (1990) performed XAS studies of wet samples to determine the structure of metal complexes adsorbed onto mineral surfaces. Since the Al and Si sites in clays are able to contract chemical interactions with the asphaltenes of the oil, the local environments around Al and Si atoms in both illite and kaolinite have been investigated by EXAFS and X-ray absorption near edge structure (XANES). The 2 clays have been studied before and after contact with asphaltenes. To our knowledge, this work is the first XAS characterization of clay samples wetted by organic compounds.

MATERIALS

The samples considered are kaolinite (Plœmeur, France) and illite (Szabadsàg, Hungary). They are hydrothermal, neoformed and well-crystallized. The samples were prepared at the Centre de Recherches sur la Physico-Chimie des Surfaces Solides de Mulhouse, France. The natural material was first purified and exchanged with Na$^+$ by the addition of the appropriate chloride salt (Robert et al. 1974) and grains smaller than 2 μm in diameter were then recovered by sedimentation. The mean structural composition formulas, the origins of the samples and the preparation method are described in Saada et al. (1995).

Asphaltenes used for the adsorption process were extracted from heavy Arabian crude oil from Safaniya, Saudi Arabia, and were supplied by the ELF-IFP-Total bank of samples. Their compositions and characteristics are also given by Saada et al. (1995). The wetting procedure followed that of Siffert et al. (1992) so that 2.4 mg/m^2 were adsorbed onto the surface of kaolinite and 1.4 mg/m^2 were adsorbed onto the surface of illite. The contact was made in presence of water to mimic the competition of the 2 fluids at the surface of the clays.

The crystallographic nature of the minerals was checked by X-ray diffraction (XRD) and differential thermal analysis. The results show that small quantities of mica and quartz are present in the kaolinite sample, and small quantities of quartz and beidellite in the illite. However, it is impossible to evaluate precisely the percentage of impurities. The diffraction patterns indicate that no modification of the grain structure or of the stacking sequence of the layers is induced by the adsorption of asphaltenes.

EXPERIMENTAL METHODS

Fourier Transform Infrared Spectroscopy

Infrared spectra were collected using a Bruker IFS66 FTIR spectrophotometer equipped with a deuterated triglycine sulphide (DTGS) detector in the middle infrared domain ranging from 4000 to 400 cm^{-1}. Fifty scans were recorded for each spectrum with a spectral resolution of 2 cm^{-1} in the transmission mode. KBr pellets were made to obtain an isotropic distribution of the grains in the samples. A mixture of 1.2 mg of clay and 300 mg of KBr was gently stirred for approximately 2 min without exerting any pressure that could induce preferential grain orientations. The resulting mixture was then pressed under 5 t to form a pellet die. The reproducibility of the results was checked with 20 samples for each compound.

X-ray Absorption Spectroscopy

Al- and Si-K edge XAS experiments were carried out on the SA32 beam line installed at the Super-ACO storage ring of LURE (Orsay, France) running at 0.8 GeV and 200 mA. A toroïdal mirror in the beamline focuses the beam into a rectangle 200 μm horizontal by 500 μm vertical, very close to that of the source. The XAS experiments used α-quartz ($10\bar{1}0$) and SbIn double crystal monochromators for Al- (1559 eV) and Si-K edge (1839 eV) measurements. The energy resolution has been estimated as approximately 0.5 eV at the Al-K edge (Ildefonse et al. 1994) and 0.7 eV at the Si-K edge (Laffon 1990). The samples were placed in a chamber at a pressure of 10^{-6} torr. Data were collected in the total electron yield mode by recording the drain current of the sample (typically a few picoamperes). This detection mode increases the sensi-
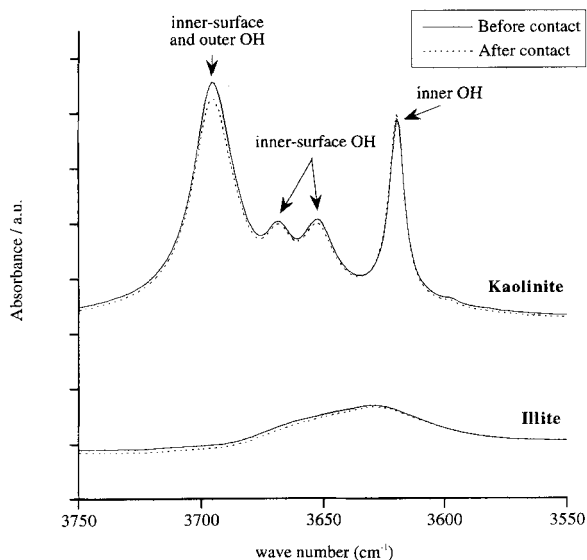
Figure 1. IR transmission spectra of Plœmeur kaolinite and illite from Hungary before and after contact with asphaltenes in the OH stretching region.

tivity to the surface of the samples, compared to transmission mode detection, which is bulk sensitive. The clays were directly pressed on indium films deposited on a copper sheet used as a support. All the spectra were collected with the samples perpendicular to the beam path.

The Si-*K* XANES spectra were collected over a photon energy range of 1830 to 1910 eV. The Al-*K* XANES spectra were recorded from 1560 to 1600 eV (0.2 eV step/2 s per point).

The XANES spectra were linearly background fitted to give a flat pre-edge region, and the intensities were normalized at the end of the spectra 60 eV above the edges.

The Si-*K* edge EXAFS spectra were collected between 1780 and 2500 eV, 1 eV step/2 s per point. Recording of EXAFS data is more challenging at the Al-*K* edge. During the energy scan, the Bragg angle of the crystals varies over at least 20° and the alignment of the crystals must be maintained throughout the scan. Furthermore, the Al-*K* edge spectra can only be recorded over a limited photon energy range of 1530 to 1830 eV (1 eV step/10 s per point) due to the presence of silicon (*K* edge at 1845 eV) both in the monochromator crystals and in the clay sample. The energy range available is thus very small compared to standard EXAFS measurements, which are often made over several hundred eV, up to 1000 eV past the edge. The extraction of structural parameters is difficult and the data treatment must be carefully performed; thus, there are relatively few EXAFS studies of the Al environment for these materials (McKeown et al. 1985; Landron et al. 1992; Roberts et al. 1993; Kamijo et al.

1994; Koningsberger and Miller 1994; Bantignies et al. 1995).

The EXAFS data were treated following the classical procedure (Teo 1986) using the programs written by Michalowicz (1991). The moduli and imaginary parts of the Fourier transforms that give a direct representation of the radial distribution of the absorber element neighborhood are shown. Examination of the imaginary part, due to phase information, is characteristic of the types of atoms that make up a given shell due to the linearity of the phase combination of the different atoms (Koningsberger and Prins 1987).

RESULTS

Infrared Spectroscopy

The spectral range corresponding to the Al-OH deformation modes, the Si-O modes and the Al-O stretching modes (1500–300 cm^{-1}) has been presented and discussed for kaolinite in Bantignies et al. (1995). For illite, the band attribution is more complicated and this part of the spectrum will not be discussed here.

Transmission IR spectra of the O-H stretching region of kaolinite and illite before and after contact with asphaltenes are shown in Figure 1. For kaolinite, 4 distinct OH stretching (v(O-H)) modes have been identified. The band at 3622 cm^{-1} is assigned to the inner OH stretching vibrational mode. The bands at 3655 and 3670 cm^{-1} are assigned to the inner-surface OH groups located on the surface of the octahedral sheet sandwiched between 2 layers. The band at 3700 cm^{-1} reflects several OH stretching contributions, the inner surface OH groups and the "outer hydroxyls" that refer to the OH groups at the surface of the micro crystals, including hydroxyl groups at the broken edges (Ledoux and White 1964). The positions and intensities of the v(O-H) bands are in agreement with previously published spectra for other kaolinites (Farmer 1974; Johnston et al. 1985; Brindley et al. 1986; Prost et al. 1989). The relative intensities of these bands show that the crystallinity of our sample is high (Johnston et al. 1990).

For illite, a broad peak centered at 3630 cm^{-1} is observed. This is mainly due to the structural inner OH stretching modes of the octahedral sheet of the layer (Oinuma and Hayashi 1965).

The XRD measurements of the 2 clays have shown that there is no modification of the cell parameters induced by asphaltene adsorption. For kaolinite, we can assume that the position, bandwidth and intensity of the intrasheet OH band at 3622 cm^{-1} is not affected by the adsorption process. The normalization of the 2 spectra has been consequently made on this peak as a reference. The adsorption process does not affect the inner-surface OH bands at 3655 cm^{-1} and 3670 cm^{-1}. However, the outer-surface OH band at 3700 cm^{-1} is affected. We observe a small but significant decrease
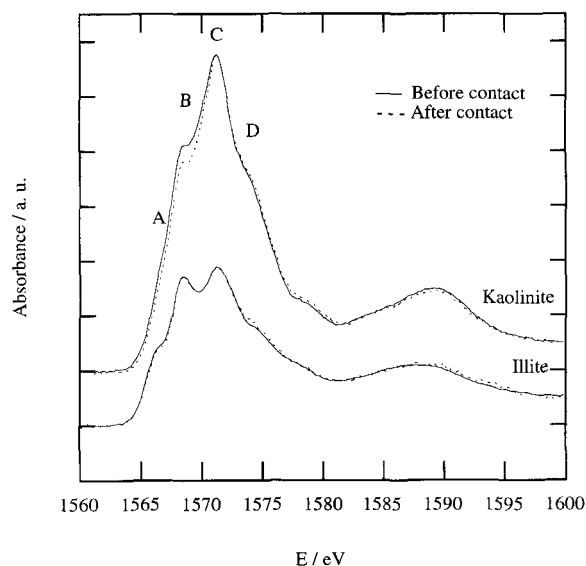
Figure 2.   Al-*K* edge XANES spectra for Plœmeur kaolinite and illite from Hungary before and after contact with asphaltenes.

of the intensity. Two types of OH groups contribute to this peak: 1) those that give vibrations from interlayer hydroxyls; and 2) those vibrating at the surface of the grains. Since contact with asphaltenes does not modify the stacking of the layer, it is therefore thought that only hydroxyl groups belonging to the surface are affected by the phenomenon. Thus, the evolution of the band at 3700 cm^{-1} can be attributed to modifications occurring to the OH located at the surface of the grain, due to the presence of adsorbed asphaltenes. This observation is in line with Ledoux and White (1964), where the band at 3700 cm^{-1} has been shown to be very sensitive to the interactions with molecules like potassium acetate.

For illite, asphaltene adsorption does not affect the OH stretching broad band. Due to the TOT structure of this material, the number of hydroxyls at the surface of the grains is much lower than for kaolinite because only the OH at the grains' broken edges can be considered. The major part of the signal is thus coming from the OH intrasheet vibrators, which are not affected by the adsorption process.

We have shown that, for kaolinite, the adsorption of asphaltenes induces a modification of the OH vibrations. The small amplitude of the variations confirms that the interactions between asphaltenes and clays are weak, probably van der Waals forces.

For the illite sample, no evolution of the OH stretching region with the asphaltene adsorption can be observed.

Proceeding further with these IR results, we performed an XAS study to characterize the Al and Si

environments and to follow their evolutions after contact with the asphaltenes.

X-ray Absorption Spectroscopy

Al-*K* EDGE XANES RESULTS. The XANES method is a direct probe of the local environment of the absorbing atom. Spectral features arise from both single and multiple scattering processes of the photoelectron with atoms surrounding the absorber; these processes involve multiple scattering centers often extending beyond the first coordination shell. Due to the low kinetic energy of the photoelectron in the XANES region, multiple-scattering contributions are very important, making this part of the spectrum particularly sensitive to the local geometrical arrangement of first and more distant neighbors around the absorber (interatomic distances, site symmetry, bond angles). Therefore, XANES can furnish direct information about the crystallographic site occupied by the selected atom.

In Figure 2, the XANES Al-*K* edge spectra of kaolinite and illite are reported before and after contact with asphaltenes. Kaolinite spectra present 4 typical features at 1566 eV (A), 1568.5 eV (B), 1571.2 eV (C) and 1574 eV (D). These features are characteristic of the Al-*K* edge XANES of oxide and aluminosilicate minerals (McKeown et al. 1985; McKeown 1989; Ildefonse et al. 1994; Cabaret et al. 1996) where Al has a coordination number of 6 (Al^{VI}). These features have been interpreted in terms of multiple scattering effects up to 14 Å around the Al atoms, reflecting the sensitivity of XANES to the medium-range order (Cabaret et al. 1996). The relative intensity and resolution of the C and B peaks are correlated to the Al^{VI}-O distance distribution (Ildefonse et al. 1994). For Al^{VI} in a regular site, C/B<1 and the resonances are well-resolved. For 2 Al^{VI} sites with an important Al-O distance distribution, we have C/B>1 and the 2 peaks are less resolved. Our data agree with the structural characteristics of kaolinite: 2 Al^{VI} sites with Al-O distances ranging from 1.868 to 1.969 Å (Bish and Von Dreele 1989).

The illite XANES spectra also present 4 features at the same energies as compared to the spectra of kaolinite. Only the relative intensities are strongly modified. Our data are consistent with the presence of tetrahedral, (Al^{IV}) and octahedral aluminum sites (McKeown et al. 1985; Ildefonse, Calas, Kirkpatrick et al. 1992, 1994; Idelfonse, Calas, Flank et al. 1995). The A peak is more intense and better resolved because it corresponds to the sharp white line observed in Al^{IV} pure tetrahedral minerals (Ildefonse et al. 1994). The B peak is also more intense and better resolved, which is consistent with the more symmetric Al^{VI} single site in illite.

Next to be considered is the influence of the asphaltene adsorption on the 2 samples. The XANES spectrum of illite after contact is superimposable onto
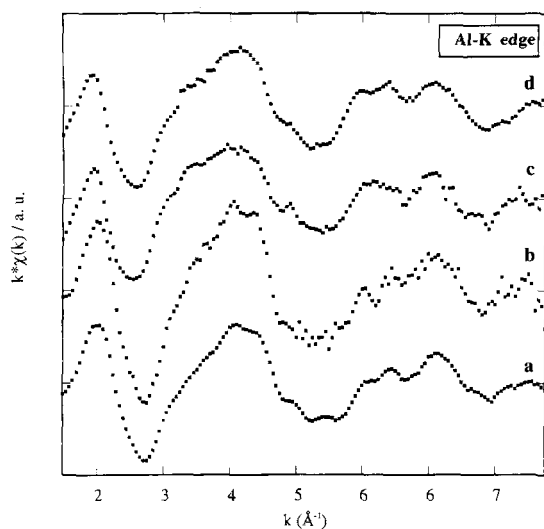
Figure 3. Al-*K* edge EXAFS spectra for illite from Hungary: a) before contact; and b) after contact; and Plœmeur kaolinite: c) before contact; and d) after contact.

Figure 4. Moduli and imaginary parts of the Fourier transforms of k-weight EXAFS spectra for Plœmeur kaolinite and illite from Hungary. Imaginary parts of the Fourier transforms of the compounds after contact with asphaltenes.

the spectrum obtained for the pure compound. This means that the electronic structure of the Al atoms and their environment are not modified by the wettability. Conversely, a small but significant modification appears for the kaolinite XANES spectrum, after contact. We observe a small decrease of the B peak intensity. This shows that the local environment of the Al is sensitive to the presence of adsorbed asphaltenes.

Our result shows that, for kaolinite, the wettability process affects the atomic arrangement around Al atoms. For the illite sample, the local atomic arrangement around the Al is not sensitive to the contact.

AL-*K* EDGE EXAFS RESULTS. The high-energy part of the XAS spectrum (up to 50 eV above the edge) corresponds to the EXAFS region. The backscattering of photoelectrons of high kinetic energy gives the EXAFS oscillations (Brown et al. 1988). Structural information about the distance, nature and number of backscatterers to the absorber can be obtained.

Figure 3 presents the Al-*K* edge EXAFS oscillations extracted from the absorption spectra of kaolinite and illite, before and after contact with the asphaltenes. The corresponding pseudo-radial distributions of the Al neighborhood are reported on Figure 4. The peak positions corresponding to the neighboring shells are displaced by the atomic-phase shifts, which are not yet introduced in the Fourier transform procedure. They are typically 0.5 Å shorter in distance compared to the crystallographic distances, differences that disappear within the analytical procedure.

The high-quality data (high signal-to-noise ratio) obtained allow us to have an accurate description of the Al environment up to 4.5 Å. The structural parameters for a kaolinite sample (from Keokuk) obtained
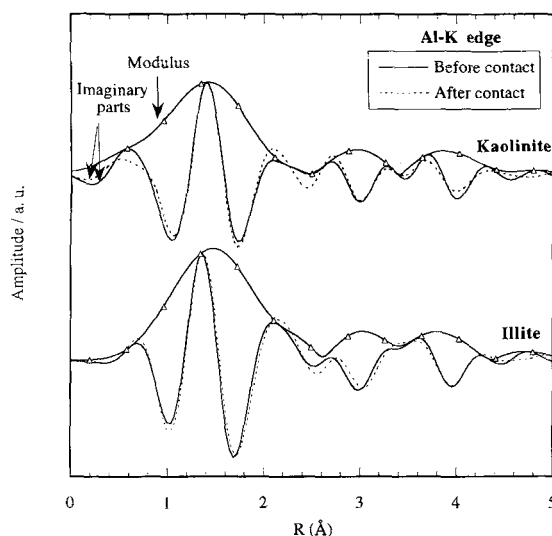
by XRD using Riedvelt analysis (Bish and Von Dreele 1989) are reported in Table 1. The structural parameters for illite are not yet clearly defined (Rothbauer 1971). Table 1 shows the structural arrangement around the Al atoms for a muscovite compound, which is structurally similar to the illite family. The first and second neighbor's shells are similar for kaolinite and illite. The first observed peak corresponds to the 6 O atoms in the first coordination sphere of Al at an average distance of 1.91 Å. The second peak corresponds to the 3 Al atoms at an average distance of 2.97 Å; 2 Si atoms for kaolinite and 4 Si atoms for illite at an average distance of 3.20 Å; and O atoms until 4 Å. The third shell corresponds to the contributions of Si and O atoms with large distance distribution (Table 1).

For kaolinite, we did not attempt to extract quantitative structural information from the EXAFS spectra because of the complexity of the structural atomic arrangement around Al atoms.

For illite, the quantitative analysis of these 3 shells is not possible because of the substitutions of Si by Al atoms in the tetrahedral sheet evaluated at 13.8% by chemical analysis. The extraction of the structural parameters would then be difficult, due to the fact that our data integrate a sum of signals coming from Al in 2 different environments.

The Fourier transforms obtained before and after contact with asphaltenes will now be compared. Figure 4 shows that the first shell around the Al atoms (6 oxygens) is not affected by the contact process (the 2 peaks are identical). Above the first shell, the imaginary part of the Fourier transform (as well as the modulus) shows a weak but significant modification. This

Table 1. Structural parameters of the Al environment for kaolinite and muscovite.

	First shell	Second shell	Third shell
Muscovite†	6 O R_{Al-O} = 1.91–1.95 Å	3 Al R_{Al-Al} = 2.99–3.00 Å 4 Si R_{Al-Si} = 3.15–3.23 Å 11 O R_{Al-O} = 3.39–4.07 Å	4 Si R_{Al-Si} = 4.37–4.49 Å 12 O R_{Al-O} = 4.25–4.54 Å
Kaolinite‡	6 O R_{Al-O} = 1.86–1.97 Å	3 Al R_{Al-Al} = 2.95–3.00 Å 2 Si R_{Al-Si} = 3.14–3.25 Å 9 O R_{Al-O} = 3.42–4.05 Å	2 Si R_{Al-Si} = 4.34–4.50 Å 11 O R_{Al-O} = 4.15–4.52 Å

† Rothbauer (1971).
‡ Bish and Von Dreele (1989).

means that at longer distances (>2 Å), the neighborhood of the Al atoms is modified by the asphaltene adsorption, a significant number of Al atoms giving a different signal in the EXAFS spectrum. This evolution is in agreement with those observed in the XANES part of the spectra and leads to the same conclusion: the contact affects the neighborhood of the kaolinite Al atoms.

For illite, the imaginary part of the Fourier transforms are superimposable before and after contact, up to 4 Å, indicating that no variation of the atomic arrangement around the Al atoms due to the adsorption process is detected. This result is also in agreement with our previous XANES investigations.

Si-K EDGE XANES RESULTS. The Si-K edge XANES spectra of kaolinite and illite, before and after contact with asphaltenes, are shown in Figure 5.
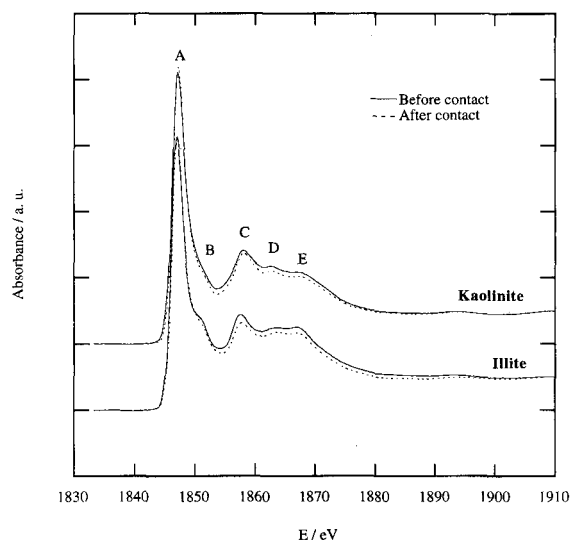

Figure 5. Si-K edge XANES spectra for Plœmeur kaolinite and illite from Hungary before and after contact with asphaltenes.

The spectra of the pure clays are in line with those previously published for the same family of compounds (Roberts et al. 1993, kaolinite; Keller-Besrest et al. 1994, illite). All of the spectra contain 1 very intense and sharp resonance (A) followed at higher energies by several oscillations with lower intensities. The peak (A) at 1847 eV is the signature of the tetrahedral Si(IV)-O_4 unit (Lagarde et al. 1992), which is the same for both spectra of the 2 clays.

At higher energies, the spectra of the 2 clays are different (positions and relative intensities of the B, C, D, E contributions). These features are attributed to the sum of single and multiple scattering processes. Multiple scattering calculations performed by Briois et al. (1993) to simulate the Si-K XANES of α-quartz have shown that a large cluster must be taken into account to reproduce all the XANES features up to 13.8 Å from the absorber. Beyond the Si(IV)-O_4 entities, which are the same for kaolinite and illite, the arrangement of the atoms at longer distances is completely different, due to the respective stacking of sheets TO and TOT. If the XANES differences between the 2 clays are small, it is because: 1) the first and second shell of neighbors around Si are identical; and 2) these closer shells are responsible for the major part of the signal. The structural differences occur after the second shell (see Table 2), primarily due to the presence of K ions.

From the spectra obtained for the 2 clays after contact with asphaltenes, we can see that they are superimposable onto those obtained from the pure compounds. This means that, during the adsorption process, the electronic structure of the Si atoms, the tetrahedral symmetry and the Si-O bonds remain the same. Furthermore, the wettability process does not affect the "short" and "medium" atomic arrangement around the Si atoms, which are not sensitive to the contact.

Si-K EDGE EXAFS RESULTS. Figure 6 presents the Si-K edge EXAFS oscillations extracted from the absorp-

Table 2. Structural parameters of the Si environment for kaolinite and muscovite.

	First shell	Second shell	Third shell
Muscovite†	4 O $R_{Si-O} = 1.63–1.65$ Å	3 Si $R_{Si-Si} = 2.96–3.07$ Å 2 Al $R_{Si-Al} = 3.15–3.23$ Å	18 O $R_{Si-O} = 3.23–4.40$ Å 3 K $R_{Si-K} = 3.73–3.82$ Å
Kaolinite‡	4 O $R_{Si-O} = 1.59–1.63$ Å	3 Si $R_{Si-Si} = 2.92–3.05$ Å 2 Al $R_{Si-Al} = 3.13–3.26$ Å	18 O $R_{Si-O} = 3.14–4.19$ Å

† Rothbauer (1971).
‡ Bish and Von Dreele (1989).

tion spectrum of kaolinite and illite, before and after contact with the asphaltenes. The corresponding pseudo-radial distributions of the neighborhoods of Si in both cases are reported in Figure 7. Table 2 reports the structural arrangement around Si for the kaolinite and the muscovite phases. The first and second neighbor's shells are similar for kaolinite and illite. The first peak of the Fourier transform corresponds to the 4 O first neighbors linked to the Si atoms at an average distance of 1.62 Å. The second peak corresponds to 3 Si atoms at an average distance of 2.98 Å. They are superimposable for illite and kaolinite. The third peak corresponds to 2 Al atoms for kaolinite and to 4 Al atoms for illite structure.

The quantitative analysis of these 3 shells has not been undertaken because our samples are not pure and a significant amount of quartz and mica is present with the kaolinite, beidellite with the illite. As a consequence, the extraction of the structural parameters is impossible, the collected signals coming from Si in kaolinite, quartz and mica. The purity of the natural samples is certainly the most important limitation of the quantitative use of the adsorption technique in earth science.

If we compare now the imaginary parts of the Fourier transforms of the EXAFS spectra before and after contact with asphaltenes, we can see that they are the same for both kaolinite and illite. The contact does not affect the local environment of the Si atoms for the 2 clays. Thus, this result confirms the XANES observations. This is not a surprise if we take into account that the sensitivity of the XANES part of the spectrum to structural changes is higher than the EXAFS one, due to the multiple scattering phenomenon, which involves more neighborhood shells.

DISCUSSION AND CONCLUSION

Fourier transform infrared spectroscopy and XAS have been used to characterize the absorption phenom-
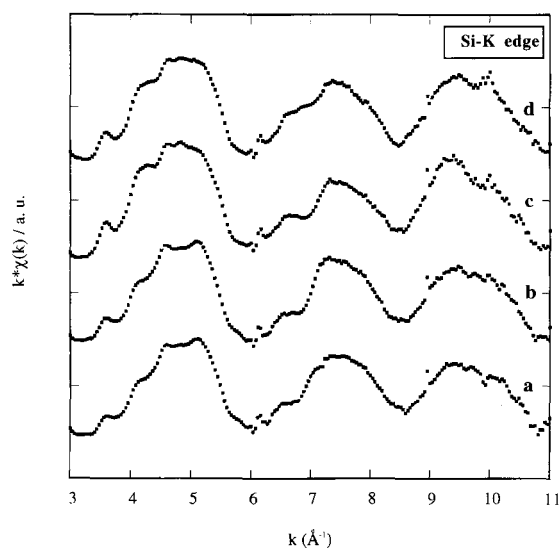

Figure 6. Si-*K* edge EXAFS spectra for illite from Hungary: a) before contact; and b) after contact; and Plœmeur kaolinite: c) before contact; and d) after contact.
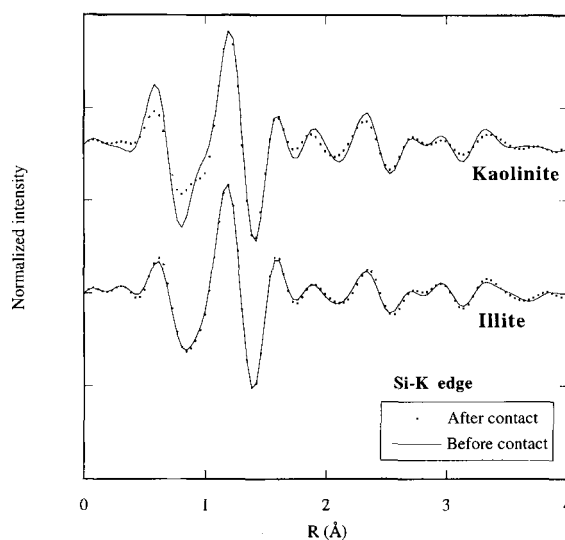

Figure 7. Imaginary parts of the Fourier transforms of k-weight EXAFS spectra for Plœmeur kaolinite and illite from Hungary. Imaginary parts of the Fourier transforms of the compounds after contact with asphaltenes.

enon of asphaltenes onto clays in the presence of water at the microscopic level.

Infrared results show that only the OH surface of the kaolinite is sensitive to the contact with asphaltenes. The XANES and EXAFS results at the Al-K edge confirm the role of these surface groups, the local order of Al (the surface OH are linked to Al atoms) in the kaolinite being the proof of the adsorption process. However, the Si environment of the kaolinite remains unsensitive to the contact; Si are not linked to OH groups.

For the illite phase, Si and Al environments are in each case not sensitive to the adsorption. Consequently, it is possible to explain the contrasts of wettability observed in the clays by structural differences between kaolinite and illite. More precisely, we pointed out the role of the Al-OH linkages located at the surface of the clays in the adsorption process. The presence of these groups at the grain surface can be associated with the preferential asphaltenes' affinity to the surface with respect to water. Our results are in line with the measurements of the OH surface groups concentration (Saada 1995), executed upon the samples studied here. They found 3.6 OH/nm^2 for the Plœmeur kaolinite and only 1.1 OH/nm^2 for the illite of Hungary.

Saada et al. (1995) explain the preferential hydrophilic character of the illite by the presence of these cations at the surface of the grain. Absent on the kaolinite surface, this mineral presents a preferential affinity for oil compared to illite. Our results are in line with these conclusions. Also, we show that only the grain surfaces containing Al-OH linkages are sensitive to the asphaltenes' contact for the kaolinite. Only these sheets generate preferential electrostatic interactions with asphaltenes rather than with water. The role of the clay grain surfaces has also been investigated by Berhouet (1994). By molecular simulations, she modelized the interactions between model compounds of petroleum and clays. Considering that the Al(OH)6−x (O)x surface groups are Lewis acids, Berhouet proved their role in the adsorption process. These groups interact preferentially with the organic wetting agent, generating an inversion of the wetting in an environment of water/oil. She proposed an interaction model to explain the wetting contrast between different clays in line with our experimental results. At the present time, it is not possible to generalize our conclusions to other wetted samples. Indeed, the behavior of the clays varies with the nature of the asphaltenes and the wetting conditions (Mercier 1994). When water is absent in the wettability process, the results obtained are quite different (Mercier 1994; Zoungrana 1994; Saada 1995).

It is now important to extend our description to the atomic scale of the oil/clay interactions by simplifying the adsorption process involved. To accomplish this, it is necessary to wet clays with model organic molecules that display simpler structures than asphaltenes. We are engaged in this work.

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