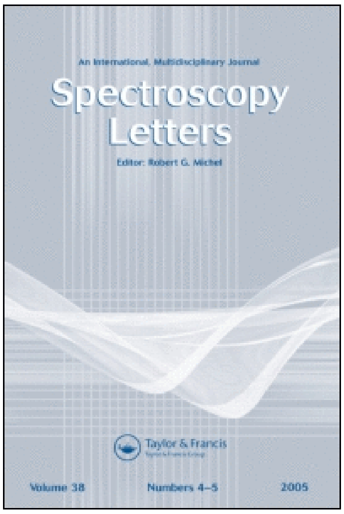

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THE ADSORPTION OF ANIONIC AND CATIONIC SURFACTANTS BY THE DIFFERENT CLAY MINERALS: FTIR SPECTROSCOPIC STUDY

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THE ADSORPTION OF ANIONIC AND CATIONIC SURFACTANTS BY THE DIFFERENT CLAY MINERALS: FTIR SPECTROSCOPIC STUDY

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ABSTRACT

The adsorption of an anionic surfactant LABS (Linear alkyl benzene-sulphonate) and a cationic surfactant DDAC (Distearly dimethyl ammonium chloride) by kaolinite, bentonite and sepiolite clays was investigated by vibrational spectroscopy. The samples prepared at different concentrations, and clay-surfactant spectra in the natural state, were recorded. The spectroscopic results indicate that the LABS and DDAC adsorbed on sepiolite and kaolinite. Bentonites are coordinated to either surface hydroxyls by H-bonding interaction (sepiolite) or to exchangeable catoins (kaolinite, bentonite) through both sulphur and nitrogen atoms as ligands. Interactions of both surfactants showed similarities, in that LABS was coordinated on clay surfaces with broken ends, and the DDAC molecule was adsorbed on the clay surface.

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Key Words: Clay minerals; Surfactant; FTIR spectroscopy

INTRODUCTION

Clay minerals are widely used in various industrial products and processes, such as paper, paints, coatings, dyes, cement, ceramics and drilling fluids, etc. An extensive literature exists with regard to the structure and chemistry of clays[1–5]. In addition, clay minerals have been commonly used as catalysts for oxidation and/or polymerisation reactions and as molecular sieves in the adsorption of some polar and non-polar molecules[6]. Although all clays are similar in some of their important properties, there are many types of clays and they can be classified in various ways. As previously stated, crystalline clays are made up of sheets of octahedra and tetrahedra of oxygen and hydroxyls. The layered aluminosilicate clay minerals are of two main types, depending upon the ratio of tetrahedral (Si-O) to octahedral (Al-O-OH) sheets, whether 1:1 or 2:1. In 1:1 minerals like kaolinite, an octahedral sheet is attached by the sharing of oxygen to a single tetrahedral sheet. In 2:1 minerals like montmorillonite (bentonite), an octahedral sheet is attached in the same way to the two tetrahedral sheets, one on each side. However, sometimes the tetravalent Si in the tetrahedral sheet is replaced by divalent Fe or Mg ions. This replacement, which is referred to as isomorphous substitution, results in a deficiency of positive charges which are compensated for by absorption of a layer of cations that are too large to be accommodated in the crystal[7–9]. In another group of clays, the phyllosilicates (sepiolite) are composed of trimorphic layers arranged in ribbons which are joined through oxygen ions. The tetrahedral sheet are continuous but the apiece of the SiO_4 tetrahedra in adjacent ribbons point in opposite directions, giving rise to a corrugated surface with open channels running parallel to the ribbons[10].

The adsorption of organic compounds to clay minerals has been studied[11–17]. Particularly, interactions of the clay-surfactants and polymers depend on the adsorption and characteristic rheological properties, such as viscosity, shear stress, yield point, gel strength, pH and the influence of surfactants on the flow behaviour of clay-water systems[14–17]. In the presence of salt and in an alkaline medium, clay mineral particles can aggregate in different ways[2,15]. At a some-what higher salt concentrations, the potential between the surfaces also becomes attractive. The particles then aggregate face-to-face (association between flat oxygen planes of two parallel platelets), in such a way that a linked structure results throughout the system[18].

The use of IR spectroscopy for the analysis of adsorbed or intercalated molecules by clays is well-known. How the sorbed molecular species are linked to surfaces can be known by studying the changes in IR spectra brought about by sorption[19,20]. Surfactants are components which reduce surface tension, when they are dissolved in water. They are used in detergents, leather production, and in the textile and cosmetic industries. As a consequence of this, when they go into water with waste water, they create various harmful effects on the natural water ecosystem; they also enhance the corrosion effect on metallic surfaces.

In this study, we analysed the adsorption of anionic and cationic surfactants by three different Anatolian clays in water.

EXPERIMENTAL PROCEDURE

Depending on the minerological investigations of clay minerals, chemical analyses carried out with XRD, classic wet chemical analysis, and atomic absorption spectroscopy are given in Table 1. The Na-peptization process was accomplished by mixing 4 weight percent $NaHCO_3$ with the natural Ca- bentonites of 45% humidity and this mixture was left for 7 days in a semi-opened stockroom where it was exposed to ambient air circulation in order to obtain better quality drilling clay[16].

For ion exchanging processes, in many rheological studies, Na-bentonite plays an important role depending upon the change in zeta potential, which affects adsorption[17].

Clay-surfactant complexes were prepared at concentrations of 5% and 20%, after a period of time at 105° C the activation processes of the clay minerals reacted with LABS and DDAC molecules. Mixtures, which are prepared by mixing in a magnetic mixer for 3 hours, then kept for 5 days; were dried following a filtration process. The FTIR spectra of KBr disks were recorded using a Shimadzu 8201/86601 PC spectrometer.

Table 1. Chemical Analyses (wt %) of the Clay Samples

Clay	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO	H_2O-LOI[a]	Total
Kaolinite	64.58	23.57	1.55	0.13	–	0.064	1.01	–	8.23	99.13
Bentonite	62.80	19.00	2.20	1.80	4.60	1.00	0.76	0.45	7.39	100
Sepiolite	51.94	2.12	1.59	20.14	0.20	0.20	0.13	–	23.67	99.99

[a] Loss on ignition.

RESULTS AND DISCUSSION

LABS-Clay Interactions

The IR spectra of LABS treated kaolinite, bentonite and sepiolite are illustrated in Figs. 1 through 3. When comparing complexes of kaolinite and bentonite-LABS, similar interactions have been observed. The sharp peak resulting from Si-O stretching at 1044 cm^{-1}, which interacts with the vibrational modes of natural LABS molecules at 1174 to 1130 cm^{-1} have been observed. The sharp carbonate mode of kaolinite and bentonite have been observed to shift from 1385 cm^{-1} to 1400 cm^{-1} as a result of complexing interactions, with a resultant reduction in its intensity. The HOH bending modes of all three clay minerals have been observed at 1638 to 1618 cm^{-1}. The interaction with the LABS surfactant caused a shift to 1660 cm^{-1} and a change into a single mode. We think that this change of clay frequencies is a result of interactions of LABS at 1466 to 1412 cm^{-1} (CH_2 symmetric and CH_3 asymmetric bending). Moreover, wide and intense structural hydroxyl stretching at 3690 to 3400 cm^{-1} are separated into two or more components, some of which are demonstrated in sharp peak modes,

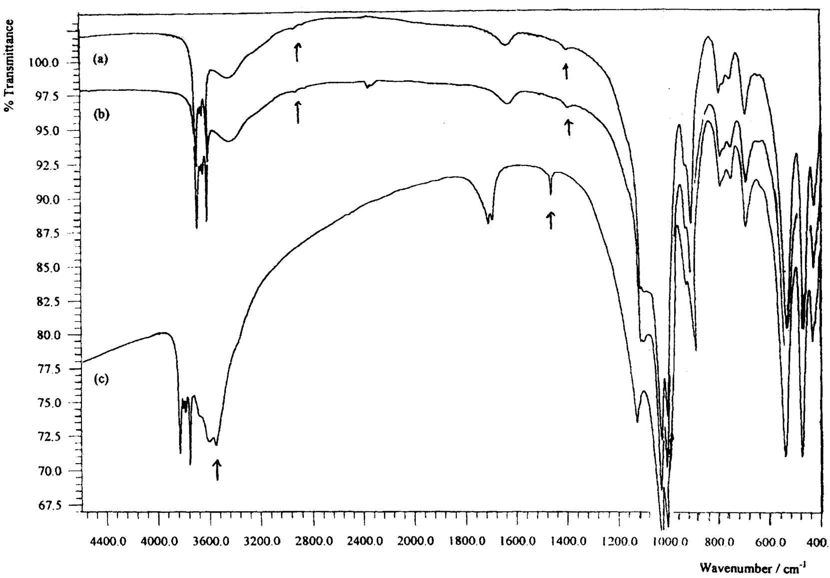

Figure 1. Infrared spectrum of (a) %5, (b) %20 LABS-treated kaolinite and (c) natural kaolinite.

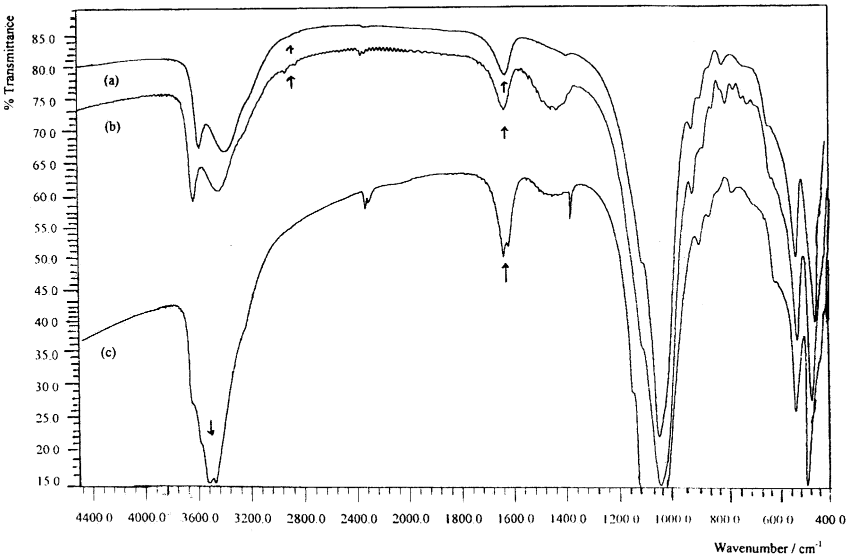

Figure 2. Infrared spectrum of (a) %5, (b) %20 LABS-treated bentonite and (c) natural bentonite.

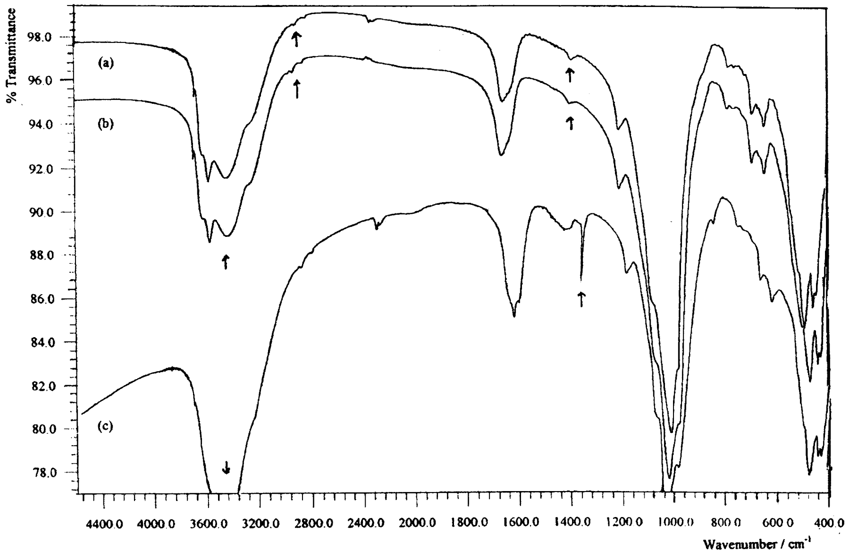

Figure 3. Infrared spectrum of (a) %5, (b) %20 LABS-treated sepiolite and (c) natural sepiolite.

within a high frequency region. The sharp and intense C-H stretching modes at 2928 to 2853 cm^1 of LABS are brought about by interaction with the hydroxyl group of clays. Depending on the increase in the concentration of surfactant, the increase of these stretching modes can be clearly seen in Figs. 1 through 3.

LABS as a result of all these interactions, have been adsorbed to surfaces of clays especially from its broken ends over benzene sulphonate. Adsorbed LABS are H-bonded to Si-OH surface groups from sulphur atoms in sepiolite and they are coordinated to exchangeable cations as ligands in kaolinite and bentonite.

DDAC-Clay Interactions

The IR spectra of DDAC treated kaolinite, bentonite and sepiolite are illustrated in Figs. 4 through 6. DDAC-clay interactions similar to LABS-Clay and the CH_2 bending modes have been observed at 2385–1487 cm^{-1}of DDAC. The intensity of these modes reduced from 1468 to 1449 cm^{-1} in the complexes of DDAC-clay. As a consequence of interaction between the N-C stretching mode at 1628 cm^{-1} of DDAC, and the HOH bending in the clay structure at 1640 to 1620 cm^{-1}, the intensity mode increases by a small

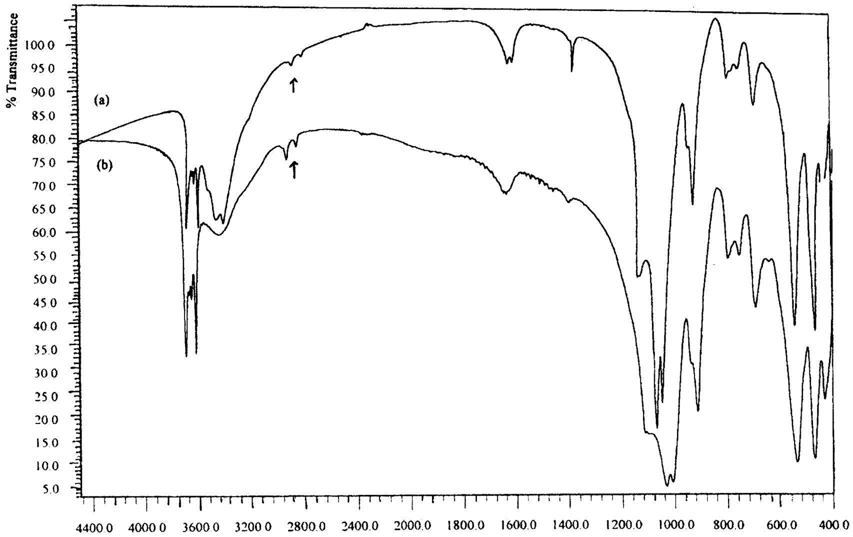

Figure 4. Infrared spectrum of (a) %5, (b) %20 DDAC-treated kaolinite.

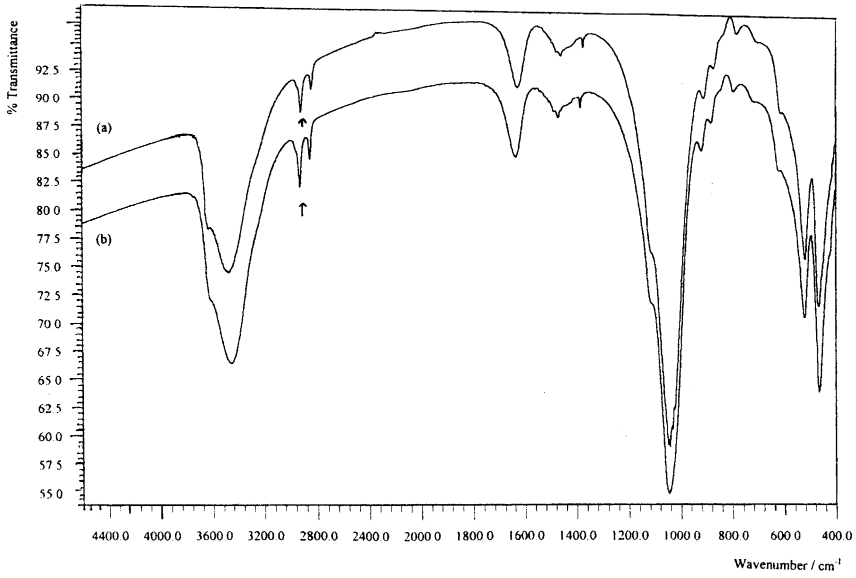

Figure 5. Infrared spectrum of (a) %5, (b) %20 DDAC-treated bentonite.

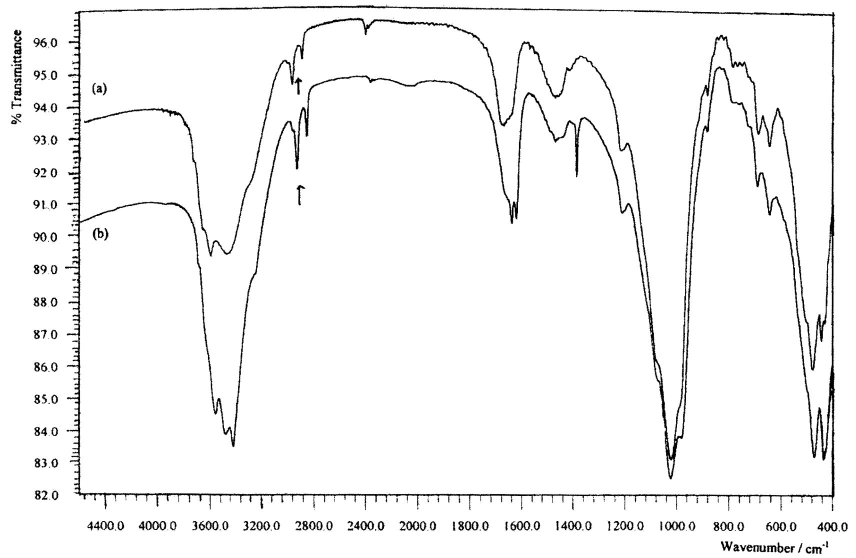

Figure 6. Infrared spectrum of (a) %5, (b) %20 DDAC-treated sepiolite.

amount. Structural hydroxyl stretching modes at 3600 cm^{-1}, which are similar to those obtained for LABS have been adsorbed, and due to this interaction the sharp and intense C-H stretching modes at 2955 to 2850 cm^{1} of DDAC show a weak band appearance. We have concluded that the hydroxyl group in the structure of clay must have had a effect on this appearance (see Figs. 4 through 6).

Cationic DDAC has been adsorbed on clays surfaces due to excess negative charge with the H-bond (sepiolite) to surface Si-OH groups from nitrogen atoms and are coordinated to exchangeable cations as ligands (kaolinite and bentonite).

As a result, we suggest that large amounts of surfactant which pour into receiver waters, could be brought under control in their present situation, thus it may be possible to reduce their harmful effects.

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