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Thermo-IR-spectroscopy study of the mechanochemical adsorption of 3,5-dichlorophenol by TOT swelling clay minerals¹

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Abstract

The mechanochemical adsorption of 3,5-dichlorophenol by laponite, saponite, montmorillonite, beidellite, and vermiculite was studied. Mixtures containing dichlorophenol and clay in the ratio 6:10 were manually ground for 1–10 min. The ground mixtures were then analyzed by thermo-IR-spectroscopy. Depending on the surface acidity of the clay two different associations between interlayer cations, water, and dichlorophenol were identified. In these associations dichlorophenol acts either as a proton acceptor or donor (configurations I and II, respectively). In laponite, montmorillonite and saponite the surface acidity of interlayer water is high; in beidellite and vermiculite it is low. Consequently, mainly configuration I was obtained for the first group of minerals and configuration II for the second group.

Keywords: Clay acidity; Clay minerals; 3,5-Dichlorophenol; Mechanochemical adsorption; Thermo-IR-spectroscopy

1. Introduction

The adsorption of phenol and substituted phenols by clay minerals and other soil components is an important environmental problem [1]. This process may slow down the migration of these hazardous chemicals in soils and sediments. Clay minerals also have good potential for use as adsorbing agents in cleaning waste water. Most previous publications on the adsorption of phenol and substituted phenols by soils or soil

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¹ Dedicated to Takeo Ozawa on the Occasion of his 65th Birthday.

components have dealt with adsorption isotherms and were related to (1) soil pH, (2) the pK_a of the phenol, and (3) the effect of the solvent or mixtures of solvents from which the adsorption took place [2–4]. The adsorption of substituted phenols by organo-clay was also investigated [5–7].

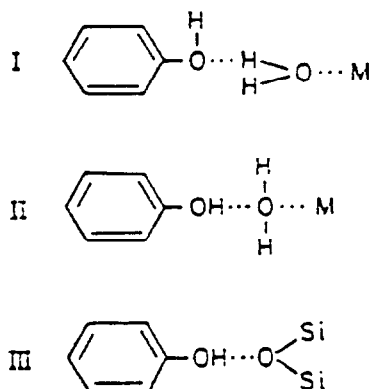
In the present paper we describe a thermo-IR-spectroscopy and X-ray study of the adsorption of 3,5-dichlorophenol (3,5DCP) by different swelling TOT clay minerals. The study was carried out in order to obtain information on the effect of surface basicity of the clay mineral on the fine-structure of the organo-clay complexes which are obtained during the adsorption process.

In the present study adsorption was effected by a mechanochemical technique. In this technique mixtures containing a volatile organic solid compound and a clay sample are ground together for different times. The ground mixtures are pressed into disks with KBr. These disks contain excess free organic compound. They are left for several days in a vacuum furnace at 115°C and the excess organic compound is evolved.

The fine-structures of complexes of nonsubstituted phenol in different expanding clay minerals have previously been investigated by thermo-IR-spectroscopy which seems to be a useful tool for the study of fine-structures of organo-clay complexes [8]. However, this technique requires that considerable amounts of the organic compound be adsorbed by the substrate. Preliminary experiments showed that when the adsorption of 3,5DCP was carried out from an organic solvent (hexane or cyclohexane) six months had to pass before the adsorbed amount was sufficient for the spectroscopic study.

Fenn and Mortland [9] studied complexes of hectorite saturated with different cations by allowing the phenol to be adsorbed from the vapor phase. The only direct phenol-cation interaction occurred with Cu- and Ag-hectorites. With other inorganic cations, hydrogen bonding through water bridges to exchangeable cations and weak π electron interactions with the silicate framework were observed. Saltzman and Yariv [10] studied the complexes which were obtained in montmorillonite when phenol was adsorbed from a CCl_4 solution. They showed that phenol behaves like an amphiprotic molecule, both donating and accepting protons. The following configurations were inferred for the phenolic group in the interlayer space where M is the exchangeable inorganic cation and O of the Si–O–Si group is an atom belonging to the oxygen plane of the tetrahedral sheet (Scheme 1).

Recently Ovadyahu et al. [11] studied the adsorption of phenol by beidellite, montmorillonite, saponite, laponite, vermiculite, and exfoliated vermiculite by using mechanochemical techniques. They showed that with this technique adsorption was very fast. The amount of phenol which was adsorbed depended on the time of grinding. With most clays it increased in the first 5 min and decreased after longer grinding. The type of association depended on the clay and the time of grinding. In most cases Configuration II predominated. In this configuration the phenol donates a proton to a water molecule, thus revealing its acidic properties. With beidellite and montmorillonite configuration I predominated after 1-min grinding. In this association the phenol accepts a proton from the water molecule and the benzene ring becomes slightly positive. Thus it may form π interactions with the oxygen plane of TOT clays with tetrahedral substitution [12,13]. In vermiculite, both configurations were detected after



Scheme 1. Arrangement of phenol in the interlayer space of montmorillonite.

1-min grinding. Longer grinding resulted in extremely high adsorption but mainly of configuration II.

In the present paper we describe the IR spectra of the 3,5DCP complexes which were obtained with beidellite, montmorillonite, saponite, laponite, vermiculite, and exfoliated vermiculite. The features of these spectra are compared with those of nonsubstituted phenol, and possible configurations of the different complexes (which are obtained in the interlayer space) are suggested.

2. Experimental

2.1. Materials

3,5DCP was supplied by Fluka. Laponite XLG (a synthetic Na-hectorite) was kindly donated by Laporte Industries, Inc. (UK). Wyoming bentonite (Na-montmorillonite) was supplied by Wards Natural Science Establishment, Inc. Saponite from California (Ca clay) and beidellite from California (Ca clay) were supplied by Source Clay Minerals Repository, Columbia, Missouri, USA. Vermiculite from Palabora Mining, South Africa and exfoliated vermiculite obtained from Habonim Industries, Israel, were kindly donated by Professor Israel Lin from the Department of Mineral Engineering (The Technion, Haifa, Israel).

2.2. Methods

Mixtures containing 30 mg of 3,5DCP and 50 mg of clay were manually ground with a mortar and pestle for different times (1,3,5, and 10 min); the ground mixtures were investigated by IR spectroscopy and X-ray diffraction.

2.3. Infrared spectra

Infrared spectra were recorded in KBr disks by means of a Nicolet FTIR spectrophotometer. Each disk was prepared by careful abrasion of the KBr (150 mg) with the ground phenol–clay mixture (3 mg). After pressing the disk, it was gently reground for a few seconds and repressed. In order to obtain reliable and reproducible IR spectra, the second preparation of the disk was essential. The regrinding process may have minor effects on the mechanochemical adsorption process, however; since our study was carried out by comparing the results obtained after different grinding periods, we assume that the small mechanochemical changes occurring during the preparation of the disks were equal in all samples and could, therefore, be neglected.

Spectra recorded immediately after the preparation of the disks showed the presence of excess free 3,5DCP. The disks were left for one week in a vacuum furnace at 115°C and the excess 3,5DCP was evolved. To prove this assumption, a KBr disk of neat 3,5DCP was prepared, reground and repressed under the same conditions. After similar thermal treatment at 115°C the IR spectrum showed that all the DCP had escaped from the disk.

2.4. X-ray diffractograms

X-ray analysis was carried out by means of a Philips Automatic Powder Diffractometer (PW 1710) with a Cu tube anode. Powder samples were placed in an aluminum sample holder in order to obtain diffractograms of similar amounts of sample.

3. Results

All the clay samples adsorbed 3,5DCP when they were ground with this compound. However, the adsorption of this phenol is very small, in contrast with the relatively great adsorption of the nonsubstituted phenol. The greatest amounts were adsorbed by laponite.

3.1. IR spectra

The OH stretching band is located at 3607 cm^{-1} (free OH) or 3250 cm^{-1} (intermolecular H-bonded) in the spectra of a dilute Nujol mull or a KBr disk of 3,5DCP, respectively. In this region the clay interlayer water absorbs IR radiation and it is not possible to detect the OH stretching band of the phenol in the spectra of the organo–clay complexes.

Two bands in the spectrum of neat 3,5DCP at 1101 and 1091 cm^{-1} are attributed to Ar–Cl [14]. It is not possible to detect these bands after adsorption because they overlap the Si–O stretching bands of the clay frameworks. Consequently, in the present study we could not obtain information on the contribution of Cl to the adsorption of this phenol.

The characteristic features of the spectrum of 3,5DCP (which may supply information on the adsorption of this molecule by the different clay minerals) appear in the region $1700\text{--}1150\text{ cm}^{-1}$. Fig. 1-4 show representative spectra of phenol–clay com-

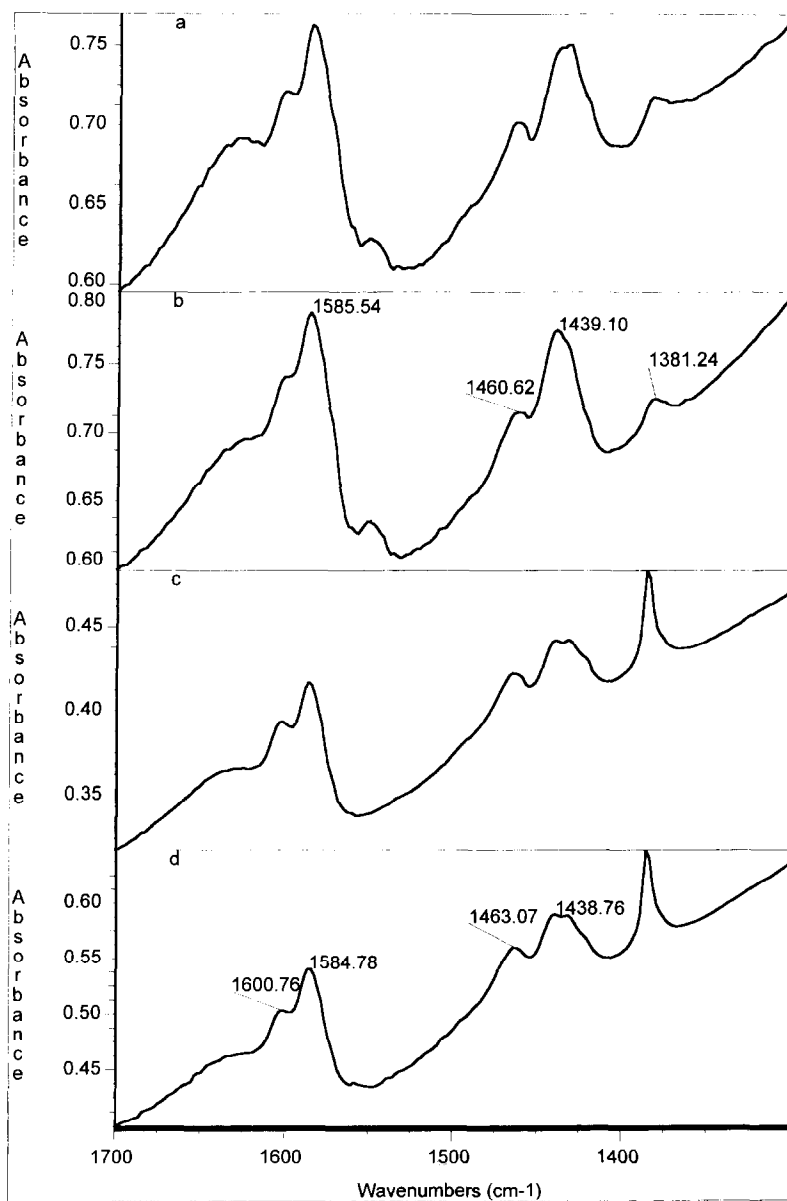


Fig. 1. Infrared spectra of 3,5DCP adsorbed by trioctahedral smectites: laponite, (a) 1-min grinding; (b) 5-min grinding, and saponite (c) 1-min grinding; (d) 5-min grinding.

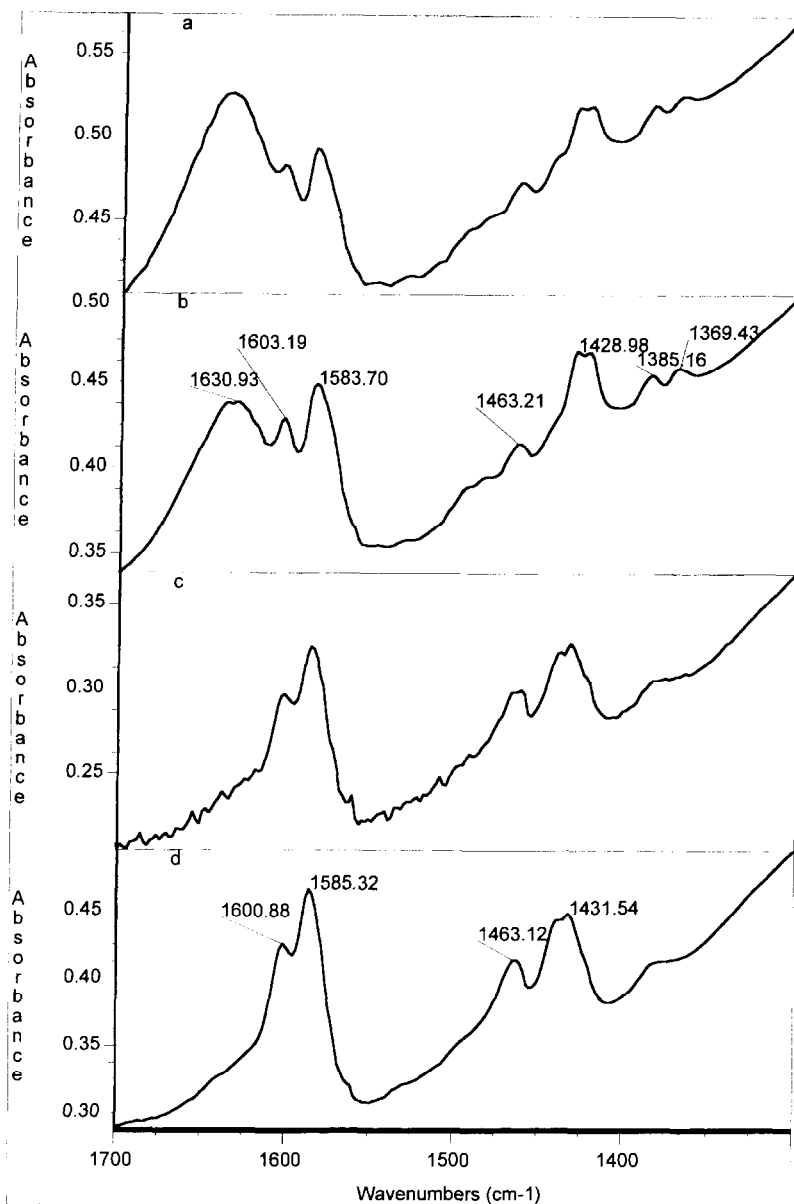


Fig. 2. Infrared spectra of 3,5DCP adsorbed by dioctahedral smectites: beidellite, (a) 1-min grinding; (b) 10-min grinding, and montmorillonite (c) 3-min grinding; (d) 5-min grinding.

plexes which were obtained during different grinding periods, after heating the disks at 115°C.

In most cases any effects of grinding on the shape or intensity of the absorption bands were not identified. In the case of the untreated Palabora vermiculite, the time of grinding affected the amounts which were adsorbed by this clay. On the other hand,

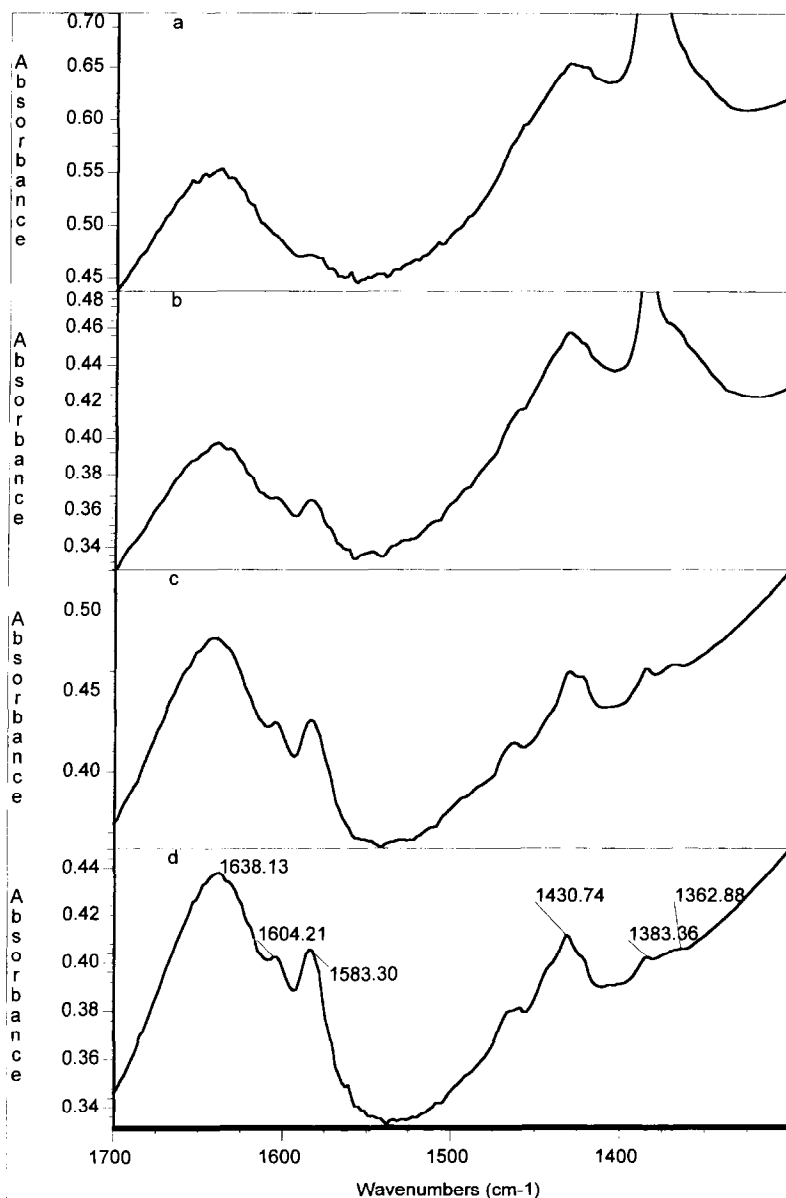


Fig. 3. Infrared spectra of 3,5DCP adsorbed by vermiculite: natural vermiculite, (a) 1-min grinding; (b) 10-min grinding, and exfoliated vermiculite (c) 1-min grinding; (d) 10-min grinding.

adsorption by the exfoliated vermiculite was not affected by the time of grinding (Fig. 3).

The adsorbed 3,5DCP replaces interlayer water. The water band at 1630 cm^{-1} , although it become small, persisted in all the samples. Beidellite and both vermiculites

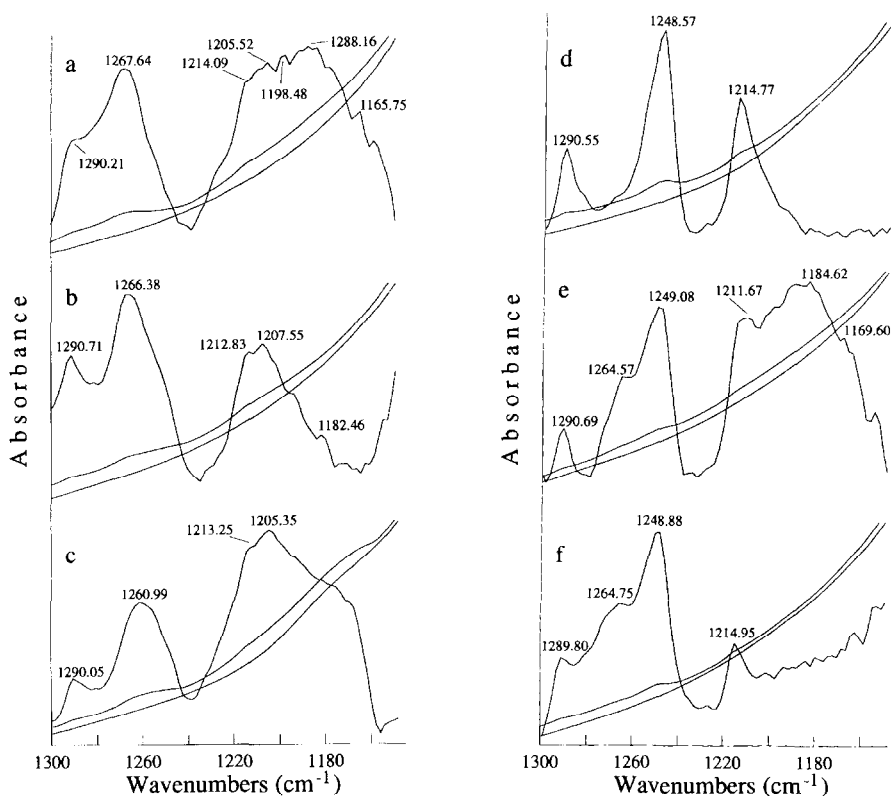


Fig. 4. Comparative infrared spectra of 3,5DCP adsorbed by different clays. The spectra of untreated clays are subtracted from the spectra of the treated clays, (a) laponite, 5-min grinding; (b) saponite, 5-min grinding; (c) montmorillonite, 5-min grinding; (d) beidellite, 10-min grinding; (e) untreated vermiculite, 10-min grinding; (f) exfoliated vermiculite, 1-min grinding. The figure also shows IR spectra of untreated clays (lower curves) and of treated clays (upper curves).

retained more water than the other clays. Table 1 shows that the locations of the ring vibrations at 1463 cm^{-1} and 1585 cm^{-1} were not affected by the type of clay. As well, the shape of the 1585 cm^{-1} band in the spectra of the clay complexes was similar to that in the spectrum of the Nujol mull. On the other hand, this band is very broad in the spectrum of the KBr disk. The KBr disk of 3,5DCP shows a broad band at 1493 cm^{-1} . This band does not appear in the spectrum of the dilute Nujol mull but is small when the Nujol mull is more concentrated. It did not appear in the spectra of the organo-clay samples.

These observations may indicate that 3,5DCP does not form π interactions with any of the clays which were investigated in this study. It should be mentioned that nonsubstituted phenol formed π interactions with the oxygen planes of beidellite, montmorillonite and also, in part, with vermiculite. This was deduced from the fading of the band at 1600 cm^{-1} and the shift of the 1470 cm^{-1} band. Both are ring vibrations

Table 1
Infrared absorption bands (in cm^{-1}) of 3,5-dichlorophenol in Nujol, in a KBr disk, and adsorbed by different clay minerals.

Band assignment	Nujol (dilute mull)	KBr disk	Clay minerals ^a					
			Laponite	Saponite	Montmorillonite	Beidellite	Vermiculite 1	Vermiculite 2
Ring vibrations	1600 1585	1602 1583	1601 1585	1601 1585	1604 1585	1604 1584	1604 1584	1604 1584
OH deformation (1 min grinding) (10 min grinding)	— 1427 ^b	— 1427–1419	— 1433	— 1431	— 1431	— 1422	— 1428	— 1422
Combinational band	—	—	—	—	—	—	—	—
C–OH	1381 ^c	1387	1381	—	—	1385	—	1384
CH in-plane deformation	—	1367	—	—	—	1369	—	1363
	1290 ^b	1290	1290	1290	1290	1290	1291	1290
	—	—	1268	1266	1261	—	1265	1265
	1254 ^{b,c}	1246	—	—	—	1249	1249	1249
	—	—	1199	1208	1205	—	—	—
	1168 ^b	—	1188	1182	1182	—	1285	—
	1214	1214	1214	1213	1213	1215	1212	1215

^aVermiculite 1 — natural vermiculite; Vermiculite 2 — exfoliated vermiculite.

^bConcentrated mull.

^cDilute mull.

[11]. The slight shift of the 1600 cm^{-1} band to higher frequencies in the present study is because this band is located in the envelope of the water band at 1630 cm^{-1} .

The OH deformation band appears in the spectrum of the dilute Nujol mull at 1381 cm^{-1} and shifts to 1427 cm^{-1} in the more concentrated mull. It is located at $1427\text{--}1419\text{ cm}^{-1}$ in the spectrum of the KBr disk. It is very broad and is accompanied by two medium bands at 1387 cm^{-1} and 1367 cm^{-1} . The different locations of the OH bands are due to different types of hydrogen bond which are obtained in the association of 3,5DCP in the crystalline state. In the spectra of the adsorbed phenol the principal OH deformation band appears at $1422\text{--}1440\text{ cm}^{-1}$ (Table 1). In the spectra of the organo-clays this band shifted to higher frequencies with increasing grinding time. Its location also depended on the type of mineral. Low frequencies were obtained with beidellite, vermiculite, and exfoliated vermiculite, whereas high frequencies were obtained with laponite and saponite. In the case of exfoliated vermiculite and beidellite two very weak bands appeared at 1385 cm^{-1} and 1368 cm^{-1} . Laponite, on the other hand, showed one absorption band at 1380 cm^{-1} . In the spectra of natural vermiculite and saponite there was a sharp band at 1385 cm^{-1} due to an impurity and this region could not be studied.

The absorption of Ar–OH is located in the region $1300\text{--}1150\text{ cm}^{-1}$ in the envelope of the Si–O stretching bands of the clay framework. Fig. 4 shows subtractions of the spectra of the neat clays from the spectra obtained after grinding the clays with 3,5 DCP. In the subtracted spectra two absorption bands could be identified, below and above 1240 cm^{-1} , named here bands A and B, respectively. In the spectra of beidellite both bands A and B were sharp with maxima at 1215 cm^{-1} and 1249 cm^{-1} , respectively. However, the intensity of band B was much greater than that of band A. In the spectra of exfoliated vermiculite band A was very weak, whereas band B was very intense, showing two maxima at 1249 cm^{-1} and 1261 cm^{-1} . In the spectra of laponite, saponite, natural vermiculite and montmorillonite ground with 3,5DCP band A was more intense than band B and was very broad, extending to frequencies below 1205 cm^{-1} . Band B in the spectra of laponite, saponite and montmorillonite showed only one maximum, at 1268 cm^{-1} , 1266 cm^{-1} and 1261 cm^{-1} , respectively. In the spectrum of vermiculite, band B had two maxima located at 1249 cm^{-1} and 1265 cm^{-1} .

3.2. X-ray diffraction

Fig. 5–7 show XRD curves of untreated laponite, beidellite and exfoliated vermiculite and of the same clays after grinding with 3,5DCP. In the diffractograms of laponite there is a very broad 001 peak extending between a 2θ angle of $<4^\circ$ and 9° , indicating that the samples were inhomogeneous and randomly interstratified. The peak maximum in the curve of untreated laponite was located at 1.30 nm and shifted slightly to 1.38 nm as a result of adsorbing 3,5DCP. The shape of the peak also changed. It first became sharper but after 10-min grinding was very broad. From the change in the shape of this peak we concluded that the phenol was adsorbed into the interlayer space of the laponite.

In the diffractograms of the other untreated clays and of the same clays ground with phenol for different periods, the 001 peak were sharper than in those of laponite,

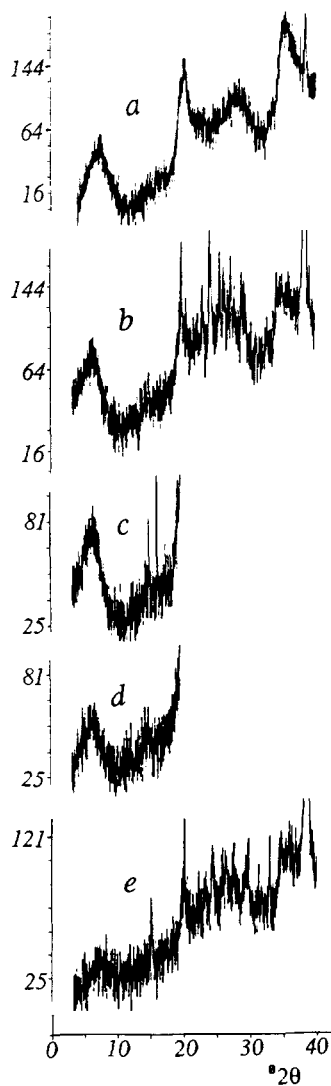


Fig. 5. X-ray diffractograms of (a) untreated laponite and of laponite ground with 3,5DCP (b–e) for 1, 3, 5, and 10 min.

indicating that the samples were relatively homogeneous and better oriented. The peak maxima shifted slightly in all samples to higher spacings as a result of adsorbing 3,5DCP. For example, this peak shifted from 1.16 nm and 1.49 nm in the diffractograms of the untreated exfoliated vermiculite and beidellite to 1.21 and 1.55 nm, respectively, after 1-min grinding with DCP. After 10-min grinding these peaks became very broad, indicating that the samples had become inhomogeneous.

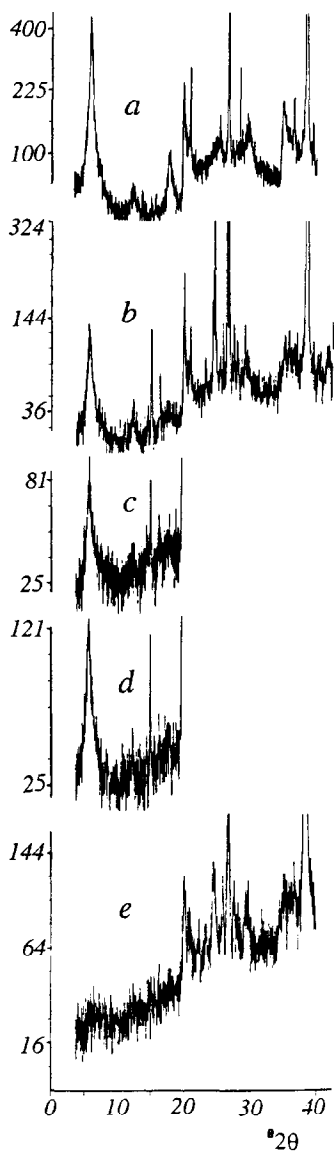


Fig. 6. X-ray diffractograms of (a) untreated beidellite and of beidellite ground with 3,5DCP (b–e) for 1, 3, 5, and 10 min.

Diffractograms were recorded up to $2\theta \approx 40^\circ$. The presence of non-adsorbed 3,5DCP was identified from its characteristic peaks. All samples, including those which were ground for 10 min contained considerable amounts of phenol. The intensities of these peaks decreased with increasing grinding time.

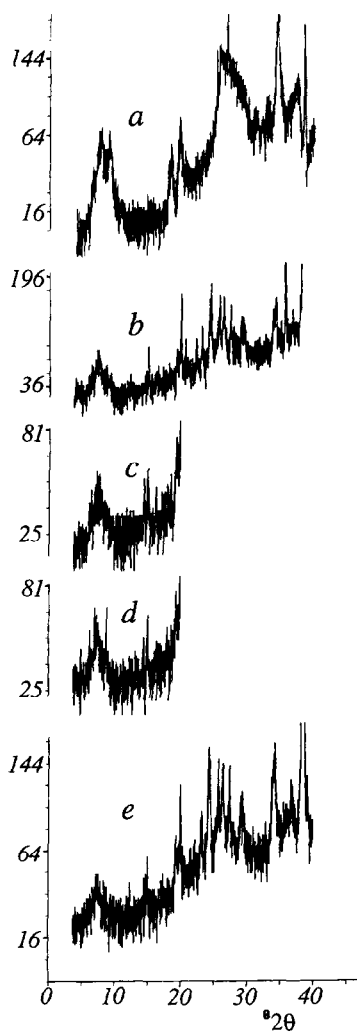


Fig. 7. X-ray diffractograms of (a) exfoliated vermiculite and of exfoliated vermiculite ground with 3,5DCP (b–e) for 1,3,5, and 10 min.

The hkl reflections of the different clay minerals persisted during the grinding, indicating that the minerals were not destroyed during the mechanochemical treatment, even after 10 min, although the 001 peaks became very broad.

4. Discussion

The location of the Ar–OH stretching vibration depends on whether the phenol group accepts or donates a proton. If it accepts a proton (Configuration I), the

double-bond character of the Ar–OH group decreases and the absorption should shift to lower frequencies. If the phenol group donates a proton (Configurations II and III) the double bond character of this group increases and the absorption shifts to higher frequencies.

Bands A and B provided information on the fine structures of the associations which were formed in the interlayer space. Band A has the contributions of the C–H in-plane deformation vibration at 1215 cm^{-1} and that of Ar–OH stretching vibration of Configuration I. This band is intense and extends to frequencies below 1205 cm^{-1} in the spectra of 3,5DCP complexes of laponite, montmorillonite, and natural vermiculite. It is therefore concluded that these clays mainly form Configuration I.

Band B represents the Ar–OH stretching vibration of Configurations II and III. This band was intense in the spectra of beidellite and exfoliated vermiculite. It is, therefore, concluded that these clay mainly formed Configurations II and/or III. Since these spectra showed intense water bands, we believe that Configuration II was the main product. In the spectra of laponite, natural vermiculite, and montmorillonite band B was also present but weak, indicating that Configuration II was formed in small amounts. In the spectra of saponite both A and B bands appeared with approximately the same intensity, indicating that both configurations were present in approximately equal amounts.

The location of band B depends on the strength of the hydrogen bonds which are formed between the phenolic OH and the water molecules.

Beidellite, vermiculite, and exfoliated vermiculite gain their charge from tetrahedral substitution and their oxygen planes serve as electron-pair donors [13]. Interlayer water molecules are hydrogen-bonded to these oxygens, in addition to ion–dipole interactions between these water molecules and the exchangeable metallic cations [15]. Consequently, the degree of freedom of water molecules in beidellite and vermiculite is smaller than that of water molecules in the other clays. The band at 1249 cm^{-1} represents weak hydrogen bonds, whereas those at 1260 cm^{-1} and 1267 cm^{-1} represent stronger hydrogen bonds. Beidellite shows only the 1249 cm^{-1} band. Exfoliated vermiculite shows bands at 1249 cm^{-1} and 1265 cm^{-1} . These two minerals, which have the highest surface basicity, form mainly Configuration II. The other clays have a lower surface basicity and they form mainly Configuration I. The small amounts of 3,5DCP which formed Configuration II, absorb at 1260 cm^{-1} or 1267 cm^{-1} .

5. Conclusions

In the adsorption of 3,5DCP by TOT swelling clay minerals the phenol reacts either as a proton acceptor, giving rise to Configuration I, or as a proton donor, giving rise to configuration II. In contrast to the nonsubstituted phenol, the 3,5DCP does not form π interactions with the oxygen planes of beidellite, montmorillonite, or vermiculite. Consequently, the mechanism of adsorption of 3,5DCP is not affected by the ability of aromatic rings to interact with the oxygen plane. As well, in contrast to the adsorption of the nonsubstituted phenol, the adsorption of 3,5DCP is not affected by the time of grinding. It depends on the acid strength of the interlayer water.

From all the clays which were studied here, beidellite and vermiculite have the highest basic strength [11]. When these minerals adsorb 3,5DCP, mainly Configuration II is obtained. Interlayer water molecules of the other clays are highly acidic and consequently, Configuration I is the principal product when 3,5DCP is adsorbed by these minerals. However, because 3,5DCP is an acid, Configuration II is also obtained to some extent.

Laponite is the most acidic clay among all the clays which were studied here and adsorbs the largest amounts of 3,5DCP. This mineral also adsorbs the largest amount of nonsubstituted phenol when mechanochemical techniques are used.

Acknowledgments

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