



Interaction of Montmorillonite with Maltol

V. LUPTÁKOVÁ

Faculty of Natural Sciences Comenius University, Mlynská dolina, 842 15 Bratislava, Slovakia

J. SITEK and I. TÓTH

Faculty of Electrical Engineering and Information Technology, Slovak Technical University, Ilkovičova 3, 812 19 Bratislava, Slovakia

(Received: 6 March 1998; in final form: 13 July 1998)

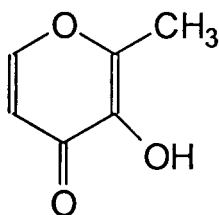
Abstract. The sorption of maltol (3-hydroxy-2-methyl-4-pyrone) by Fe-montmorillonite from aqueous solutions is pH dependent. IR and Mössbauer spectroscopy indicate bonding of maltol oxygen ligands to the interlayer Fe(III). Simultaneously maltol releases part of the Fe(III) into the solution. The interaction of the Fe-maltolato complex with Na-montmorillonite occurs by ion exchange.

Key words: montmorillonite, maltol, sorption, infra-red spectroscopy, Mössbauer spectroscopy

1. Introduction

Clay minerals such as montmorillonite are layered aluminosilicates which are known for their ability to interact with various inorganic and organic compounds and thus markedly change their properties.

Maltol (3-hydroxy-2-methyl-4-pyrone) is a natural heterocyclic compound which forms coordination compounds with various metal ions [1–3]. It is found in pine-needles, is created in the production of malt and by decomposition of cellulose. Maltol is a bidentate (O,O) monobasic ligand which has the ability to form complexes of moderate lipophilicity and hydrophilicity.



Maltol

On the other hand iron is an important element in inorganic chemistry, mineralogy, biology and technology. Its coordination chemistry is dominated by ligands

Table I. Sorption of maltol by Fe-montmorillonite

| Sample | c(ML) (mol dm ⁻³) | pH | ML _{ads} (mmol g ⁻¹) | Fe _{rel} (mmol g ⁻¹) | Fe _{MMT} (mmol g ⁻¹) | d ₀₀₁ (nm) |
|--------|----------------------------------|------|--|--|--|--------------------------|
| Fe-MMT | – | – | – | – | 1.21 | 1.55 |
| 1 | 0.01 | 3.00 | 0.61 | 0.47 | 0.74 | 1.42 |
| 2 | 0.02 | 3.00 | 0.72 | 0.52 | 0.69 | 1.48 |
| 3 | 0.03 | 3.06 | 0.46 | 0.67 | 0.54 | 1.37 |
| 4 | 0.06 | 3.00 | 0.43 | 0.70 | 0.51 | 1.37 |
| 5 | 0.06 | 9.40 | Traces | 0.38 | 0.83 | 1.24 |
| 6 | 0.06 | 9.50 | Traces | 0.36 | 0.85 | 1.26 |

that are O-atom donors. Maltol and its complexes with Fe(III) are almost redox stable because they undergo photoredox reactions with the lowest efficiency [4].

The aim of this study is to describe the interaction between montmorillonite, Fe(III) and maltol. All mentioned substances occur in nature but derivatives of pyrone are used in agriculture as pesticides and sorption complexes with Fe(III) and montmorillonite may be formed in soils.

2. Experimental

Montmorillonite (MMT) from Jelšovský Potok (Slovakia) was used [5] in this study. A powder grain fraction of size less than 2 μm was obtained by sedimentation. The chemical composition of montmorillonite was (in wt %): SiO₂, 62.66; Al₂O₃, 20.52; Fe₂O₃, 2.35; TiO₂, 0.12; CaO, 2.44; MgO, 4.21; K₂O, 0.1; Na₂O, 0.6; MnO, 0.02; H₂O, 14.73.

Na⁺ and Fe³⁺ exchanged samples were prepared by repeated immersion of the clay in a 0.1 M solution of the corresponding metal chloride. For the preparation of Fe-montmorillonite a partially hydrolysed solution (pH = 2.5) containing polymeric hydroxy-Fe(III) cations was used [6, 7]. Excess salt was removed with deionized water until the Cl⁻ test was negative. The cation exchange capacity of Na-montmorillonite determined following literature methods [8] was 1.01 mmol/g. The content of the interlayer Fe(III) in Fe-montmorillonite was 1.21 mmol/g. Maltol (ML) was supplied by Aldrich and the other chemicals of analytical grade by Lachema.

The sorption of maltol by Fe-montmorillonite was realised by mixing of an aqueous solution of maltol and 1 g of montmorillonite suspended in distilled water. The total volume of this suspension was 100 mL (samples 1–4) or 150 mL (samples 5 and 6). The concentration of maltol in the suspensions is given in Table I. The pH values were adjusted with 1 M HNO₃ or NaOH (sample 5) or tetramethylammonium hydroxide (sample 6).

Table II. Mössbauer parameters of Fe-montmorillonite after sorption of maltol

| Sample | Outer | | | Inner | | | χ^2 |
|--------|-----------------------------|-----------------------------|-----------------------|-----------------------------|-----------------------------|-----------------------|----------|
| | IS (mm s ⁻¹) | QS (mm s ⁻¹) | A _{rel} % | IS (mm s ⁻¹) | QS (mm s ⁻¹) | A _{rel} % | |
| Fe-MMT | 0.35 | 0.93 | 50 | 0.36 | 0.57 | 50 | 513 |
| 1 | 0.38 | 1.33 | 56 | 0.35 | 0.64 | 44 | 536 |
| 2 | 0.31 | 1.26 | 54 | 0.35 | 0.64 | 46 | 578 |
| 3 | 0.32 | 1.22 | 52 | 0.35 | 0.65 | 48 | 572 |
| 4 | 0.31 | 1.18 | 52 | 0.35 | 0.63 | 48 | 570 |
| 5 | 0.34 | 0.82 | 56 | 0.35 | 0.56 | 44 | 520 |
| 6 | 0.35 | 0.79 | 56 | 0.35 | 0.56 | 44 | 522 |

IS is given relative to Fe metal; A_{rel} is relative amount of Fe corresponding to outer and inner components.

The sorption of the maltolate Fe(III) complex (samples 7–9) was realised by mixing 150 mL of its solutions with 50 mL of a 2% suspension of Na-montmorillonite. Solutions of the Fe complex were prepared by a subsequent dissolution of maltol (1.5–4.5 mmol) and Fe(NO₃)₃·9H₂O (1.5 mmol). The pH was adjusted with 1 M HNO₃ or NaOH. The suspensions were stirred for 3 hours and were centrifuged after 24 hours, washed with 200 mL H₂O and dried at 40 °C.

The amount of Fe(III) was determined from the difference between the initial and final concentration of Fe(III) in solution by a titrimetric method [9]. The Fe(III) content of the Fe-maltolato-montmorillonites was determined by acid decomposition. The maltol content was estimated by elemental analysis on a CHN analyser (Carlo Erba).

The infra-red spectra in nujol mulls and KBr pellets were recorded on a Nicolet 750 Magna spectrometer. The basal distances were recorded with a Philips PW 1050 X-ray diffractometer.

Mössbauer spectroscopy was carried out at room temperature in transmission geometry using a constant acceleration spectrometer and a ⁵⁷Co source in a Rh matrix. The activity of the source was approximately 1.5 × 10³ MBq. The absorber was prepared in powder form. The spectra were collected with a count of 4 mill. imp./channel. The Mössbauer spectra were fitted with the NORMOS programs [10]. The goodness of the fit, χ^2 , are given in Tables II and IV.

3. Results and Discussion

During the study of the interaction of maltol we focused our attention on the conditions by which maltol is bonded to Fe(III) in the interlayer space of montmorillonite. It is known that depending on the pH value maltol and Fe(III) form the [FeML(H₂O)₄]²⁺, [Fe(ML)₂(H₂O)₂]⁺ or [Fe(ML)₃] complexes in which Fe(III)

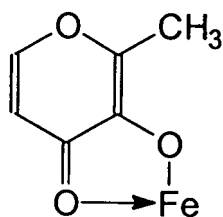
has an octahedral coordination [11, 12]. Two methods for studying the interaction of maltol with montmorillonite were used.

Firstly the sorption of maltol by montmorillonite at pH = 3, which is the existence region of the complex cation $[\text{Fe}(\text{ML})_2(\text{H}_2\text{O})_2]^+$ was studied. Solutions of maltol with Fe-montmorillonite form a dark violet colour suspension. Therefore, after sorption we analysed not only montmorillonite but also the solution. We found that by this interaction as maltol is sorbed in the interlayer space some of the Fe(III) is simultaneously released into the solution (samples 1–4). Values of sorbed maltol (ML_{ads}), released iron (Fe_{rel}) and the amount of interlayer Fe in montmorillonite after sorption (Fe_{MMT}) are given in Table I.

The results show that a higher concentration of maltol does not increase the sorption, as expected, but we observed a decrease of the sorption. The bonding of the maltol in the interlayer space was identified by IR spectroscopy.

The characteristic frequencies of the IR spectra of Fe-montmorillonite, maltol and sample 1 are shown in Figure 1. The assignments follow the works by Katričky and Jones [13, 14] on 4-pyrone and its derivatives and more recent studies on maltolato complexes [2, 3, 12].

The important point is that $\nu(\text{OH})$, found at 3257 cm^{-1} in maltol, is absent in the spectra of all samples. The disappearance of this vibration confirms the deprotonation of the OH groups of maltol and the coordination of the maltolato ligand to Fe(III) via this oxygen atom. The other important feature in the spectra of maltol and its complexes is the set of four bands in the region $1660\text{--}1460\text{ cm}^{-1}$ attributed to mixed C=O and C=C stretching modes of the maltol. This pattern of strong absorptions is retained in the spectrum of the interlayer complex with a significant shift of the order of $50\text{--}60\text{ cm}^{-1}$ in the three higher frequency absorptions. The shifting of the mixed $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{C})$ bands to lower wavenumbers confirms the coordination of maltolato ligand to Fe(III) via the oxygen atom of the carbonyl group [15]. Maltol acts in the interlayer space as a monobasic bidentate (O,O) ligand and dark violet Fe-maltolato-montmorillonites are formed (samples 1–4).



The weakening of the C=O and C=C bonds is associated with electron donation from the ring to the Fe(III) [15]. The other bands in the region $1200\text{--}1400\text{ cm}^{-1}$ are slightly affected by the coordination, but the vibrations of the CH groups, such as $\delta(\text{CH})_{\text{ring}}$ out-of-plane at 851 cm^{-1} are almost unaffected.

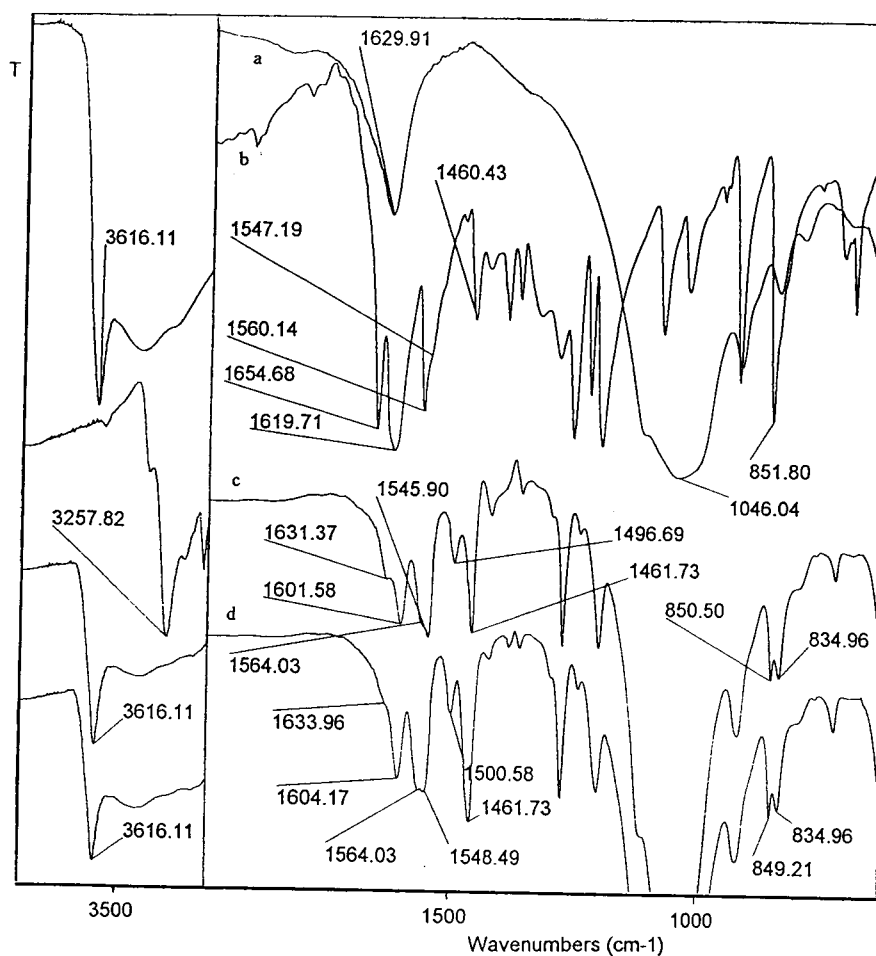


Figure 1. The IR-spectra of (a) Fe-montmorillonite; (b) maltol; (c) Fe(ML)-montmorillonite (sample 1); (d) Fe(ML)-montmorillonite (sample 7).

In the spectra the band at 835 cm^{-1} which can be ascribed to vibrations of Fe—O bonding was present. In the IR spectra of all samples the additional bands at 728 , 430 and 410 cm^{-1} were found. This indicates that part of Fe(III) was hydrolysed and $\text{Fe}(\text{H}_2\text{O},\text{OH})_x$ was probably formed [15–17].

Changes in characteristic montmorillonite bands were not observed. Only the band of sorbed H_2O was found as a weak shoulder at $1631\text{--}1633\text{ cm}^{-1}$ on the band of maltol. This is caused by the partial release of the H_2O molecules from the coordination sphere of the Fe(III) with the organic ligand.

The molar ratio Fe : ML in the interlayer space is approximately 1 : 1. On the basis of the results obtained it can be assumed that maltol is directly coordinated to the interlayer Fe(III) and a monoligand Fe-maltolato complex is formed in the interlayer space although the coordination of two ligands was expected at pH = 3.

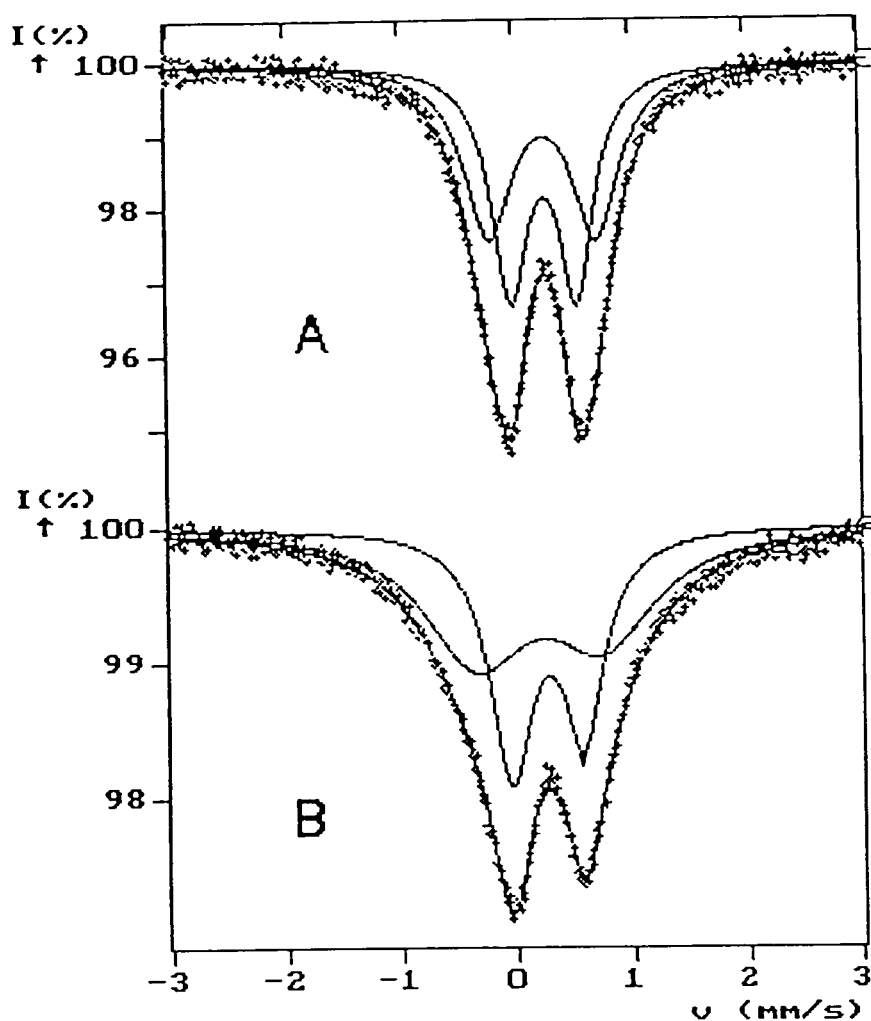


Figure 2. The Mössbauer spectra of (A) Fe-montmorillonite and (B) Fe(ML)-montmorillonite (sample 1).

With a view to increase the number of coordinated ligands, the greater volume of the alkaline maltol solution was used for the preparation of samples 5 and 6. In the case of sample 6, the pH was adjusted with organic base to exclude cation exchange of the Fe(III) by the sodium. In alkaline solutions the tris(maltolate)-Fe(III) complex is formed, but under these conditions the maltol is not sorbed.

The Mössbauer spectrum of montmorillonite consists of outer and inner doublets [18]. The doublets correspond to Fe(III) originally present in the octahedral site of montmorillonite. The component corresponding to Fe(II) was not found in the Mössbauer spectra. The Mössbauer parameter is given in Table II. After treatment with maltol the values of the quadrupole splitting (QS) and the isomer shift

Table III. Sorption of Fe-maltolato complex by Na-montmorillonite

| Sample | pH | ML _{ads} (mmol g ⁻¹) | Fe _{ads} (mmol g ⁻¹) | d ₀₀₁ (nm) |
|--------|-----|--|--|--------------------------|
| Na-MMT | – | – | – | 1.49 |
| 7 | 1.8 | 1.12 | 0.89 | 1.52 |
| 8 | 4.9 | 0.15 | 0.41 | 1.25 |
| 9 | 7.9 | 0.09 | 0.10 | 1.26 |

Table IV. Mössbauer parameters after sorption of the Fe-maltolate complex by Na-montmorillonite

| Sample | Outer | | | Inner | | | χ^2 |
|--------|-----------------------------|-----------------------------|-----------------------|-----------------------------|-----------------------------|-----------------------|----------|
| | IS (mm s ⁻¹) | QS (mm s ⁻¹) | A _{rel} % | IS (mm s ⁻¹) | QS (mm s ⁻¹) | A _{rel} % | |
| Na-MMT | 0.37 | 0.92 | 50 | 0.32 | 0.51 | 50 | 520 |
| 7 | 0.35 | 1.23 | 54 | 0.35 | 0.61 | 46 | 566 |
| 8 | 0.36 | 1.20 | 53 | 0.35 | 0.58 | 47 | 522 |
| 9 | 0.34 | 0.85 | 56 | 0.35 | 0.55 | 44 | 530 |

(IS) of the inner doublet remained nearly constant. The increase of the quadrupole splitting and decrease of the isomer shift of the outer doublet indicates that maltol is coordinated to the iron in the interlayer space. Decreasing of sorbed maltol in montmorillonite causes a decrease of the quadrupole splitting and also a slight decrease of the relative area of the outer doublet (samples 1–4). In alkaline conditions, when no maltol is sorbed, the values of the quadrupole splitting were lower than those for the original montmorillonite.

Na-montmorillonite and the Fe-maltolato complex prepared in aqueous solution was also used to study the interaction. The results are given in Table III. In strong acid conditions (pH = 1.8) where the $[\text{FeML}(\text{H}_2\text{O})_4]^{2+}$ complex is present in a solution, an interaction by ion exchange occurs and $\text{FeML}(\text{H}_2\text{O})_x$ montmorillonite is formed (sample 7). The molar ratio Fe : ML of the sample is nearly 1 : 1 and the IR spectrum is almost identical with the spectra of samples 1–4 (Figure 1). Thus, it can be concluded that in the interlayer space of samples 1–4 and 7 the same monoligand Fe(III) is present. In the solution at pH = 4.9 a mixture of the bisligand and trisligand complexes is formed. But the ion exchange under these conditions decreases and the amount of the maltolato complex in the interlayer is low (sample 8). The ion exchange is practically nonexistent at pH = 7.9.

Mössbauer parameters (Table IV) also confirm that the quadrupole splitting of the outer doublet is higher in acid conditions than in alkaline conditions. This means that the maltolato complex is sorbed in the interlayer spaces in acid conditions.

The basal spacings d_{001} of samples 1–4 and 7, in which the maltolato Fe(III) complex was identified, were in the range 1.37–1.52 nm. Comparison with the solution data shows that the interlayer space is determined by the content of the maltolato-Fe complex. There has been no report on the crystal structure of maltol, though the maltolato ligand was found to be quite planar in its complexes [1, 12]. It can be assumed that the heterocyclic ring of the maltol bonded to the Fe(III) is not coplanar with the basal plane of the montmorillonite. Since in the interlayer space the hydrolytic Fe(III) products were also found the orientation of $[\text{FeML}(\text{H}_2\text{O})_x]^{2+}$ cannot be proposed just on the basis of the d_{001} spacings.

Acknowledgements

This work was supported by NATO Linkage grant HTECH.LG95/560 and partly by National grant 1/4286/97.

References

1. M.M. Finnegan, S.J. Rettig, and C. Orvig: *J. Am. Chem. Soc.* **108**, 5033 (1986).
2. H. Luo, S.J. Rettig, and C. Orvig: *Inorg. Chem.* **32**, 4491 (1993).
3. M.M. Finnegan, T.G. Lutz, W.O. Nelson, A. Smith, and C. Orvig: *Inorg. Chem.* **26**, 2171 (1987).
4. J. Šima, B. Chochulová, M. Veverka, J. Makáňová, H. Hajšelová, and A. Bradiaková: *Polish J. Chem.* **67**, 1369 (1993).
5. K. Jesenák and V.Š. Fajnor: *Mineralia Slov.* **27**, 221 (1995).
6. R. Herrera and M. Peech: *Soil Sci. Soc. Am. Proc.* **34**, 740 (1970).
7. T.G. Spiro, S.A. Allerton, J. Renner, A. Terzis, R. Bils, and P. Saltman: *J. Am. Chem. Soc.* **88**, 2721 (1966).
8. W.H. Hendershot and M. Duquette: *Soil Sci. Soc. Am. J.* **50**, 605 (1986).
9. R. Příbyl: *Komplexometrie*, pp.143–149, SNTL Prague (1977).
10. R.A. Brand: *NORMOS Program*, Interval Report, Universität Duisburg (1987).
11. A. Stefanović, J. Havel, and L. Sommer: *Collect. Czech. Chem. Commun.* **12**, 4198 (1968).
12. M.T. Ahmet, C.S. Frampton, and J. Silver: *J. Chem. Soc., Dalton Trans.* 1159 (1988).
13. A.R. Katritzky and R.A. Jones: *J. Chem. Soc.* 2947 (1960).
14. A.R. Katritzky and R.A. Jones: *Spectrochim. Acta* **17**, 64 (1961).
15. T.A. Annan, C. Peppe, and D.G. Tuck: *Can. J. Chem.* **68**, 1598 (1990).
16. L. Heller-Kallai, S. Yariv, and M. Riemer: *Clay Minerals* **10**, 35 (1973).
17. J.E. Amonette and D. Rai: *Clays Clay Minerals* **38**, 129 (1990).
18. V. Luca and C.M. Cardile: *Clays Clay Minerals* **37**, 375 (1989).