

INFRARED SPECTRAL INVESTIGATIONS OF ADSORPTION AND OXIDATION OF N,N-DIMETHYLANILINE BY SEPIOLITE, LOUGHLINITE AND DIATOMITE

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ABSTRACT. The adsorption behaviour of sepiolite, loughlinite (Na-sepiolite) and diatomite for N,N-dimethylaniline (DMA) and its catalytically formed oxidation products are studied using IR spectroscopy. It is found that sepiolite and loughlinite adsorb DMA and then react with it more easily than diatomite. The adsorption capacity sequence of DMA for the minerals studied is sepiolite > loughlinite > diatomite.

I. INTRODUCTION

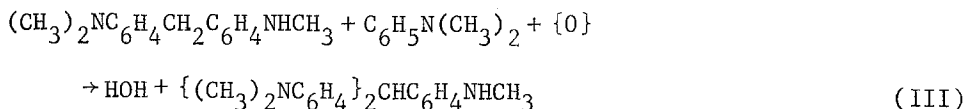
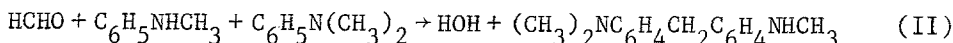
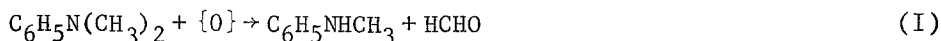
Sepiolite is a hydrated magnesium silicate having an internal structure of channels which can accommodate zeolitic water and other molecules. The magnesium ion in sepiolite crystal is exchangeable with various metal ions(1). Loughlinite has a similar structure to sepiolite and is known as natural Na-sepiolite(2). Sepiolite is an effective catalyst for hydrorefining of hydrocarbons, fuel oils(3) and conversion of ethanol into ethylene or bute-1,3-diene(1).

Diatomite is a siliceous rock made largely from the skeletons of aquatic plants (mainly planktonic) called diatoms. It is used as an absorber of dangerous chemicals in handling and storage, and for the refining of various acids(4).

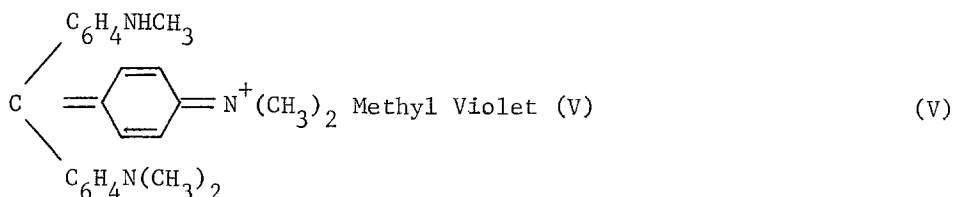
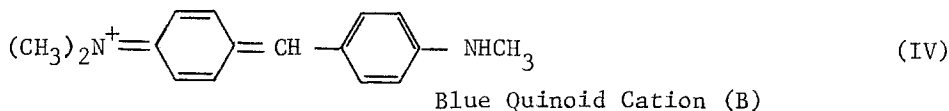
Oxidative properties of clay minerals have been studied previously using simple organic molecules which are absorbed and then react at the surface yielding colored products(5,6).

In this study, the coloration of sepiolite, loughlinite and diatomite by the oxidation products of N,N-dimethylaniline (DMA) have been investigated using IR spectroscopy.

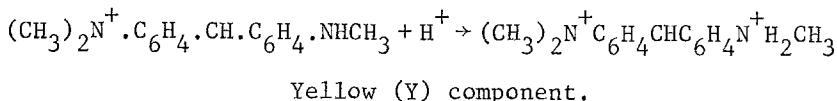
The oxidation of DMA by various oxidation agents (e.g. cupric sulphate) and the formation of methyl violet is a well known process used in the manufacture of the dye. The coloration and oxidation process is described by the following stages(6) : **(a)** sorption of DMA, **(b)** oxidation to N,N-dimethyl-N'-methylbenzidine and bis 4-(N,N-dimethylaminophenyl)-4-(N'methylaminophenyl) methane and **(c)** further oxidation to a blue quinoid cation or its protonated yellow component and finally to methyl violet. The reaction can be formulated as follows :



Further oxidation of (II) and (III) in an acidic environment results in the formation of blue quinoid cation (B or IV) and methyl violet (V), respectively.



Yellow component is formed by protonation of B (IV) species :



In order to verify that the oxidation reaction sequence is also valid for sepiolite, loughlinitite and diatomite, the adsorption of DMA by these minerals have been performed.

2. EXPERIMENTAL

Sepiolite and loughlinitite were obtained from the Mihaliccik region of Eskisehir (Turkey) and diatomite was obtained from the Kızılcahamam region of Ankara(Turkey). The samples were first investigated by X-ray diffraction, differential thermal analysis and elemental analysis. In loughlinitite, analcime and dolomite were detected as significant impurities.

DMA-treated samples were prepared by immersing them in liquid DMA in sealed bottles for different periods of time at room temperature. They were then filtered and washed several times with benzene and dried.

IR spectra of the KBr disks of unwashed and benzene washed samples were recorded on Perkin-Elmer 621 and Nicolet MX-IE spectrometers.

3. RESULTS AND DISCUSSION

All the samples used in the present study were colored by DMA.

In the cases of sepiolite and loughlinite the samples turned to a green color immediately on immersion in liquid DMA. In longer treatments (1 week or more) the color turned to a dark bluish green. Sepiolite was found to be quickly affected by DMA vapour. The sample which was left in the open air near to a DMA bottle which was opened for few seconds also turned to a green color.

The IR spectrum of sepiolite which was treated with DMA for one week at room temperature and then washed with benzene several times is given in figure 1a. We do not observe vibrational bands of DMA(6,7), however we do observe vibrational bands of the V and Y components of the oxidation products of DMA(6). The IR spectrum of the same DMA-treated sepiolite sample, this time unwashed with benzene, is given in figure 1b. When the spectrum is compared with the IR spectra of DMA-treated laponite(6), it is found that the sample contains tetramethylbenzidine (tetrabase, TB) in addition to the V and Y components of the oxidation products of DMA. The IR spectrum of the loughlinite which was treated with DMA for two weeks and then washed with benzene several times is given in figure 1c. The vibrational bands of the V and Y components of the oxidation products of the DMA(6) are observed. We also observe the TB vibrational bands in the IR spectrum of the unwashed sample of the DMA-treated loughlinite.

The reaction of DMA with diatomite is found to be slower than in the cases of sepiolite and loughlinite. Diatomite turns slowly to a light blue color when it is contacted with DMA. If it is left under DMA vapour for a month at room temperature the color gets deeper. Figure 2 shows DMA-treated diatomite which is kept under DMA vapour for a month. We observe only the V component of the oxidation products of DMA. We do not observe any changes in the IR spectrum of DMA-treated diatomite after washing the sample with benzene. It is noted that the V and Y components of the oxidation products of DMA are not desorbed during the washing with benzene but the excess DMA and tetramethylbenzidine (TB) are washed out with benzene. IR spectroscopic analysis shows that sepiolite and loughlinite absorb DMA and then react with it more easily than diatomite. The adsorption capacity sequence of DMA for the minerals studied is found to be sepiolite > loughlinite > diatomite.

4. ACKNOWLEDGEMENTS

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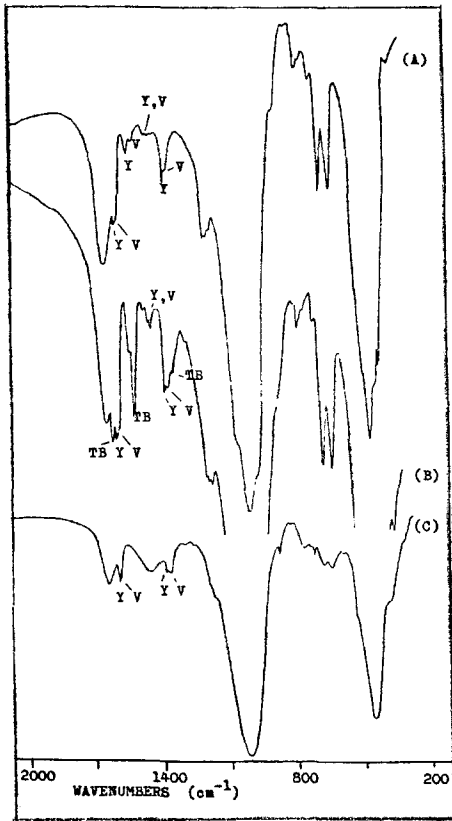


Figure 1. IR spectra of sepiolite and loughlinite samples treated with DMA. (a)(b) Sepiolite treated with DMA for one week, benzene washed (a), and unwashed(b). (c) Loughlinite treated with DMA for two weeks, benzene washed.

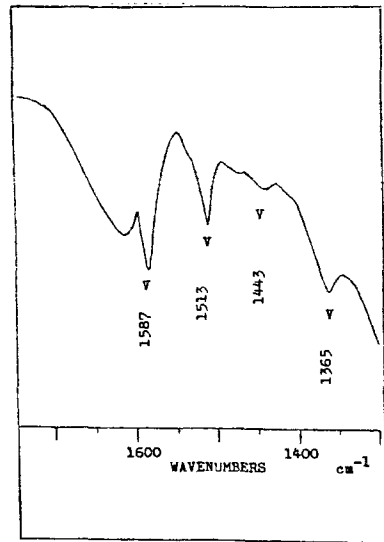


Figure 2. IR spectrum of diatomite treated with DMA for one month.

REFERENCES

1. Y.Kiyatama and A. Michishita, *J.Chem.Soc.Chem.Comm.*, 401-2(1981)
2. W.Echle, *Contrib.Mineral Petrology*, **14**,86(1967).
3. A.J.Dandy and M.S. Nadiye-Tabbiruka, *Clays and Clay Min.*, **30**,347(1982).
4. T.Dickson, *Industrial Minerals*, **141**,33(1979).
5. B.K.G. Theng, *Clay,Clay Min.*, **19**,383(1971).
6. E.F.Vansant and S.Yariv, *J.Chem.Soc.Far.*, **I**,**73**,1815(1977).
7. P.N.Gates, R.A.R.Pearce and K.Radcliffe, *J.Chem.Soc.Perkin Trans.II*, **11**,1607(1972).