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STABILITY OF METHYLENE-BLUE - MONTMORILLONITE IN HCl SOLUTION

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Abstract. The aim of this paper was to investigate the effect of methylene blue adsorbed at the exchange positions of montmorillonite on the solubility of this mineral in HCl solution. Accordingly, 10, 30, 50 and 70 mval of methylene blue/100 g of mineral was introduced into montmorillonite, which was then treated with 1:1 HCl. The reaction products were investigated by X-ray diffractometry, IR spectroscopy and atomic absorption spectroscopy. It was found that the greater the amount of organic cations on the exchange positions of montmorillonite, the lower was its solubility in HCl solution.

INTRODUCTION

The modification of physico-chemical properties of montmorillonite with organic compounds has been the subject of many papers. Several publications have also been concerned with the reactions of montmorillonite with acid solutions. The present author investigated the effect of methylene blue adsorbed in cationic form on montmorillonite on the solubility of this mineral in HCl solution.

EXPERIMENTAL

Investigations were carried out on montmorillonite separated from the Chmielnik bentonite and converted into hydrogen form. The mineral was introduced into methylene blue aqueous solutions containing respectively 10, 30, 50 and 70 mval of dye per 100 g of montmorillonite, and stirred for 3 days. Then the suspensions were centrifuged, washed with distilled water and dried at 60°C. The montmorillonite complexes obtained in this way, as well as untreated H-montmorillonite, were heated in 1:1 HCl solution for 8 hours. Then the samples were centrifuged and washed with distilled water until the reaction for Cl⁻ ion was negative. The solid

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reaction products were subjected to infrared spectroscopic and X-ray investigations whilst the resulting solutions were analysed for Mg, Al and Fe using atomic absorption spectroscopy.

RESULTS

X-ray investigations

In the X-ray diffraction pattern of H-montmorillonite, the 001 reflection corresponds to $d_{001} = 15.9$ (Fig. 1). Upon introducing methylene blue onto the exchange positions, the d_{001} value initially decreases to 15.1 and 14.2 for samples containing 10 and 30 mval of methylene blue per 100 g of montmorillonite, respectively. Further increase in the amount of organic cations on the exchange positions to 50 and 70 mval/100 g of montmorillonite causes the interlayer spacing to expand to 15.8 and 16.9. The values of further $00l$ reflections (Fig. 1) indicate that mixed-layer structures made up of H-montmorillonite and MB*-montmorillonite layers presumably form in samples containing 10 and 30 mval of methylene blue/100 g of montmorillonite. The organic cations are distributed as a single sheet (Pham Thi Hang, Brindley, 1970). In the sample containing 50 mval of methylene blue/100 g of montmorillonite, the series of $00l$ reflections with values of 15.8, 5.28 and 3.16 suggests the presence of two sheets of flat-lying organic cations (Pham Thi Hang, Brindley, 1970). Further introduction of methylene blue onto the exchange positions (70 mval/100 g) does not cause any significant changes in d_{001} values (16.9, 5.30, 3.19).

The X-ray diffraction pattern of montmorillonite heated with 1:1 HCl displays a slight inflection at about $3^\circ \theta$. Moreover, the 110 reflection (4.48) has been found to be considerably less pronounced than for untreated montmorillonite (Fig. 2). These facts testify to intense amorphization of the mineral.

X-ray diffractograms of montmorillonite samples modified with methylene blue and then treated with acid are presented in Fig. 2. In the case of sample containing 10 mval of organic cations per 100 g of montmorillonite, the intensity of basal and general (110) reflections is markedly higher than in the powder pattern of initial montmorillonite treated with HCl. The former reflection for samples containing 10, 30, 50 and 70 mval of methylene blue/100 g of montmorillonite corresponds respectively to values $d = 13.7, 13.4, 13.6$ and 13.8 . The intensity of basal and general (110) reflections increases with the increasing content of methylene blue (Fig. 2).

Infrared spectroscopic investigations

Infrared spectra of H-montmorillonite show absorption bands associated with AlMgOH (850 cm^{-1}) and AlAlOH (930 cm^{-1}) bending vibrations, and OH stretching vibrations of adsorbed water molecules (3430 cm^{-1}) and OH structural groups (3630 cm^{-1}). The intense absorption at 1635 cm^{-1} corresponds to bending vibrations of water molecules. The weak absorption bands at 810 and 3750 cm^{-1} testify to the presence of a trace admixture of amorphous substance of the silica gel type (Fig. 3).

The infrared spectrum of montmorillonite containing 10 mval of methylene

* MB - methylene blue.

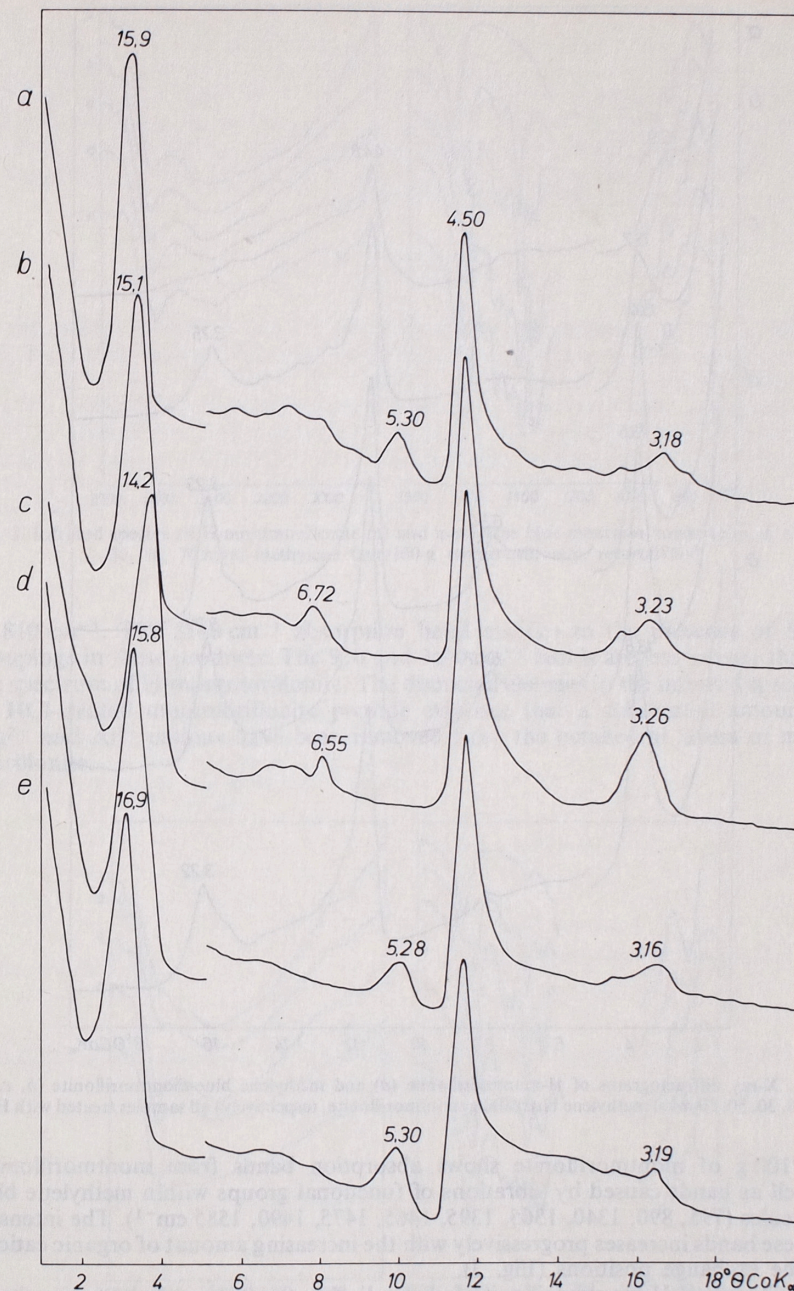


Fig. 1. X-ray diffractograms of H-montmorillonite (a) and methylene blue-montmorillonite (b, c, d, e - 10, 30, 50, 70 mval methylene blue/100 g montmorillonite, respectively)

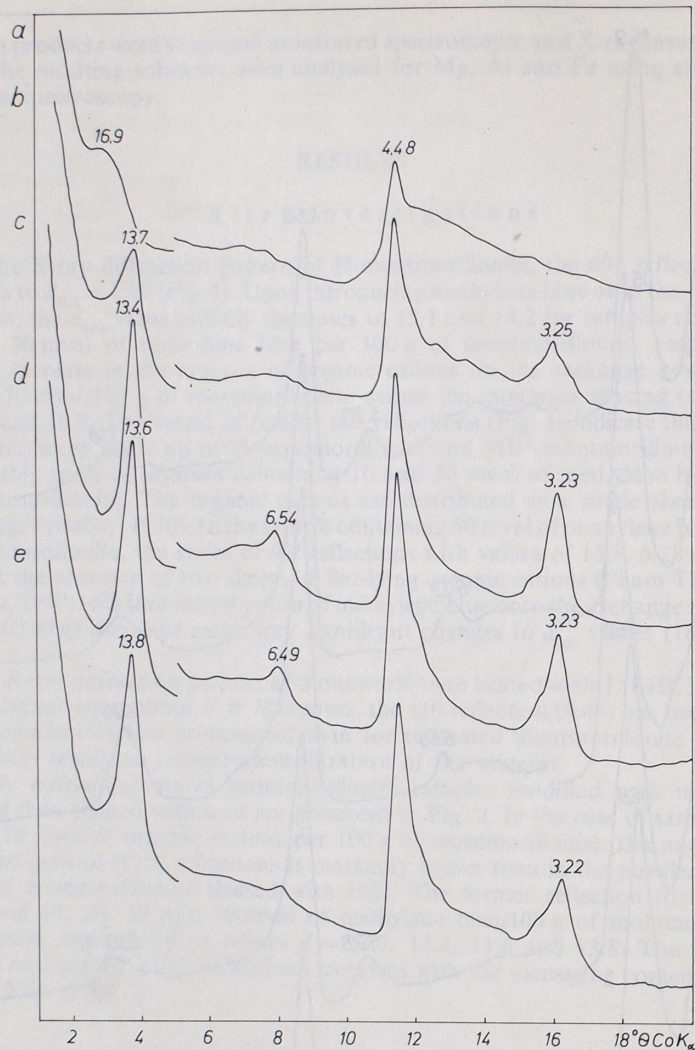


Fig. 2. X-ray diffractograms of H-montmorillonite (a) and methylene blue-montmorillonite (b, c, d, e - 10, 30, 50, 70 mval methylene blue/100 g montmorillonite, respectively) all samples treated with HCl

blue/100 g of montmorillonite shows absorption bands from montmorillonite, as well as bands caused by vibrations of functional groups within methylene blue molecules (795, 890, 1340, 1365, 1395, 1465, 1475, 1490, 1585 cm^{-1}). The intensity of these bands increases progressively with the increasing amount of organic cations on the exchange positions (Fig. 3).

HCl-treated H-montmorillonite fails to display the 850 cm^{-1} absorption band characteristic of AlMgOH groupings (Fig. 4). On the other hand, a pronounced absorption band typical of the dissolution products of montmorillonite appears

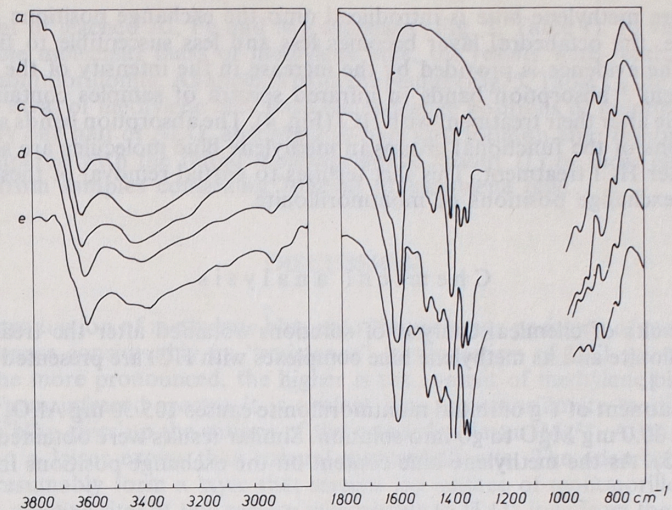


Fig. 3. Infrared spectra of H-montmorillonite (a) and methylene blue-montmorillonite (b, c, d, e - 10, 30, 50, 70 mval methylene blue/100 g montmorillonite, respectively)

at 810 cm^{-1} . The 3740 cm^{-1} absorption band testifies to the presence of SiOH groupings in these products. The 930 and 3630 cm^{-1} bands are less intense than in the spectrum of H-montmorillonite. The discussed changes in the infrared spectrum of HCl-treated montmorillonite provide evidence that a substantial amount of Mg^{2+} and Al^{3+} cations have been removed from the octahedral layers of montmorillonite.

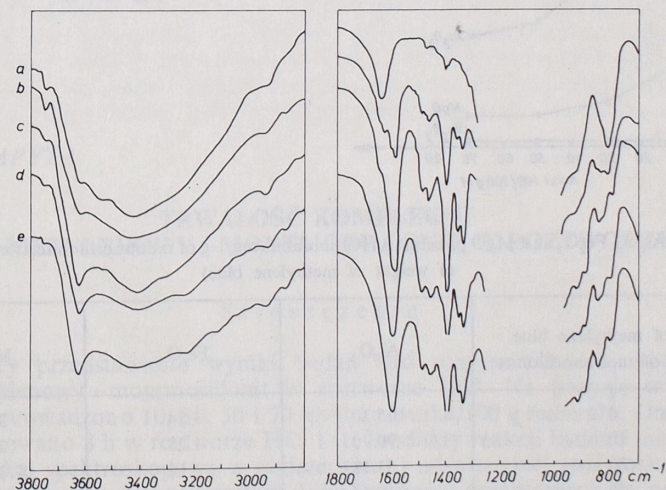


Fig. 4. Infrared spectra of H-montmorillonite (a) and methylene blue-montmorillonite (b, c, d, e - 10, 30, 50, 70 mval methylene blue/100 g montmorillonite, respectively) all samples treated with HCl

As more methylene blue is introduced onto the exchange positions of montmorillonite, the octahedral layer becomes less and less susceptible to the action of HCl. The evidence is provided by the increase in the intensity of the 850, 930 and 3630 cm^{-1} absorption bands in infrared spectra of samples containing methylene blue after their treatment with HCl (Fig. 4). The absorption bands attributed to vibrations of the functional groups in methylene blue molecules are somewhat weaker after HCl treatment. This fact testifies to partial removal of these cations from the exchange positions of montmorillonite.

Chemical analysis

The results of chemical analysis of solutions obtained after the treatment of montmorillonite and its methylene blue complexes with HCl are presented in Fig. 5 and Table 1.

The treatment of 1 g of initial montmorillonite causes 105.30 mg Al_2O_3 , 1.84 mg Fe_2O_3 and 30.0 mg MgO to go into solution. Similar results were obtained by Fijał *et al.* (1975). As the methylene blue content on the exchange positions increases,

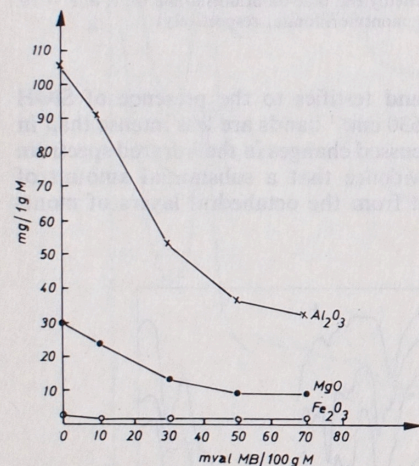


Fig. 5. Relationships between the amount of Al_2O_3 , Fe_2O_3 , MgO passing to HCl solution and the content of methylene blue in montmorillonite (M) (see tab. 1)

Table 1

Amount of Al_2O_3 , Fe_2O_3 and MgO passing to HCl solution (mg/1 g of montmorillonite after subtracting of weight of methylene blue)

| Mval of methylene blue in 100 g of montmorillonite | Al_2O_3 | Fe_2O_3 | MgO |
|--|-------------------------|-------------------------|--------------|
| 0 | 105.30 | 1.84 | 30.0 |
| 10 | 90.70 | 1.28 | 24.6 |
| 30 | 53.18 | 1.18 | 13.0 |
| 50 | 36.44 | 1.18 | 9.2 |
| 70 | 32.38 | 1.18 | 9.0 |

the amount of leached Al, Fe and Mg decreases (Fig. 5, Table 1). In view of the considerable molecular mass of methylene blue, the results were recalculated to 1 g of H-montmorillonite. As appears from the results (Fig. 5, Table 1), the introduction of 30 mval of methylene blue onto the exchange positions of montmorillonite causes only one half of Al_2O_3 and MgO to pass into solution after treatment with HCl. Compared with the initial montmorillonite, about 1/3 of these cations are removed from samples containing 70 mval of methylene blue.

DISCUSSION

The introduction of methylene blue onto the exchange positions of montmorillonite enhances considerably its "resistance" to the action of HCl solution. This effect is the more pronounced, the higher is the content of methylene blue in the sample. From infrared spectra it is evident that montmorillonite modified with methylene blue gives up the cations of the octahedral layer (Mg^{2+} , Al^{3+}) into HCl solution to a lesser extent than natural montmorillonite. The adsorbed organic cations presumably form a layer that screens the surface of montmorillonite and makes the reactive sites at this surface inaccessible to H_3O^+ ions from the solution.

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Zenon KLAPYTA

TRWAŁOŚĆ KOMPLEKSU BŁĘKIT METYLENOWY – MONTMORILLONIT W ROZTWORZE HCl

Streszczenie

W pracy przedstawiono wyniki badań nad rozpuszczalnością kompleksu błękit metylenowy-montmorillonit w roztworze HCl. Na pozycje wymienne minerału wprowadzono 10, 30, 50 i 70 mval barwnika/100 g minerału. Otrzymane próbki ogrzewano 8 h w roztworze HCl 1:1. Produkty reakcji badano metodami: rentgenowską, spektroskopową w podczerwieni i adsorpcyjnej spektroskopii atomowej. Stwierdzono, że ze wzrostem ilości kationów organicznych na pozycjach wymiennych montmorillonitu maleje ilość jonów Al^{3+} , Mg^{2+} i Fe^{3+} przechodzących do roztworu.

OBJAŚNIENIA FIGUR

- Fig. 1. Dyfraktogramy rentgenowskie H-montmorillonitu (a) i kompleksu błękit metylenowy-montmorillonit (b, c, d, e — odpowiednio 10, 30, 50, 70 mval błękitu metylenowego /100 g montmorillonitu)
- Fig. 2. Dyfraktogramy rentgenowskie H-montmorillonitu (a) i kompleksu błękit metylenowy-montmorillonit (b, c, d, e — odpowiednio 10, 30, 50, 70 mval błękitu metylenowego /100 g montmorillonitu) po traktowaniu próbek HCl
- Fig. 3. Spektrogramy w podczerwieni H-montmorillonitu (a) i kompleksu błękit metylenowy-montmorillonit (b, c, d, e — odpowiednio 10, 30, 50, 70 mval błękitu metylenowego /100 g montmorillonitu)
- Fig. 4. Spektrogramy w podczerwieni H-montmorillonitu (a) i kompleksu błękit metylenowy-montmorillonit (b, c, d, e — odpowiednio 10, 30, 50, 70 mval błękitu metylenowego /100 g montmorillonitu) po traktowaniu próbek HCl
- Fig. 5. Zależność pomiędzy ilością Al_2O_3 , Fe_2O_3 i MgO przechodzących do roztworu HCl a zawartością błękitu metylenowego w montmorillonicie (M) (Tab. 1).

Зенон КЛАПЫТА

ПРОЧНОСТЬ КОМПЛЕКСА МЕТИЛОВАЯ СИНЬ— —МОНТМОРИЛЛОНИТ В РАСТВОРЕ HCl

Резюме

В труде представлены результаты испытаний растворимости комплекса метиленовая синь-монтмориллонит в растворе HCl. На обменные позиции минерала введено 10, 30, 50 и 70 мвал красителя/100 г минерала. Полученные образцы выгревались в течение 8 часов в растворе HCl. Продукты реакции испытывались методами: рентгеновским, ик-спектроскопическим и абсорбционной атомной спектроскопии. Обнаружено, что в связи с увеличением количества органических катионов на обменные позициях монтмориллонита уменьшается количество ионов Al^{3+} , Mg^{2+} и Fe^{3+} , переходящих в раствор.

ОБЪЯСНЕНИЯ К ФИГУРАМ

- Фиг. 1. Рентгеновские дифрактограммы H-монтмориллонита (a) и комплекса метиленовая синь-монтмориллонит (b, c, d, e — соответственно 10, 30, 50, 70 мвал метиленовой сини/100 г монтмориллонита)
- Фиг. 2. Рентгеновские дифрактограммы H-монтмориллонита (a) и комплекса метиленовая синь-монтмориллонит (b, c, d, e — соответственно 10, 30, 50, 70 мвал метиленовой сини/100 г монтмориллонита) после обработки образцов HCl
- Фиг. 3. Ик-спектры H-монтмориллонита (a) и комплекса метиленовая синь-монтмориллонит (b, c, d, e — соответственно 10, 30, 50, 70 мвал метиленовой сини/100 г монтмориллонита)
- Фиг. 4. Ик-спектры H-монтмориллонита (a) и комплекса метиленовая синь-монтмориллонит (b, c, d, e — соответственно 10, 30, 50, 70 мвал метиленовой сини/100 г монтмориллонита/после обработки образцов HCl)
- Фиг. 5. Зависимость между количеством Al_2O_3 , Fe_2O_3 и MgO , переходящих в раствор HCl и содержанием метиленовой сини в монтмориллоните (M) (таб. 1)