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## BLEACHING PROPERTIES OF NON-BENTONITIC CLAY MATERIALS AND THEIR MODIFICATION

### III. MODIFICATION OF BLEACHING PROPERTIES OF KRAKOWIEC CLAYS FROM MACHÓW WITH SOME ORGANIC COMPOUNDS

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**Abstract.** The ability of  $H_2SO_4$  - activated clays to decolorize oils can be enhanced by saturating them with appropriately selected organic compounds of the amine type. These compounds coat the surfaces of clay minerals, combining simultaneously with the molecules of colouring matter present in oils. It has been found that the interlayer surface of smectites does not participate in the decolorization of oils.

## INTRODUCTION

Clay minerals form hybrid complexes of variable properties with a great number of organic compounds (Theng, 1974). These complexes find application in several fields of technology.

Organic compounds can be sorbed on both the external and internal (interlayer) surfaces of smectites. Compounds of large molecular size are sorbed only on the external surfaces. When the sorption takes place in the interlayer spaces, they replace exchange cations and/or interlayer water molecules.

It is to be expected that the coating of the surface of clay minerals with appropriately selected organic compounds will enhance their bleaching properties because the molecules of such a compound will form an intermediate layer reacting with the adsorbent surface on one hand and, on the other, combining with the adsorbate molecules, i.e. with the colouring matter present in substances refined with active earths (Stoch *et al.*, 1975).

The organic compounds introduced into the interlayer spaces expand them, rendering them accessible to other compounds of large molecular size, of the type of colouring matter.

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## EXPERIMENTAL

The experiments aiming to test the usefulness of organic compounds as agents enhancing the bleaching ability of active earths were carried out on clay derived from the overburden layer of a sulphur deposit in the Machów mine. Its main constituents are montmorillonite, illite and chlorite. The mineralogical composition of this clay and the studies of its activation with sulphuric acid were presented in earlier papers (Stoch *et al.*, 1977, 1979).

The experimental material was the fraction < 10  $\mu\text{m}$ , separated from this clay. It was treated with 16% sulphuric acid solution at 95°C for 3 hours. The activated clay was then saturated with the following organic compounds: N, N-diethyl-p-phenylenediamine hydrochloride, L-cysteine, safranine T, methyl violet, diethylamine hydrochloride, ethylamine hydrochloride. 2% aqueous solutions of these compounds were prepared and mixed with clay in such proportions that the dissolved matter made up 20 wt. % of the clay.

In another experimental series, the acid-activated clay was converted into the sodium form prior to its saturation with organic compounds. In each case the excess reagent was carefully washed off, and the samples were subjected to X-ray and infrared absorption spectroscopic investigations to determine the mode of binding of the organic compounds to clay minerals. Then the decolorizing action of these samples on sulphur, rape oil and P-3 inorganic oil was investigated<sup>1</sup>. Bleaching earth was introduced into these substances in an amount of about 1 wt. %.

## RESULTS

### X-ray investigations

Changes in the interlayer spacing  $d_{001}$  in response to the saturation of the clay with an organic compound indicate the manner of filling of interlayer spaces of smectite with the molecules of this compound. The magnitude of these changes is expressed by the difference in 001 interplanar spacing of unsaturated montmorillonite ( $d = 15.4$ ) and montmorillonite saturated with a specified organic compound. Data referring to the organic compounds under study are listed in Table 1 whereas changes in the position of the 001 lines are shown in Figure 1. As appears from these data, the sorption of organic compounds is attended by the reduction in the interlayer spacing of montmorillonite from the Machów clay. The greatest contraction is caused by safranine and methyl violet. The marked contraction of the crystal lattice of montmorillonite indicates that when the compound is introduced into the lattice, water is simultaneously removed from the interlayer spaces. Samples in the sodium form show greater contraction, which evidences that the interlayer spaces are better filled with organic molecules.

### Infrared absorption spectroscopy

Infrared spectroscopic analysis permits ascertaining whether the sorption of organic compounds has taken place in the interlayer spaces of montmorillonite. Moreover, the infrared spectrum provides information whether, and to what

<sup>1</sup> Studies of the decolorization of sulphur, rape oil and P-3 oil were made at the Research and Development Centre of Sulphur Industry „Siarkopol” in Machów near Tarnobrzeg.

Table 1  
 $d_{001}$  values and changes ( $\Delta d$ ) of  $d_{001}$  for montmorillonite from the fraction < 10  $\mu\text{m}$  of the miocene clay from Machów, saturated with organic compound

Sample No	Organic compound	$d_{001}$	$\Delta d$	Remarks
0	non-treated clay material	15.4	0.0	
1	N, N-diethyl-p-phenylenediamine hydrochloride	15.2	-0.2	removing of water
1-Na	Na-form	14.9	-0.5	removing of water
2	L-cysteine	15.9	+0.5	
2-Na	Na-form	14.9	-0.5	
3'	methyl violet	(10.5) 9.8	(-4.9) -5.6	removing of water
3-Na	Na-form	(10.5) 9.8	(-4.9) -5.6	removing of water
4	diethylamine hydrochloride	13.2	-2.2	removing of water
4-Na	Na-form	13.1	-2.3	removing of water
5	ethylamine hydrochloride	12.8	-2.6	partial removing of water
6-Na	safranine T, Na-form	9.9	-5.5	partial removing of water

extent, water has been removed from the interlayer spaces. The results can be summed up as follows:

*Samples saturated with N, N-diethyl-p-phenylenediamine hydrochloride.* Both samples yield nearly identical spectra (Fig. 2). Besides absorption bands belonging to the mineral component of the samples, there occur bands owing to the presence of hydrochloride. Its absorption bands are centered close to 1520  $\text{cm}^{-1}$  (N-H bending vibrations), 835, 860, 1400  $\text{cm}^{-1}$  (C-H vibrations). A comparison of the spectra reveals that hydrochloride is more intensely sorbed by the sample in sodium form. This observation is also confirmed by the disappearance of the 1630  $\text{cm}^{-1}$  absorption band caused by vibrations of water molecules partly coordinated by exchange cations. This also proves that the amine is incorporated in the interlayer spaces of montmorillonite in ionic form, dislodging simultaneously the interlayer water.

*Samples saturated with L-cysteine.* Both infrared spectra are similar, but the manner of L-cysteine sorption cannot be determined unequivocally. Absorption bands arising from L-cysteine (730, 740, 840, 850, 1340, 1410, 1495, 1950  $\text{cm}^{-1}$ ) are pronounced. However, the presence of the 1625  $\text{cm}^{-1}$  band (attributed to vibrations of  $\text{H}_2\text{O}$  molecules) suggests that the compound in question causes the organic molecules to be bound to the outer surface of the mineral rather than to be absorbed in the interlayer spaces of montmorillonite.

*Samples saturated with methyl violet.* Methyl violet combines extensively with the clay, which is evidenced by the intensity of the absorption bands produced

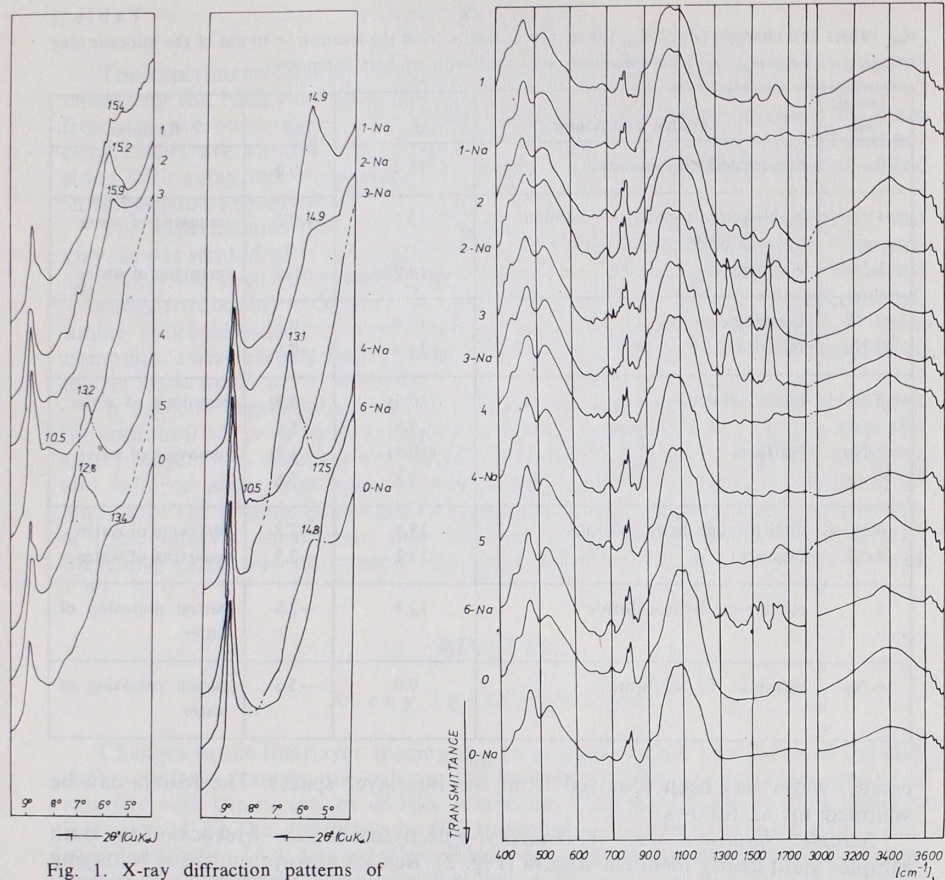


Fig. 1. X-ray diffraction patterns of <10 μm fraction of the clay from Machów saturated with various organic compounds

0 - sample treated with 16% H<sub>2</sub>SO<sub>4</sub> for 3 hr. 1-6 - samples treated with 16% H<sub>2</sub>SO<sub>4</sub> for 3 hr and then saturated with: 1 - N, N-diethyl-p-phenylenediamine hydrochloride, 2 - L-cysteine, 3 - methyl violet, 4 - diethylamine hydrochloride, 5 - ethylamine hydrochloride, 6 - safranin

by this substance, i.e. 725, 745, 765, 835, 1300, 1368, 1488, 1590 cm<sup>-1</sup>. Methyl violet is sorbed in the interlayer spaces in cationic form, displacing the exchange cations and water molecules. The 1630 cm<sup>-1</sup> band from water is virtually imperceptible in the spectrum.

*Sample saturated with diethylamine hydrochloride.* It can be inferred from the spectra that the sorption of this amine proceeds in the interlayer spaces of montmorillonite. This process is attended by the removal of water from the interlayer spaces. In the case of the sample in Na form, the degree of water removal is higher (almost complete disappearance of the 1630 cm<sup>-1</sup> band). It appears then that it

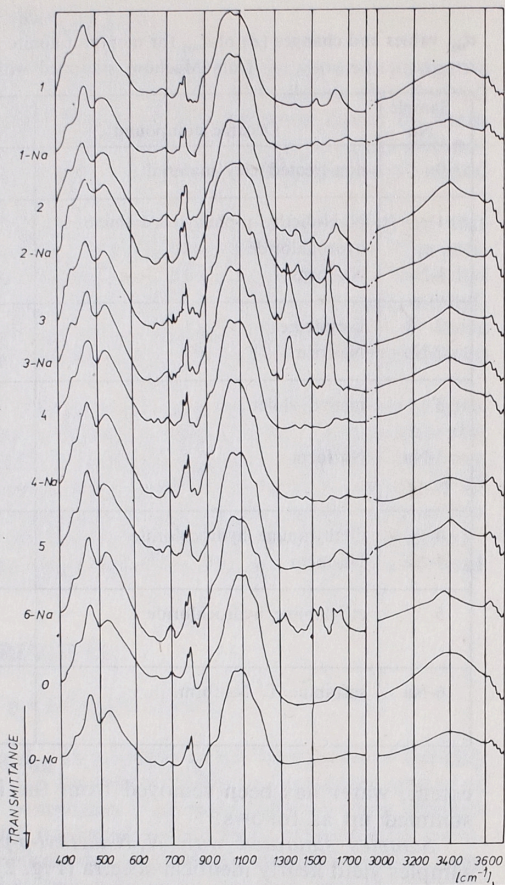


Fig. 2. Infrared absorption spectra of <10 μm fraction of the clay from Machów saturated with various organic compounds (symbols as in Fig. 1)

facilitates the introduction of the organic cation into the interlayer spaces of montmorillonite.

*Sample saturated with ethylamine hydrochloride.* The amount of sorbed amine seems to be inconsiderable as there are no pronounced absorption bands that could be attributed to this compound. Besides, the 1630 cm<sup>-1</sup> band, arising from H<sub>2</sub>O molecules, is still visible in the infrared spectrum, and this implies that water has not been completely removed from the interlayer spaces.

The spectrum of the clay in Na form displays intense absorption bands produced by safranin at 830, 1295, 1330, 1425, 1490, 1532 and 1645 cm<sup>-1</sup>. The latter band strongly coincides with the 1630 cm<sup>-1</sup> band from water molecules, which makes it difficult to determine the degree of removal of water molecules from the interlayer spaces.

From the above investigations it is evident that the organic compounds, added to the H<sub>2</sub>SO<sub>4</sub>-activated clays from Machów in order to enhance their bleaching ability, combine with montmorillonite present in these clays. In most cases, they enter the interlayer spaces in cationic form and, removing partially or completely water and exchangeable cations, form organo-mineral complexes. The sorption of organic compounds is particularly intense when the clay has been converted into the sodium form prior to saturation.

#### Bleaching properties of organo-mineral complexes

The formation of organo-mineral complexes enhances considerably the bleaching ability of sulphuric-acid activated clays with respect to rape oil (Tab. 2),

Table 2  
Bleaching properties of the fraction <10 μm of the miocene clay from Machów, saturated with organic compounds

Sample No	Organic compound	Degree of bleaching in (%)		
		rape oil	P-3 oil	sulphur
0	activated clay by 16% H <sub>2</sub> SO <sub>4</sub>	43.7	64.3	74.8
1	N, N-diethyl-p-phenylenediamine hydrochloride	67.8	38.6	55.4
1-Na	Na-form	71.4	33.3	56.8
2	L-cysteine	78.7	43.2	78.4
2-Na	Na-form	78.7	38.0	59.4
3	methyl violet	75.0	38.6	51.0
3-Na	Na-form	75.0	47.6	53.9
4	diethylamine hydrochloride	67.7	53.6	60.0
4-Na	Na-form	61.8	50.0	64.7
5	ethylamine hydrochloride	77.8	27.3	78.8
6-Na	safranin T, Na-form	78.7	41.4	51.1

Table 3

Specific surface area and pore volume of the fraction  $< 10 \mu\text{m}$  of the Miocene clay from Machów saturated with organic compounds

Sample No	Organic compound	Specific surface area ( $\text{m}^2/\text{g}$ )	Pore volume $\text{Ncm}^3(\text{Ar})/\text{g}$
2	L-cysteine	150.5	50
4	diethylamine hydrochloride	212.5	51
5	ethylamine hydrochloride	362.9	115
6-Na	safranin T, Na-form	37.7	0

which amounts to 78% (L-cysteine, safranin, ethylamine hydrochloride). The addition of organic compounds little affects, on the other hand, the decolorizing ability of clays with respect to P-3 mineral oil. Except for L-cysteine and ethylamine hydrochloride, the compounds used deteriorate significantly the ability of clays to decolorize sulphur.

BET measurements of the specific surface area and pore volume from argon sorption (Tab. 3) revealed that they vary over a wide range, depending on the kind of compound saturating the interlayer spaces of montmorillonite. However, no relationship has been found to exist between the size the specific surface area and the ability of clays saturated with organic compounds to decolorize oils or sulphur. This fact implies that most of the surfaces covered by argon molecules do not participate in the bleaching process.

## DISCUSSION

Both the results of the present experiments and the earlier studies (Stoch *et al.*, 1979) imply that the refining of sulphur and oils involves the sorption of the constituent hydrocarbons on the external surfaces of clay minerals. By coating the surface of clay minerals, particularly of montmorillonite, with molecules of an appropriately selected organic compound of the amine type, their decolorizing ability can be enhanced. The bleaching properties are presumably enhanced by those compounds whose molecules are bound to the surface of clay minerals on one hand and, on the other, have the ability to combine with molecules of the compounds which give the colour to the substance being refined. L-cysteine, methyl violet, ethylamine hydrochloride and safranin appeared to be the suitable amines for rape oil.

As the amines in question become incorporated in the interlayer spaces of montmorillonite, they either increase the interlayer spacing ( $d_{001}$ ) and retain interlayer water molecules (L-cysteine), or reduce the  $d_{001}$  and cause the interlayer water to be removed (methyl violet, ethylamine hydrochloride). Safranin, on the other hand, causes not only the removal of water but also a complete breakdown of the structure of montmorillonite ( $d_{001} = 9.9$ ). Nevertheless, the clay saturated with safranin decolorizes rape oil in the same degree as L-cysteine. This fact shows that the interlayer spaces of montmorillonite do not participate in the sorption of oil-colouring matter.

The data listed in Tables 1 and 3 also permit one to make certain inferences regarding the effect of the filling of the interlayer spaces of montmorillonite on the size of the surface area accessible to argon molecules. The surface area increases

depending on the kind of molecules occupying the interlayer spaces in the sequence: L-cysteine, diethylamine hydrochloride, safranin, i.e. it increases with the decreasing interlayer distance and the attendant removal of water. In the case of complete contraction of the lattice and the closing of interlayer spaces, which phenomena are caused by the introduction of safranin molecules, the surface area diminishes rapidly, and the BET pore volume equals zero. Then the interlayer spaces become inaccessible to organic molecules.

From the above considerations it appears that no relationship should exist between the specific surface area size determined from argon sorption and the degree of decolorization of oils by clays saturated with exchange organic compounds. The results of bleaching tests have, in fact, fully confirmed this hypothesis (Tab. 2).

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## WŁASNOŚCI ODBARWIAJĄCE ILASTYCH SUROWCÓW NIEBENTONITOWYCH I ICH MODYFIKOWANIE

### III. MODYFIKOWANIE WŁASNOŚCI ODBARWIAJĄCYCH ILÓW KRAKOWIECKICH Z MACHOWA NIEKTÓRYMI ZWIĄZKAMI ORGANICZNYMI

#### Streszczenie

Podjęto próbę zwiększenia zdolności odbarwiających ilów krakowieckich z Machowa, aktywowanych kwasem siarkowym, przez nasywanie ich związkami organicznymi typu amin. Jak się przypuszcza właściwości odbarwiające ulegają polepszeniu pod wpływem tych związków, których drobinny wiążą się z jednej strony z powierzchnią minerałów ilastych, z drugiej zaś mają zdolność łączenia się z drobinami związków wywołujących barwę rafinowanej substancji. Dla oleju rzepakowego takimi aminami okazały się L-cysteina, fiolet krystaliczny, chlorowodorek etyloaminy i safranina. Substancje te w budując się w przestrzenie międzypakietowe montmorillonitu zwiększają odległości  $d_{001}$  i zatrzymują drobinę wody międzypakietowej (L-cysteina) lub też zmniejszają  $d_{001}$  i powodują usunięcie wody (np. fiolet krystaliczny i chlorowodorek etyloaminy). Safranina powoduje natomiast nie tylko usunięcie wody, lecz również całkowite zapadnięcie się struktury

ры montmorillonitu ( $d_{001} = 9,9$ ). Насычены nią ил одбарива jednak olej rzepakowy w takim samym stopniu jak L-cysteina. Dowodzi to, że przestrzenie międзпакетовые montmorillonitu nie uczestniczą w procesie сорпции субстанции барвящих олеје.

Dane zestawione w tabelach 1 i 3 pozwalają równоcześnie на poczynanie pewnych spostrzeżeń odnosnie wpływu obsady przestrzeni międзпакетовой montmorillonitu на wielkość поверхности доступной для дробин аргону. Rоśnie она в зависимости от rodzaju дробин, obsadzających przestrzenie międзпакетовые, в kolejności: L-cysteina, chlorowodorkiem dwuetyлоамини, safranina. Wielkość tej поверхности wzrasta więc ze zmniejszaniem się odległości międзпакетовыми i związanym z tym usuwaniem воды. W przypadku całkowитей контракции sieci i zamknięcia przestrzeni międзпакетовой, wywołаней wprowadzeniem дробин safraniny, wielkość tej поверхности spada gwałtownie, а objętość пор wyznaczona методом BET wynosi zero. Przestrzeń międзпакетовая staje się wówczas niedostępна для дробин органических. Nie powinna zatem istnieć zależność wielkości поверхности właściwej, określonej на podstawie сорпции аргону, а stopniem одбаривания олеи przez ил насыены wymiennymi związkami органическими. Potwierdzają to całkowicie rezultaty badań (tab. 2).

#### ОБЪАШНИЕНИЯ ФИГУР

Fig. 1. Dyfraktogramy фракции  $< 10 \mu\text{m}$  илу з Махова насыеных разными związkami органическими  
0 — próbka актиwowана 3 h 16-procentowym  $\text{H}_2\text{SO}_4$ ; 1—6 próbki актиwowане 3 h 16-procentowym  $\text{H}_2\text{SO}_4$ , а następnie насыены: 1 — chlorowodorkiem N,N-dwuetyло-p-fenylene-dwuамини, 2 — L-cysteina, 3 — fioletem krystalicznym, 4 — chlorowodorkiem dwuetyлоамини, 5 — chlorowodorkiem etyлоамини, 6 — safranina

Fig. 2. Widma absorpcyjne в подчервении фракции  $< 10 \mu\text{m}$  илу з Махова насыеных разными związkami органическими (oznaczenia jak на fig. 1)

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### ОТБЕЛИВАЮЩИЕ СВОЙСТВА ГЛИНИСТОГО НЕБЕНТОНИТОВОГО СЫРЬА И ИХ МОДИФИЦИРОВАНИЕ

#### III. МОДИФИЦИРОВАНИЕ ОТБЕЛИВАЮЩИХ СВОЙСТВ КРАКОВЕЦКИХ ГЛИН С МАХОВА НЕКОТОРЫМИ ОРГАНИЧЕСКИМИ СОЕДИНЕНИЯМИ

#### Резюме

Были предприняты попытки увеличения отбеливающей способности краковецких глин с Махова, активированных серной кислотой, путём насыщения их органическими соединениями типа аминов. Как предполагается, отбеливающие свойства улучшаются под влиянием тех соединений, молекулы которых связываются с поверхностью глинистых минералов с одной

стороны, с другой стороны имеют способность соединяться с молекулами соединений, вызывающих окрашивание рафинированного вещества. Для суперного масла такими аминами оказались L-цистеин, кристаллвиолет, хлористоводородный этиламин и сафранин. Эти вещества, встраиваясь в межпакетное пространство монтмориллонита, увеличивают расстояние  $d_{001}$  и задерживают молекулы межпакетной воды (L-цистеин) либо уменьшают  $d_{001}$  и вызывают удаление воды (нп. кристаллвиолет и хлористоводородный этиламин), Сафранин вызывает зато не только удаление воды, но также и совершенный провал структуры монтмориллонита ( $d_{001} = 9,9 \text{ \AA}$ ). Насыщенная нею глина отбеливает однако, суперное масло в такой же степени, как L-цистеин. Это доказывает то, что межпакетное пространство монтмориллонита не принимает участия в процессе сорбирования веществ, отбеливающих масла.

Данные, приведенные в таблицах 1 и 3 разрешают одновременно произвести определённые наблюдения относительно влияния выполнения межпакетного пространства монтмориллонита на величину поверхности, доступной для молекул аргона. Она растёт в зависимости от вида молекул, выполняющих межпакетные пространства, в очерёдности: L-цистеин, хлористоводородный двуэтиламин, сафранин. Величина этой поверхности растёт с уменьшением расстояния между пакетами связанным с этим удалением воды. В случае полной контракции сети и закрытия межпакетного пространства, вызванного введением молекул сафранина, величина этой поверхности резко уменьшается, а объём пор, определённый методом BET, составляет нуль. Межпакетное пространство становится тогда недоступным для органических молекул. Таким образом, не должна существовать зависимость между величиной удельной поверхности, определённой на основании сорбции аргона и степенью отбеливания масел глиной, насыщенной перечисленными органическими соединениями. Это полностью подтверждают результаты исследования (таб. 2).

#### ОБЪАСНЕНИЕ К ФИГУРАМ

Фиг. 1. Дифрактограммы фракции  $< 10 \mu\text{m}$  глины с Махова, насыщенной разными органическими соединениями

0 — глина активированная 3 час. 16-процентным раствором  $\text{H}_2\text{SO}_4$ ; 1—6 — глины активированные 3 час. 16-процентным раствором  $\text{H}_2\text{SO}_4$ , а затем насыщенные: 1 — хлористым водородом N, N-двуэтил-p-фенил-двуамини, 2 — L-цистеини, 3 — кристаллвиолетом, 4 — хлористоводородным двуэтиламини, 5 — хлористоводородным этиламини, 6 — сафранини

Фиг. 2. Инфракрасные спектры фракции  $< 10 \mu\text{m}$  глины из Махова, насыщенной разными органическими соединениями (обозначения как на рис. 1)