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## MODIFICATION OF SORPTION PROPERTIES OF H-MONTMORILLONITE WITH UREA, PYRIDINE AND RHODAMINE

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**Abstract.** The paper presents investigations of sorption properties of H-montmorillonite modified by urea, pyridine and rhodamine. Adsorption of organic cations in the interlayer region has been determined basing on X-ray and IR spectroscopic investigations. The sorption properties of samples (after heating at 50 and 550°C) with respect to water and benzene vapours were investigated.

### INTRODUCTION

The replacement of the inorganic cations present on the clay surface by organic ions brings about a modification of sorption properties of the mineral. The degree of modification depends on the amount and chemical nature of organic cations.

In earlier publications (Żyła, Kłapyta, 1976; Kłapyta, Żyła, 1977) the sorption properties of montmorillonite modified with long-chain organic cations were determined. This paper presents the studies of sorption properties of H-montmorillonite modified by urea, pyridine and rhodamine.

### EXPERIMENTAL

Investigations were carried out on montmorillonite from Chmielnik. The mineral was transformed into H-form by treatment with 0.1 n HCl solution. Excess acid was washed out in a centrifuge with distilled water until the reaction to Cl<sup>-</sup> ion was negative. Aqueous solution of urea, pyridine and rhodamine was added to H-montmorillonite suspension, and the mixture was stirred for two days. The samples were centrifuged and the excess of organic compounds was washed out with distilled water.

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The specimens thus obtained were subjected to X-ray and infrared spectroscopic analysis and their sorption properties were determined. The samples were investigated after heating at 50 and 550°C.

## RESULTS

### X-ray investigations

The diffraction patterns of H-montmorillonite treated with urea, pyridine and rhodamine (Fig. 1) show intense basal reflections 001 with the  $d_{hkl}$  values of 15.9, 14.6 and 18.0 Å\*, respectively. This is due to protonation of urea and pyridine on the clay surface and adsorption of the cationic forms in the interlayer region. Rhodamine is adsorbed by replacement of interlayer  $\text{H}_3\text{O}^+$  ions.  $d_{001}$  values are conformable to the data for these montmorillonite complexes (Theng, 1974).

Heating of samples at 550°C causes a displacement of basal reflection on the X-ray diffractograms of urea- and pyridinium-montmorillonite to  $d_{hkl} = 10$  Å. This reflection is broadened as the reflection of H-montmorillonite. On the X-ray diffraction patterns of H-montmorillonite treated with rhodamine and calcinated at 550°C the position of the basal reflection 001 corresponds to  $d_{001} = 13.0$  Å. This reflection is sharp and not broadened.

### Infrared spectroscopic investigations

Infrared spectra of the samples studied are presented in Fig. 2. The spectrum of urea adsorbed by H-montmorillonite (Fig. 2a) reveals the presence of ab-

Fig. 1. X-ray diffraction patterns of H-montmorillonite treated with urea (a), pyridine (b), rhodamine (c) and of the same samples heated at 550°C (d, e, f, respectively)

\* 1 Å = 0.1 nm (SI).

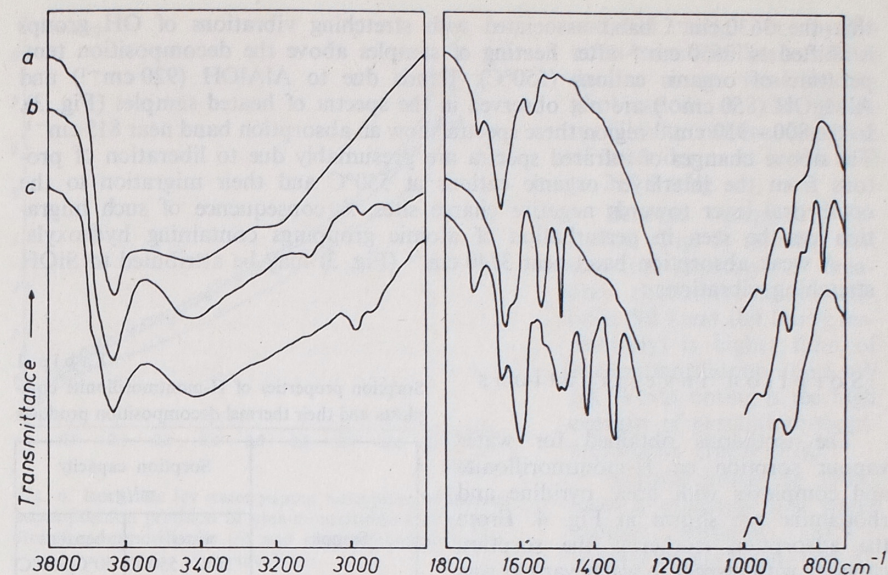
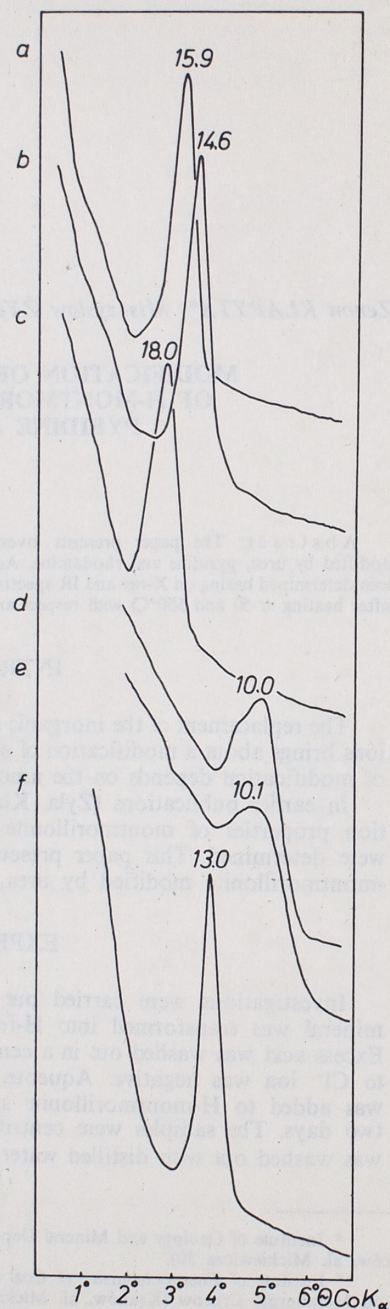


Fig. 2. Infrared spectra of H-montmorillonite treated with urea (a), pyridine (b) and rhodamine (c)

sorption bands at 1565, 1634, and 1710  $\text{cm}^{-1}$  typical of urea-cation. The protonation of adsorbed pyridine is observed in Fig. 2b. The absorption bands at 1490 and 1545  $\text{cm}^{-1}$  are due to the presence of pyridinium cations.

Thermal decomposition of organic cations adsorbed on the clay surface causes disappearance of their absorption bands (Fig. 3). It is interesting to note

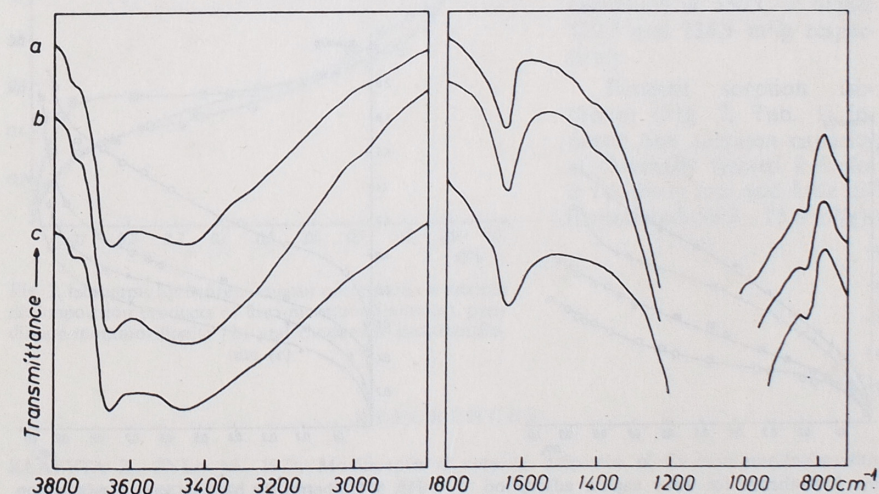


Fig. 3. Infrared spectra of thermal decomposition products of urea-montmorillonite (a), pyridinium-montmorillonite (b) and rhodamine-montmorillonite (c)

that the  $3630\text{ cm}^{-1}$  band associated with stretching vibrations of OH groups is shifted to  $3650\text{ cm}^{-1}$  after heating of samples above the decomposition temperature of organic cations ( $550^\circ\text{C}$ ). Bands due to  $\text{Al}(\text{OH})_3$  ( $920\text{ cm}^{-1}$ ) and  $\text{AlMgOH}$  ( $850\text{ cm}^{-1}$ ) are not observed in the spectra of heated samples (Fig. 3). In the  $800\text{--}950\text{ cm}^{-1}$  region these spectra show an absorption band near  $815\text{ cm}^{-1}$ . The above changes of infrared spectra are presumably due to liberation of protons from the interlayer organic cations at  $550^\circ\text{C}$  and their migration to the octahedral layer towards negative charge sites. A consequence of such migration can be seen in perturbation of atomic groupings containing hydroxyls.

A weak absorption band near  $3740\text{ cm}^{-1}$  (Fig. 3) may be attributed to SiOH stretching vibrations.

## Sorption investigations

The isotherms obtained for water vapour sorption on H-montmorillonite and complexes with urea, pyridine and rhodamine are shown in Fig. 4. From the adsorption isotherms the sorption capacity with respect to water vapour was calculated (Tab. 1).

As appears from the above results, adsorption of urea on H-montmorillonite brings about a small increase in the sorption of water. The pyridinium cations cause a notable decrease in sorption capacity with respect to water. This capacity is  $314.2\text{ m}^2/\text{g}$  for H-montmorillonite

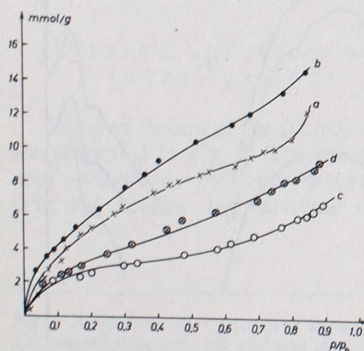


Fig. 4. Isotherms for water vapour adsorption on H-montmorillonite (a), urea-montmorillonite (b), pyridinium-montmorillonite (c) and rhodamine-montmorillonite (d).

Table 1  
Sorption properties of H-montmorillonite complexes and their thermal decomposition products

| Sample                     | Sorption capacity<br>$\text{m}^2/\text{g}$ |                              |                               |                                |
|----------------------------|--------------------------------------------|------------------------------|-------------------------------|--------------------------------|
|                            | water<br>$50^\circ\text{C}$                | water<br>$550^\circ\text{C}$ | benzene<br>$50^\circ\text{C}$ | benzene<br>$550^\circ\text{C}$ |
| H-montmorillonite          | 314.2                                      | 81.9                         | 66.5                          | 73.4                           |
| Urea-montmorillonite       | 348.7                                      | 64.9                         | 99.3                          | 58.7                           |
| Pyridinium-montmorillonite | 136.2                                      | 122.5                        | 162.4                         | 60.9                           |
| Rhodamine-montmorillonite  | 218.9                                      | 124.9                        | 104.1                         | 75.0                           |

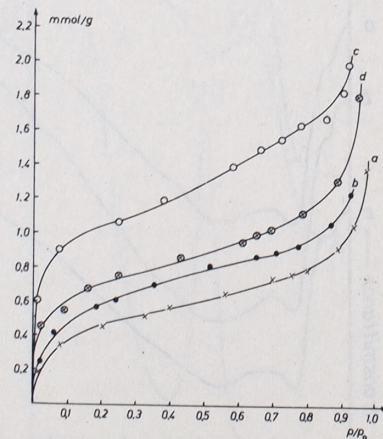


Fig. 5. Isotherms for benzene vapour adsorption on H-montmorillonite (a), urea-montmorillonite (b), pyridinium-montmorillonite (c) and rhodamine-montmorillonite (d).

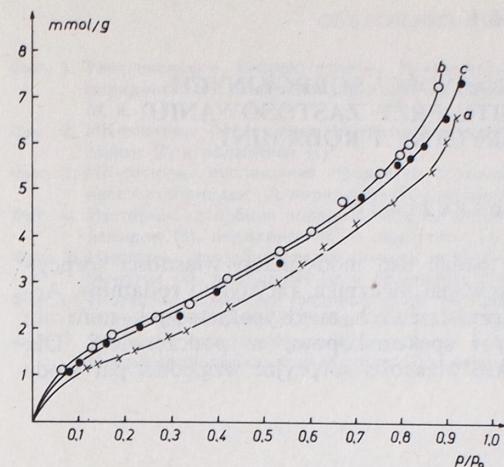


Fig. 6. Isotherms for water vapour adsorption of thermal decomposition products of urea-montmorillonite (a), pyridinium-montmorillonite (b) and rhodamine-montmorillonite (c).

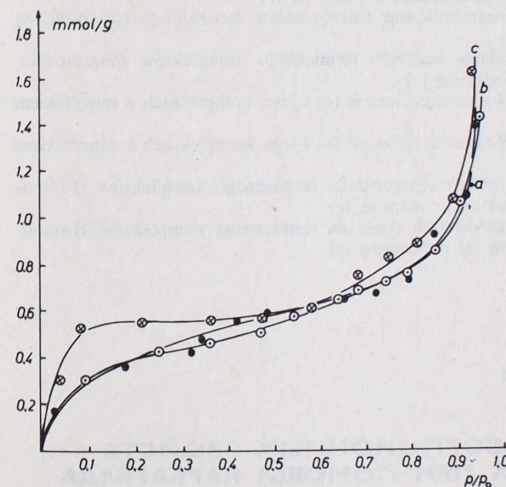


Fig. 7. Isotherms for benzene vapour adsorption on thermal decomposition products of urea-montmorillonite (a), pyridinium-montmorillonite (b) and rhodamine-montmorillonite (c).

and  $136.2\text{ m}^2/\text{g}$  for pyridinium-montmorillonite. Rhodamine causes weak hydrophobization of the montmorillonite surface. Sorption of water decreases in this case to  $218.9\text{ m}^2/\text{g}$ .

Benzene sorption isotherms (Fig. 5) indicate that sorption capacity of urea- and rhodamine-montmorillonite ( $99.3$  and  $104.1\text{ m}^2/\text{g}$  respectively) is higher than of H-montmorillonite ( $66.5\text{ m}^2/\text{g}$ ). Worth noting is the high capacity of pyridinium-montmorillonite ( $162.4\text{ m}^2/\text{g}$ ).

Samples heated at  $550^\circ\text{C}$  show a relatively low water vapour sorption ( $81.9\text{--}124.9\text{ m}^2/\text{g}$ ) (Fig. 6, Tab. 1). It may be interesting to mention that a thermal decomposition product of urea-montmorillonite shows lower sorption capacity with respect to water than H-montmorillonite heated at  $550^\circ\text{C}$ . This capacity for pyridinium- and rhodamine-montmorillonite calcinated at  $550^\circ\text{C}$  is higher  $122.5$  and  $124.9\text{ m}^2/\text{g}$  respectively.

Benzene sorption isotherms (Fig. 7, Tab. 1) indicate that sorption capacity of thermally treated samples is relatively low and little differentiated ( $58.7\text{--}75.0\text{ m}^2/\text{g}$ ).

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# **MODYFIKACJA WŁASNOŚCI SORPCYJNYCH H-MONTMORILLONITU PRZY ZASTOSOWANIU MOCZNIKA, PIRYDYNY I RODAMINY**

## **Streszczenie**

W pracy przedstawiono wyniki badań nad modyfikacją własności sorpcyjnych H-montmorillonitu przy zastosowaniu mocznika, pirydyny i rodaminy. Adsorpcję kationów organicznych w przestrzeniach międzypakietowych minerału stwierdzono metodą rentgenowską i spektroskopową w podczerwieni. Dla otrzymanych próbek oznaczono także własności sorpcyjne względem par wody i benzenu.

## **OBJAŚNIENIA FIGUR**

- Fig. 1. Dyfraktogramy rentgenowskie H-montmorillonitu traktowanego mocznikiem (a), pirydyną (b), rodaminą (c) oraz tych samych próbek po prażeniu w 550°C (d, e, f)
- Fig. 2. Spektrogramy w podczerwieni H-montmorillonitu traktowanego mocznikiem (a), pirydyną (b) i rodaminą (c)
- Fig. 3. Spektrogramy w podczerwieni produktów rozkładu termicznego kompleksów montmorillonitu z mocznikiem (a), pirydyną (b) i rodaminą (c)
- Fig. 4. Izotermy adsorpcji pary wodnej na H-montmorillonicie (a) i jego kompleksach z mocznikiem (b), pirydyną (c) i rodaminą (d)
- Fig. 5. Izotermy adsorpcji par benzenu na H-montmorillonicie (a) i jego kompleksach z mocznikiem (b), pirydyną (c) i rodaminą (d)
- Fig. 6. Izotermy adsorpcji pary wodnej na produktach rozkładu termicznego kompleksów H-montmorillonitu z mocznikiem (a), pirydyną (b) i rodaminą (c)
- Fig. 7. Izotermy adsorpcji par benzenu na produktach rozkładu termicznego kompleksów H-montmorillonitu z mocznikiem (a), pirydyną (b) i rodaminą (c)

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# **МОДИФИКАЦИЯ АДсорПЦИОННЫХ СВОЙСТВ Н-МОНТМОРИЛЛОНИТА ПРИ ПОМОЩИ КАРБАМИДА ПИРИДИНА И РОДАМИНА**

## **Резюме**

В статье представлены результаты исследований модификации адсорпционных свойств Н-монтмориллонита при помощи карбамида, пиридина и родамин. Адсорбция органических катионов в междупакетных пространствах была обнаружена рентгенографическим и ИК-спектроскопическим методами. Для изучаемых образцов были тоже обозначены адсорпционные свойства по отношению к парам воды и бензола.

## **ОБЪЯСНЕНИЯ К ФИГУРАМ**

- Фиг. 1. Рентгеновские дифрактограммы Н-монтмориллонита, обработанного карбамидом (а), пиридином (b), родамином (с) и тех же образцов после обжига при температуре 550°C (d, e, f)
- Фиг. 2. ИК-спектры поглощения Н-монтмориллонита, обработанного карбамидом (а), пиридином (b) и родамином (с)
- Фиг. 3. ИК-спектры поглощения продуктов термического распада комплексов монтмориллонита с карбамидом (а), пиридином (b) и родамином (с)
- Фиг. 4. Изотермы адсорбции водяного пара на Н-монтмориллоните (а) и его комплексах с карбамидом (b), пиридином (с) и родамином (d)
- Фиг. 5. Изотермы адсорбции паров бензола на Н-монтмориллоните (а) и его комплексах с карбамидом (b), пиридином (с) и родамином (d)
- Фиг. 6. Изотермы адсорбции водяного пара на продуктах термического распада комплексов Н-монтмориллонита с карбамидом (а), пиридином (b) и родамином (с)
- Фиг. 7. Изотермы адсорбции паров бензола на продуктах термического распада комплексов Н-монтмориллонита с карбамидом (а), пиридином (b) и родамином (с)