

STUDY OF UREA COMPLEXES WITH MONTMORILLONITE

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Received January 10th, 1972

Complexes of urea with montmorillonite were studied by means of infrared spectroscopy. The comparison of the obtained results with the spectra of complex compounds of urea with Cu(II) leads to the assumption of formation of complex compounds of the type $[M(\text{CO}(\text{NH}_2)_2)_4]^{2+}$ in the interlayer space of montmorillonite, if $M = \text{Cu(II)}, \text{Co(II)}$. The metal in that compound is bonded to the oxygen of urea. For Na(I) and Ca(II) montmorillonites, urea is bonded mainly to the outer surface of the mineral. The complex formation did not appear markedly.

The interaction between clays and organic compounds¹ (including urea) with the surface of a silicate mineral² is explained by the formation of hydrogen bonds between the carbonyl or amide groups of urea and the surface oxygen atoms of the silicate. The effect of the exchange cation and its possible participation in the urea — silicate bond has not been considered^{1,2}.

In the paper³ we pointed out the different shape of the sorption isotherms of urea

TABLE I

Results of Analyses of the Na(I)-, Ca(II)-, Cu(II)-, and Co(II)-Forms of Montmorillonite

Component	Content (%) in the form			
	Na	Ca	Co	Cu
SiO ₂	55.91	57.80	55.80	55.50
CaO	2.23	2.60	—	—
MgO	2.43	2.23	2.41	2.33
Fe ₂ O ₃	5.78	5.77	5.36	5.53
Al ₂ O ₃	22.60	22.50	21.80	21.90
Na ₂ O	4.02	1.01	0.82	0.04
MO	—	—	6.61	106.0
annealing loss	6.62	8.13	8.32	5.70

on the cation-exchange forms of montmorillonite in dependence on the exchange cations. If the exchange cations are Cd(II), Zn(II), Ni(II), Co(II), Cu(II), or Fe(III), urea is bonded in the interlayer space of montmorillonite under the formation of complex compounds of the type $[M(\text{CO}(\text{NH}_2)_2)_4]^{n+}$, where M is the metal. If $M = \text{Na(I)}, \text{Ca(II)}$, no considerable formation of interlayer complexes can be inferred from the shape of the sorption isotherms. Infrared spectroscopic study of the complex compounds of urea with various cations was performed by Penland⁴; he suggested the possibility of the bonding of the metal through the oxygen or nitrogen atoms of urea. The bonding of the metals to the urea oxygen is reflected in the infrared spectrum by a decrease of the wavenumber of the stretching vibration of the C=O bond and an increase of that of the CN bond. The bonding through the urea nitrogen leads to an increase of the wavenumber of the stretching vibration of the CO bond and to a decrease of that of the CN bond. From the results of⁴ it follows that in the urea complexes, Cu(II) is bonded to the urea oxygen, whereas in Pd(II) complexes the metal is bonded to the urea nitrogen.

EXPERIMENTAL

Infrared spectra were measured on a double-beam spectrophotometer IKS-14 (USSR), the interplanar spacings on an X-ray goniometer GON 3 (Chirana, Prague).

For the preparation of the complexes of montmorillonite with urea, montmorillonite isolated from bentonite from the locality Lastovce⁵ was used for the preparation of the cation-exchange forms⁶. The preparation of urea complexes with montmorillonite as well as the investigation of the sorption isotherms of urea on cation-exchange montmorillonites has been described³. Bonded urea was determined according to⁷. The samples for the measurements of the infrared

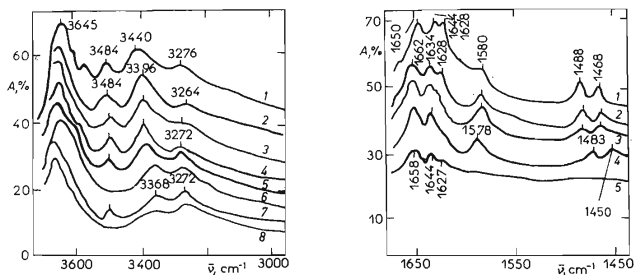


FIG. 1

Infrared Spectrum of the Complex of Cu(II)-Montmorillonite with Urea

1 20°C (on air); 2—8 (in vacuo): 2 20°C; 3 50°C; 4 100°C; 5 150°C; 6 200°C; 7 250°C; 8 300°C.

spectra were prepared by drying a thin layer of aqueous suspension on a calcium fluoride window at room temperature. The spectra were measured in an evacuable cell⁸ at the pressure of 10^{-2} Torr and temperature 20–300°C. The contents of SiO_2 , Al_2O_3 , Fe_2O_3 , MgO , CaO , and CuO were determined complexometrically⁹ and that of Na_2O flame-photometrically¹⁰ in the samples prior to urea sorption. The results of the chemical analysis are given in Table I.

RESULTS AND DISCUSSION

The infrared spectra of Cu(II) , Co(II) , Ca(II) , and Na(I) complexes of montmorillonite with urea are given in Fig. 1–4, resp. From the comparison of the spectra

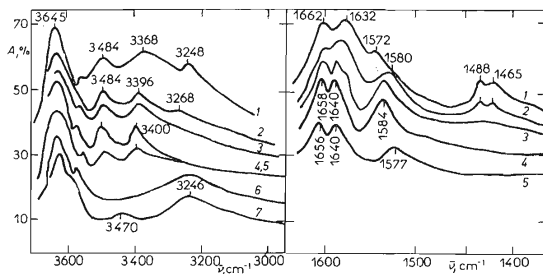


FIG. 2

Infrared Spectrum of the Complex of Co(II) -Montmorillonite with Urea

1 20°C (on air); 2–7 (in vacuo): 2 20°C; 3 50°C; 4 100°C; 5 150°C; 6 200°C; 7 250°C.

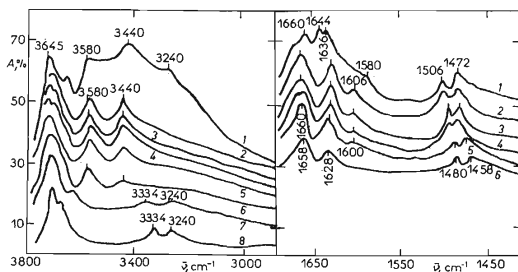


FIG. 3

Infrared Spectrum of the Complex of Ca(II) -Montmorillonite with Urea

1 20°C (on air); 2–8 (in vacuo): 2 20°C; 3 50°C; 4 100°C; 5 150°C; 6 200°C; 7 250°C; 8 300°C.

with the results given in Table II it can be concluded that, if the exchange cations of montmorillonite are Cu(II) or Co(II), the cation is bonded to urea through the oxygen atom, since the stretching vibration of the C=O bond appears at 1580 cm^{-1}

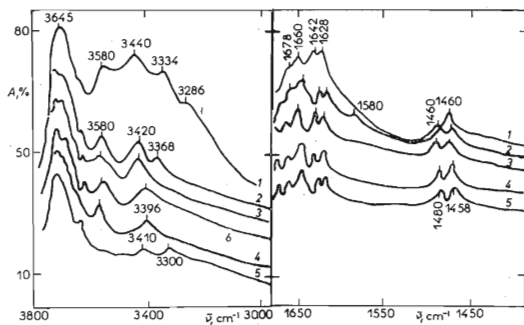


FIG. 4

Infrared Spectrum of the Complex of Na(I)-Montmorillonite with Urea
1 20°C (on air); 2–6 (*in vacuo*): 2 20°C ; 3 50°C ; 6 100°C ; 4 150°C ; 5 200°C .

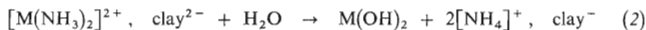
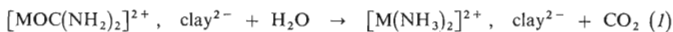
TABLE II

Absorption Bands of Urea and the Urea Complex-Cu(II) (cm^{-1})^a

$\text{CO}(\text{NH}_2)_2$	$[\text{Cu}(\text{OC}(\text{NH}_2)_2)_4]\text{Cl}_2$	Assignment
3 450	3 425	NH stretch
3 355	3 340	
3 265	3 275	
3 210		
1 670	1 655	NH bend
1 622	1 620	
1 605	1 580	CO stretch
1 468	1 485 1 470	CN stretch

^a Ref.⁴.

and that of the CN bond at 1488 cm^{-1} . The bands in the region of $3500\text{--}3400\text{ cm}^{-1}$, attributed to the stretching vibrations of the NH bonds, are found at higher wavenumbers as compared with nonbonded urea. Figures 3 and 4 represent the infrared spectra of the complexes of Na(I) and Ca(II) montmorillonite with urea, resp. A detailed analysis of those urea complexes based on infrared spectroscopy is rather difficult. The sorption isotherms of those forms have indicated that adsorption on the surface predominates, so that the bands of the complexes formed do not appear clearly. The figures show also the spectra measured *in vacuo* at the temperatures 20, 50, 100, 150, 200, 250, and 300°C , resp. The spectra indicate a gradual decomposition of the urea complexes occurring on increasing the temperature. The bands at 3410 and 3300 cm^{-1} for the Na-form and at 3334 and 3240 cm^{-1} for the Ca-form were attributed to the NH vibrations of ammonia adsorbed on the surface¹¹. The band at 1600 cm^{-1} vanishes in the case of the Ca-form on increasing the temperature. The thermal decomposition of the urea complex in the presence of a certain amount of interlayer water can be expressed, in accordance with Mortland¹², by the following equations:



where $\text{M} = \text{Cu(II)}, \text{Co(II)}, \text{Ca(II)}, \text{Na(I)}$.

By means of X-ray analysis we followed the changes in the values of the interplanar spacing before and after the sorption of urea. The sorption of urea was achieved by treating the cation-exchange forms of montmorillonite with an aqueous solution of urea. The values d_{001} (in Å) and the amounts of bonded urea, n (in mmol/g), are given in Table III. The values of the interplanar spacing evidence penetration

TABLE III

Values of Interplanar Spacing (Å) Before and After the Sorption of Urea (n , mmol/g) on Montmorillonite

Cation	n	d_{001}	Cation	n	d_{001}
Na(I)	0.0	12.6	Cu(II)	0.0	12.2
	60.0	14.5		56.6	17.7
Ca(II)	0.0	14.6	Co(II)	0.0	13.9
	60.0	15.1		61.6	16.5

of urea into the interlayer space of montmorillonite. The differences in those values can be explained by the different arrangement of the interlayer complexes. The lower values of interplanar spacing for the Na- and C-forms after the sorption of urea, as compared with those for the Cu- and Co-forms with an approximately equal amount of adsorbed urea, can be explained by the adsorption of urea on the surface of the former forms. In the case of the latter forms a marked increase of the d_{001} values appears, which is obviously due to the penetration of urea into the interlayer space of montmorillonite.

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Translated by P. Adámek.