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INVESTIGATION OF THE ADSORPTION OF NONPOLAR ADSORBATE MOLECULES ON THE ILLITE SURFACE

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ABSTRACT

The full thermodynamic characteristics of CO_2 and CH_3OH adsorption on the mineral illite were obtained using the adsorption - calorimetric method. The crystal chemistry of illite was studied using the polar CH_3OH molecule and the quadrupole CO_2 molecule as a molecular probe. The mechanism of adsorption of these molecules, the conformation of the resulting ion/molecular complexes, and the thermokinetics of adsorption were revealed. The adsorption isotherms are studied and described by their corresponding equations. The molecular mechanism of CO_2 and CH_3OH adsorption on illite was studied in the entire filling area. It has been established that under the influence of a polar methanol molecule, K^+ migrate to the basal and lateral faces of illite, filling vacant holes with six-dimensional CH_3OH/K^+ complexes of illite, the state of molecules on the surface is close to liquid - like. The process of migration of cations is completely reversible. It was found that the adsorption of a quadrupole CO_2 molecule on illite does not lead to the migration of cations. Adsorption proceeds on K^+ cations, which occupy the basal one third of the illite surface.

Keywords: *adsorption, adsorbate, thermodynamics, illite, carbon dioxide, methanol, isotherm.*

INTRODUCTION

The widespread use of minerals such as montmorillonite, muscovite, vermiculite, illite and others as adsorbents and catalysts for a number of technological processes of purification, drying, as well as in engineering and other areas of industry is possible due to the peculiarities of their adsorption properties. Many works have been devoted to the research of the adsorption properties of the mineral illite. Some publications have adopted the terminology of G. Brown, which suggests that all forms of clay micas, including illite, should be attributed to hydrosludes.

Among the publications of recent years, it should be noted works on the detailed study of the surface properties of these minerals, the possibilities of their modification, studies of the structures of adsorbed substances and ion exchange on these mica minerals [1 - 6]. The authors of all these work studied the adsorption of hydrate water on the mica surface under environmental conditions using the Monte Carlo method. It is shown that water molecules are adsorbed near ditrigonal cavities on the mica surface, being distributed between K^+ counter ions (approximately one water molecule per potassium pair). Most of these water molecules form a layer perpendicular to the plane with a distance of about 2.5 Å from the surface oxygen atoms. The calculated oxygen atom density profile of water corresponds well to the experimental data obtained by X-ray reflection, indicating a strong transverse ordering of hydrate water in mica, characterized by a generally undirected liquid structure.

The study of adsorption centers on the surface of illite and other clay minerals using radioactive isotopes was carried out in [7 - 9]. The adsorption centers and dynamics of Cs and Na atoms, as well as their mixtures on the surface of illite, kaolinite, belite and silica gel reacted with 0.1 M NaCl solution and a mixture of NaCl and CsCl solutions were studied by ^{23}Na and ^{133}Cs NMR. The ^{23}Na spectra obtained at humidity levels from 0 to 100 % were compared with the Cs spectra. According to chemical analysis, Cs^+ is better adsorbed on illite than on silica gel, which is due to the large surface charge of illite. Illite belongs to the group of phyllosilicates. Any data is not found in the literature that reveals the exact mechanism of hydration of this mineral [10, 11].

EXPERIMENTAL

The studies were carried out on illite - $K_{1-1,5}Al_4[Si_{7-6,5}Al_{1-1,5}O_{20}](OH)_4$. To study the adsorption properties of the mineral, CO_2 and CH_3OH were selected as adsorbates. Carbon dioxide is a technical gas from a cylinder, purified by passing through P_2O_5 и Na_2CO_3. It was frozen and distilled in a glass U-shaped tube connected to an adsorption unit. The purity of the adsorbate was checked by mass spectrometric analysis. Methanol is of the "chemical pure for chromatography" brand, purified from impurities by distillation on a distillation column. The purity of alcohol was determined by the coincidence of the refractive index with the tabular data. The listed nonpolar adsorbents were thoroughly cleaned from heavy and light impurities by the adsorption - evacuation method, by repeated pumping during freezing, alternating with melting.

The adsorption - calorimetric method used in this work allows us to obtain high precision molar thermodynamic characteristics, as well as to reveal in detail the mechanisms of adsorption processes occurring on adsorbents and catalysts. The adsorption measurements and the dosage of the adsorbate were carried out using a universal high vacuum adsorption unit, in the working part of which only mercury valves were used, replacing valves with lubrication. The installation allows for the dosage of adsorbate by both gas - volume and volume - liquid methods. A modified DAK 1-1 calorimeter with high accuracy and stability was used as a calorimeter.

RESULTS AND DISCUSSION

Illite is similar in composition to the mineral muscovite, the main difference is a deficiency of K^+, which is compensated by a lower content of A1^{1V}. Usually, but not always, A1^{1V} is partially replaced by Mg, Fe^{3+} и Fe^{2+}.

Herein, we conduct a detailed study of the process of hydration of illite from zero fillings to saturation. Previous studies revealed that the adsorption of water on muscovite leads to the migration of cations from neighboring layers to the basal and lateral surfaces and the filling of vacant centers [12 - 15].

In order to study the initial surface, which is not complicated by the process of cation migration, our investigation started with the adsorption of CO_2 on the illite (Fig. 1). Given the relatively large size of CO_2 and the fact that a linear quadrupole molecule has relatively small charges on oxygen atoms compared to a polar water molecule, a sharp decrease in the energy of the ion-quadrupole interaction should be expected, and also that the CO_2 molecule is not able to extract cations from the illite volume. The sample was pumped out at a temperature of 723 K. In the initial region, the heat drops sharply, starting from 53 to 40 kJ·mol^{-1} at 4.3 μmol·g^{-1}.(Fig. 2). Then the drop becomes smoother

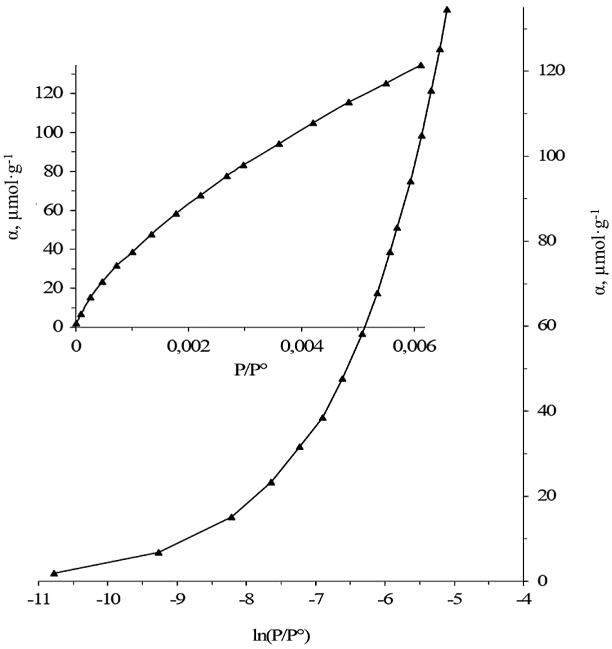

Fig. 1. Isotherm of CO_2 adsorption on illite at 303 K.

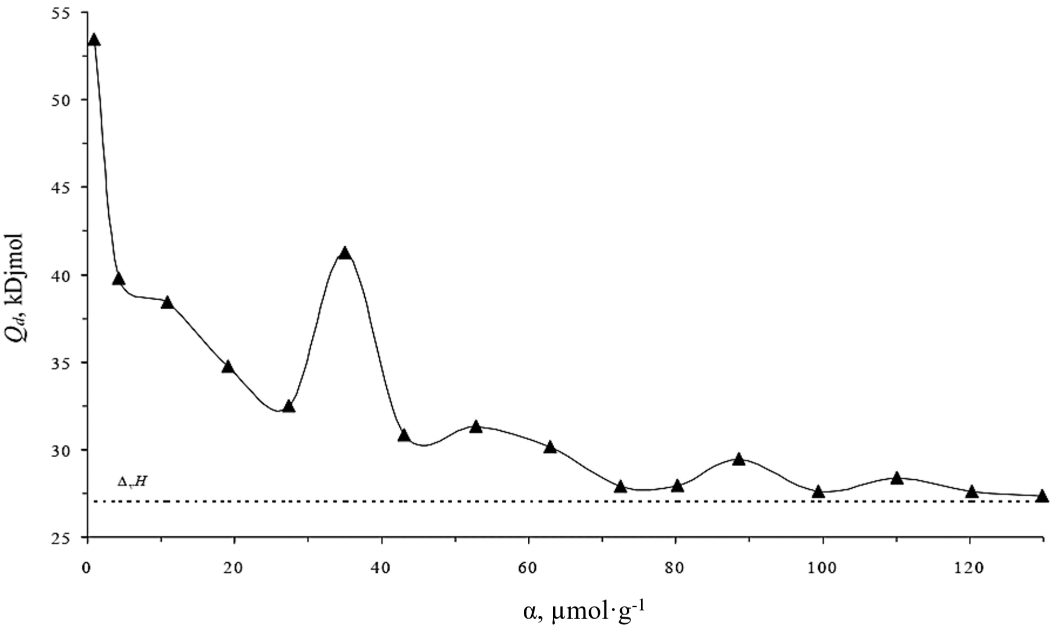

Fig. 2. Differential heat of CO_2 adsorption on illite at 303 K. (Dashed line - heat condensation of methanol at 303 K).

to 31 kJ·mol^{-1} at a = 27.4 µmol·g^{-1}. As in the case of muscovite, the curve passes through a sharp maximum (*Qd* = 35 kJ·mol^{-1}), then falls to 30.8 kJ·mol^{-1} at a = 40.1 µmol. Then the curve passes through another gentle maximum, ending at 77 µmol·g^{-1}. Further, the adsorption takes place at the level of the heat of condensation. The region of inhomogeneity (0 - 4.3 µmol·g^{-1}) at small fillings of the surface of the illite with CO_2 is apparently due to the presence of defective and/or impurity cations on the surface, with which CO_2 is adsorbed with increased heats. Such high adsorption energy (53 kJ·mol^{-1}) assumes that polyvalent cations are impurities, since the mono-valence Na^+ or Li^+ cations located in hexagonal wells are adsorbed with a heat of ~36 kJ·mol^{-1} [15]. Further, the adsorption is carried out on K^+ up to 77 mmol·g^{-1}. The reason for the appearance of the maximum is the tendency of the adsorbed CO_2 molecules to self-associate. In this case, the energy of the adsorption of CO_2 on the illite is additionally superimposed on the energy of the adsorbate - adsorbate interaction, which leads to an increase in heat.

Such a high maximum on the Q_d curve is explained by the fact that first of all, CO_2 molecules adsorbed on high-energy defect and/or impurity centers and on the neighboring K^+ cation are associated, and then on two neighboring potassium cations. On the Q_d curve, these mechanisms are implemented on the left and on the right side of the maximum, respectively. Thus, the basal surface of the illite contains ~77 µmol·g^{-1} of K^+ cations. Extrapolation of Q_d to zero filling cuts off on the axis the heat equal to the heat of adsorption of CO_2 with a potassium cation, equal to 31 kJ·mol^{-1}. Fig. 3 shows the molar differential entropy of CO_2 adsorption on illite, calculated from the differential heat of adsorption and the adsorption isotherm. The straight dashed line is the

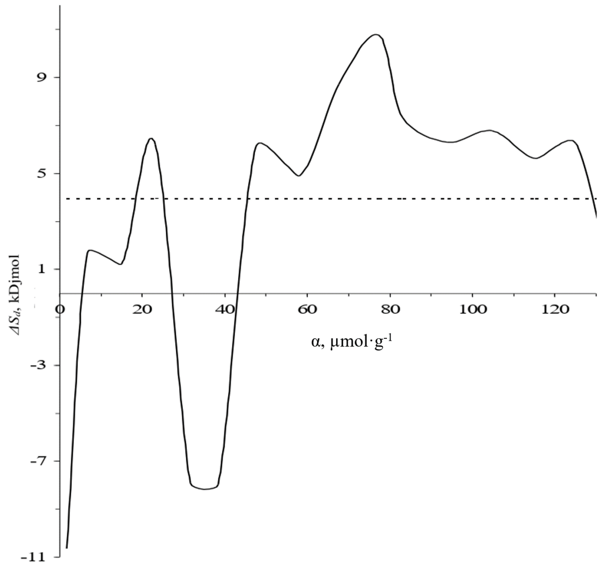

Fig. 3. Mole differential entropies of CO_2 adsorption on illite at 303 K.

average mole integral entropy. The entropy of liquid CO_2 is taken as zero. The mean molar integral entropy is equal to + 3.94 J $mol^{-1}K^{-1}$.

The mobility of adsorbed CO_2 is slightly higher than the entropy mobility of liquid CO_2. Thus, it could be concluded, that the state of CO_2 on the surface of the illite is liquid - like. To test the surface properties of illite, methanol was used. It differs from water in the size and the ability to additionally participate into hydrophobic interaction with the surface. The isotherm of methanol adsorption on the fly out was measured at 303 K (Fig. 4).

The isotherm in the coordinates of the BET equation is linear in the range of relative pressures of $0.04 < P/P < 0.26$. The capacity of the monomolecular layer (a_m) was 1169 μmol·g^{-1}, and the specific surface area for methanol was 140 m^2 g^{-1}, if the area occupied by a methanol molecule in a dense monomolecular layer (ω_m) is taken as $Å^2$. Fig. 4 shows that the isotherm has a stepped form. The equilibrium pressure at small fillings reaches $P/P° = 1.5\times10^{-6}$, which indicates a strong adsorption of methanol.

In the initial region of methanol adsorption on the illite, the pressure increases slowly, then an exponential increase in pressure is observed until the illite is saturated with methanol. As expected, the Q_d curve has a stepped form (Fig. 5). Dashed line shows the heat condensation of methanol at 303 K.

Adsorption begins with a high heat of 95 kJ·mol^{-1} and drops sharply to 62 kJ·mol^{-1} at 230 μmol·g^{-1}. From the adsorption of CO_2, it was found that the initial surface contains 77 μmol·g^{-1} of K^+ cations. However, we got a figure 3 times higher. Consequently, the vacant centers, as in the case of muscovite, were filled with K^+ cations due to the adsorption of methanol [15, 16].

At this stage, a monomeric H_2O/K^+ complex is formed on the basal surface. Further, the heat decreases from 62 to 54.6 kJ·mol^{-1} in the adsorption range from 230 to 469 μmol·g^{-1}, at which a two-dimensional complex is formed. Three-dimensional and four-dimensional complexes are formed in the adsorption range from 469 to 922.5 μmol·g^{-1} with a heat decreasing from 54.6 to 53.3. Five-and six-dimensional complexes are formed

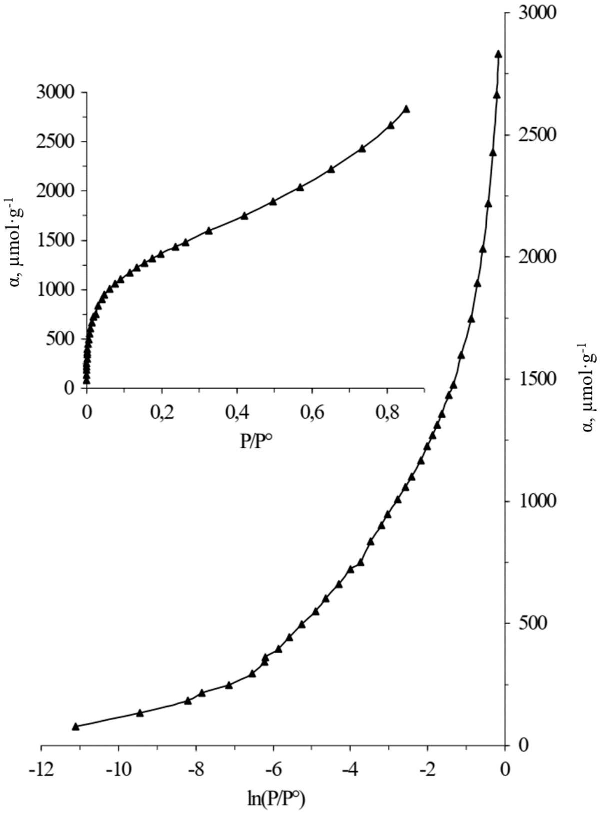

Fig. 4. Isotherm of CH_3OH adsorption on illite at 303 K.

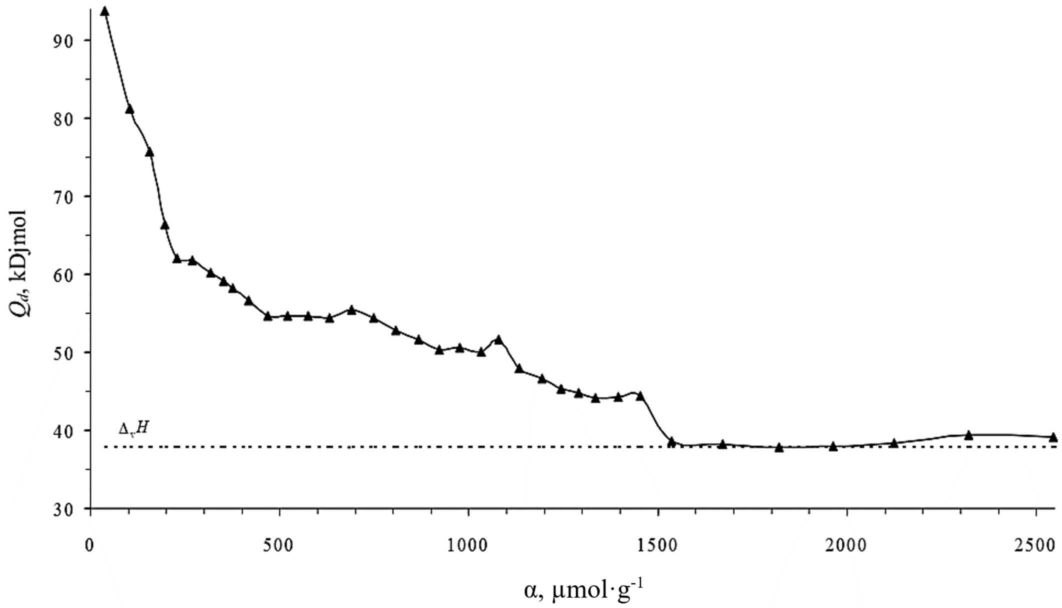

Fig. 5. Differential heat of methanol adsorption on illite at 303 K.

in the adsorption range from 922.5 to 1382 μmol·g^{-1} with a heat varying from 53.3 to 44.2 kJ·mol^{-1}. Further, the adsorption proceeds without the direct participation of cations with the formation of hydrogen bonds with pre-adsorbed methanol molecules.

Using the isotherm and the differential heat of adsorption of methanol on illite, the molar differential entropy of adsorption (*ΔS_a*) was calculated using the Gibbs-Helmholtz equation (Fig. 6). The dashed line is the mean molar integral entropy. The entropy of liquid CH_3OH is assumed to be zero.

Fig. 6 shows the differential entropies of adsorption at 303K, deferred from the entropy of liquid methanol. In accordance with the stepwise nature of the heat curve, the entropy has a polyextremal form. Up to a = 1500 μmol·g^{-1}, it is located below the entropy of liquid methanol. And above-it crosses the zero line and rises up and immediately slowly decreases due to the interaction of adsorbate-absorbate. The mean-value differential entropy is equal to -11.7 J·mol^{-1} ·K. The mobility of methanol molecules on the illite surface is lower than in liquid methanol. The thermokinetic data are presented in Fig. 7.

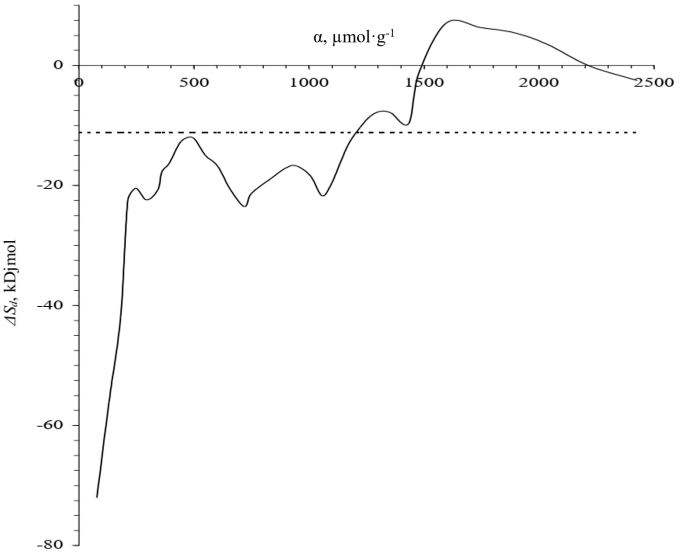

Fig. 6. Differential entropies of CH_3OH adsorption on illite at 303 K.

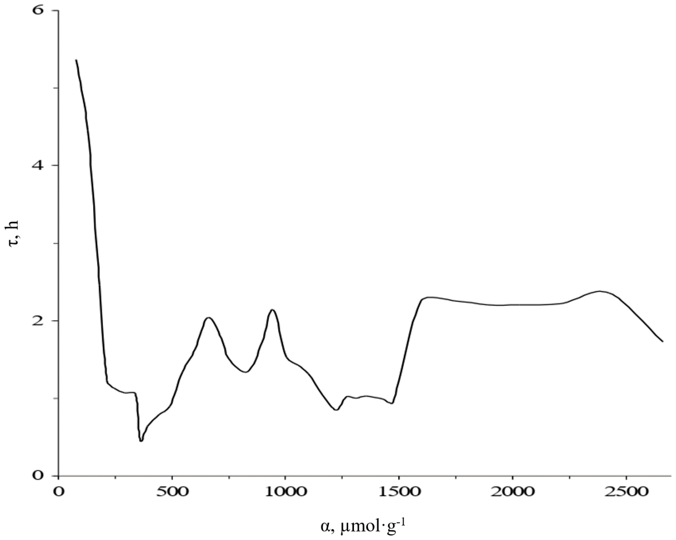

Fig. 7. The time of establishing the adsorption equilibrium depending on the value of the adsorption of CH_3OH on the illite at 303 K.

It is possible to trace the dependence of the time of establishing the adsorption equilibrium on the filling of the surface, taking into account the obtained data. The dependence shows that the formation of the monocomplex proceeds at a very slow rate - 5.5 hours. The deceleration of the velocity is associated not only with the redistribution of methanol molecules on the surface, but also with the migration of cations from neighboring layers to the surface. The speed deceleration is also observed during the formation of the third and fourth layers. Then the speed increases again. An interesting fact is that the formation of the second adsorption layer proceeds at a slow speed.

CONCLUSIONS

In this paper, the complete thermodynamic characteristics of the adsorption of systems of nonpolar (quadrupole) CO_2 and CH_3OH molecules with illite are studied in detail. The correlation between the adsorption - energy characteristics and the crystal - chemical structure of adsorbents is found and the molecular mechanism of adsorption of CO_2 and CH_3OH on illite in the entire region of pore space filling is revealed.

It is established that when polar methanol molecules interact with K^+ illite cations, six-dimensional CH_3OH/K^+ complexes are formed that fill the vacant wells of illite. It is established that the adsorption of a quadrupole CO_2 molecule on the illite does not lead to cation migration. The adsorption proceeds on K^+ occupying one third of the illite surface.

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