

Adsorption Isotherm, Differential Heat, Entropy and Thermokinetics of Benzene Vapor in Pakistan Bentonite

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Abstract As a result of changes in the chemical structure of rocks under various influences, clay minerals are formed in nature. Aluminum oxide and silicon oxide serve as the basis of clay minerals. By determining the specific surface area of mineral adsorbents of molecular adsorption in different shapes and structures, the study of the laws of surface chemistry on the basis of the laws awakens a great interest. Based on the energy properties formed during the adsorption of adsorbate molecules, it is possible to determine the structure of the bentonite-forming layers, the migration of cations. Owing to the low charge value and weak electrostatic interaction between the three-layer surface and the multi-layer cations, minerals of the montmorillonite group are capable of multilayer sorption of various substances - cations, water molecules and many organic compounds. Saying differently, the processes of metabolism, absorption and desorption of substances in this group of minerals can occur not only on the outer but also on the inner surfaces of crystallites. The data obtained contribute greatly to the development of the theory of adsorption forces and intermolecular interactions. Determination of adsorption isotherm, differential heat and thermokinetics of benzene in Pakistan bentonite was carried out using adsorption calorimetry method in high vacuum adsorption device. They are based on differential molar entropy and free adsorption energy. The mechanism of benzene adsorption on this bentonite has been fully elucidated. Adsorption isotherms were described using BET and Langmuir equations.

Keywords Isotherm, Differential heats, Differential entropies, Thermokinetics, Pakistani bentonite, Ammonia, Adsorption calorimetry

1. Introduction

Clays are mainly composed of microcrystalline particles of a small group of minerals called clay minerals [1]. Clay minerals involve in naturally occurring layered and layered chain silicates, and allow to add layers that are mainly formed during chemical decomposition of rocks, accumulation of sediments, as well as their post-sedimentation, including in the process of hydrothermal action or in other ways [2]. One of the important features of the crystal structure of clay minerals is their active interaction with water.

Bentonite clays (bentonites) are considered mineral products adjuncting of the class of aluminosilicates [3]. Originally, bentonites are formed as a result of changes in volcanic rocks or are considered autigenic minerals [4], i.e., minerals of sedimentary rocks are formed as a result of sedimentation or subsequent sedimentation [5].

The most actual mineralogical component of bentonite

clays is smectite (clay mineral). For this reason, the great attention is paid to the mineralogical analysis of smectites. Smectite minerals are divided into two subgroups: dioctahedron and trioctahedron [6].

Only 2/3 of all octahedral cavities are filled with cations in dioctahedral smectite, and Al^{3+} cations are mainly located in the center of the octahedrons. Whereas, in trioctahedral smectites, all octahedral areas are filled with cations, and Mg^{2+} cations are located mainly in the center of the octahedron [7].

The high absorption capacity of clays composed of minerals of the montmorillonite group is widely used in various fields [9].

Vermiculite and montmorillonite have the highest absorption capacity of all clay minerals (80–150 mg-eq/100 g). The high sorption capacity of montmorillonite is associated with the exchange of ions not only on the outer surface of its crystals, but also inside the crystal lattice in the spaces between the silicon-oxygen tetrahedral layers. The mechanism of sorption of water contaminants from clay minerals is very complex and is caused by various chemical effects: hydrogen bonds, ion-dipole and ion-ion interactions, coordination bonds, acid-base reactions, and

Van-Der Waals forces [4,9].

2. Object and Methods of Research

The differential heat of adsorption was measured on DAK 1-1 calorimeter of a Tean-Calvet model. The volumetric method was used in the determination of adsorption isotherm. The accuracy error of the adsorption isotherm is 0.1% and of the heat is up to 1% [10].

Benzene obtained as an adsorbate was purified and dried under vacuum conditions before using in sorption. Dissolved gases were removed until its vapor pressure was the same as the vapor pressure data given in the tables for pure benzene. Then, it was determined to be consistent with the data presented in the literature [11].

Benzene adsorption on Pakistan bentonite was carried out at 303 K.

3. Results and Discussions

In Figure 1, the isotherm of benzene adsorption in Pakistani bentonite is presented in semi-logarithmic coordinates. The initial logarithmic value of the adsorption isotherm is -9.58. In the later stages of benzene adsorption in bentonite, the isothermal lines gradually rise. The logarithmic value of the isotherm of 200 $\mu\text{mol/g}$ of sorbed benzene molecules is -5.5, in which the adsorbates are localized. The inner adsorption layer of 200 $\mu\text{mol/g}$ clay minerals is filled with benzene. When the adsorption reaches 800 μmol , the isotherm value is -1.32. In the subsequent absorption of benzene molecules tends towards the adsorption axis, and when it reaches 1600 $\mu\text{mol/g}$, benzene reaches saturation levels.

The adsorption isotherm is linear in the coordinates of the BET equation in the range of relative pressures $0.017 < P/P^0 < 0.39$. The capacity (a_m) of the monomolecular layer was 605 mkmol/g and the energy constant was 1.01. If the

specific surface area for benzene is $174 \text{ m}^2/\text{g}$, the area occupied by the benzene molecule in the dense monomolecular layer (ω_m) is assumed to be 48 \AA^2 . These values are expressed in the Langmuir equation.

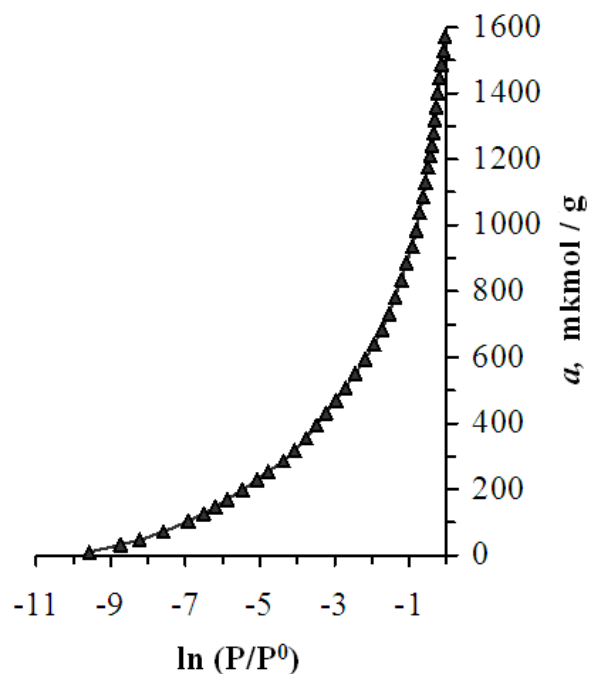


Figure 1. Benzene vapor adsorption isotherms in Pakistan bentonite at 303 K

In the surface monomolecular filling area of benzene molecules, the differential heat (Q_d) in Pakistani bentonite decreases in a wavy manner (Figure 2). In the adsorption of benzene in bentonite, the differential heat initially decreases from 82.9 kJ/mol to 64.80 kJ/mol in the initial fields. Adsorption is 72 kJ/mol at 59.2 mkmol/g . At benzene adsorption up to 213 mkmol/g , cations of alkali and alkaline earth metals (Na^+ , Ca^{2+}) in bentonite are characterized by the formation of π -complexes. Usually bentonites are divided into three layers.

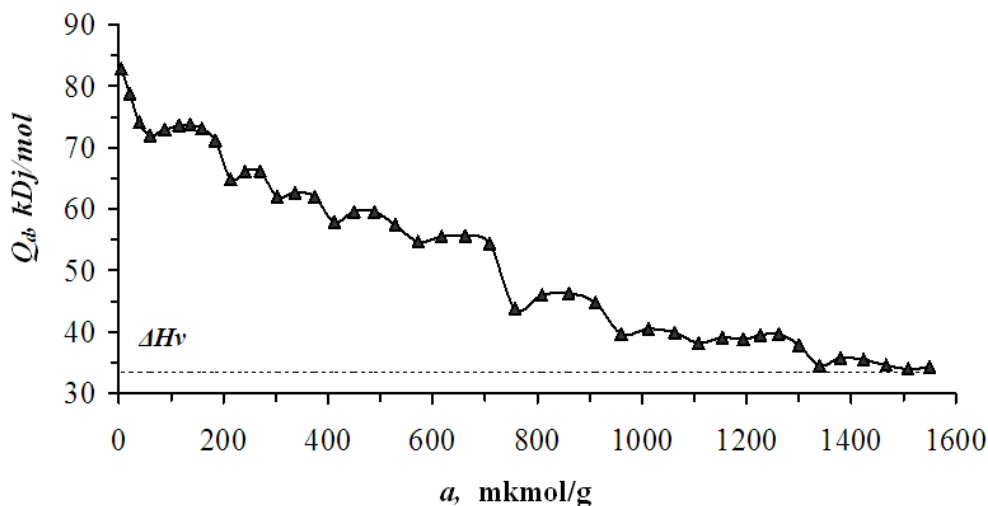


Figure 2. Differential heat of benzene adsorption on Pakistan bentonite at 303 K. Benzene adsorption at 303 K Horizontal dashed lines - heat condensation

When the amount of absorbed benzene molecules reaches 200 mkmol/g, adsorption differential heat indicators indicate that sorption of the clay mineral to the inner interlayer surface occurs. In the next step, the benzene molecules go to the edge surface layer and their adsorption ranges from 200 kDj/mol to 750 kDj/mol. At the same time, the adsorption heat decreases from 82.9 kDj/mol to 43.8 kDj/mol. The adsorption process in this layer has a complex character, mainly due to the migration of cations. In this case, the empty cells are filled with π -complexes of benzene with cations due to the migration of cations in the adjacent layer. Therefore, in the Q_d curve, a decrease in the adsorption heat in the form of a wave is observed. In the next stages, benzene adsorption is observed in the outer, ie the adsorption process in the basal layer. At this stage, it gradually reaches a value of thermal condensation of 43.8 kDj/mol. In this case, the low adsorption heat occurs under conditions of insignificant participation of cations in benzene molecules.

In Figure 3, the differential entropy of benzene adsorption on Pakistani bentonite was presented. The formula of the Gibbs-Helmholtz equation was used to calculate the differential entropy using the differential heat and isotherm

values of benzene adsorption in Pakistani bentonite [12].

$$\Delta S_d = \frac{\Delta H - \Delta G}{T} = \frac{-(Q_d - \lambda) + A}{T}$$

λ - condensation of the heat, ΔH and ΔG - enthalpy and free energy change, T - temperature, Q_d - average differential heat.

The entropy curve, which corresponds to the waveform curve of adsorption heat, also has a polyextrimal shape. In the surface monomolecular area, the curve is close to the entropy of the liquid benzene, indicating that the mobility of the benzene is close to that of the liquid. When layer 2 is filled, the entropy is lower than the liquid benzene entropy. Consequently, the mobility of benzene in this layer is slightly slower than that of liquid benzene. Adsorption without the participation of cations leads to an increase in entropy, and it passes through the zero level and grows in the positive region, which indicates an increase in the mobility of benzene relative to the movement in the liquid. The average molar integral entropy is -36.54 Dj/mol*K, so the state of benzene in a benzene bentonite system is similar to that of a liquid.

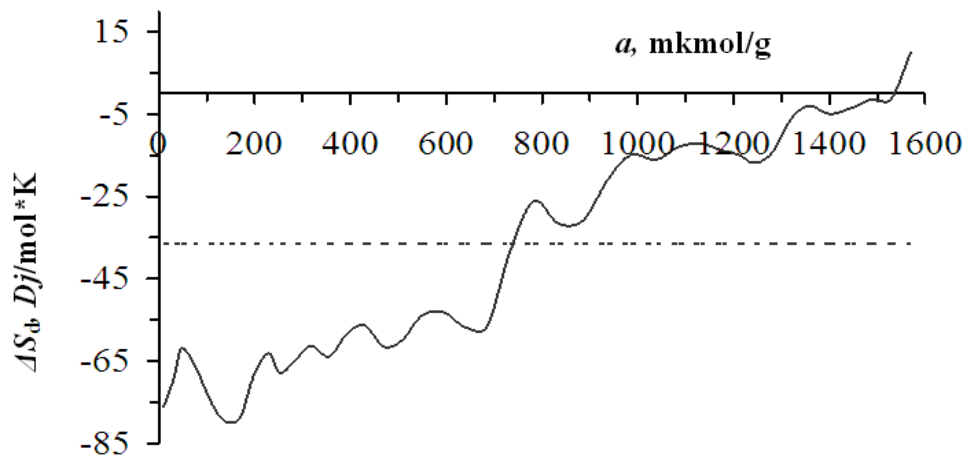


Figure 3. Differential entropy of benzene adsorption on Pakistan bentonite at 303K temperature. Horizontal bar lines are the mean integral entropy

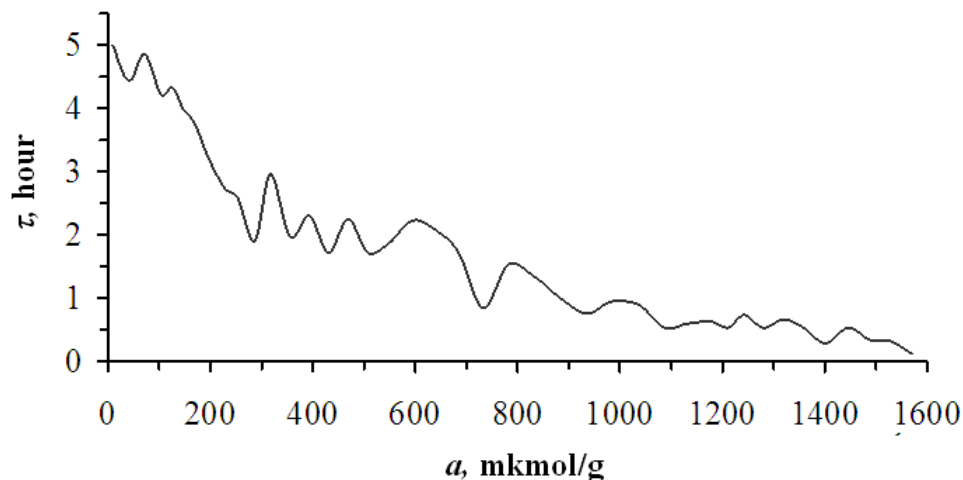


Figure 4. Equilibrium time of benzene adsorption in Pakistan bentonite at 303 K temperature

The adsorption equilibrium time shows that the equilibrium time is as high as the differential heat of adsorption in the interlayer until it reaches 200 mkmol/g (Figure 4). At this stage, the benzene molecules go away in 3-5 hours. In the next stage layer, the equilibrium appears in 1 hour. In the last outer basal layer, equilibrium is reached in 20 minutes during the final stages of adsorption.

4. Conclusions

It was found from the low sorption of benzene molecules in the inner layer of bentonite that the number of sorption cells was less than in other layers. The adsorption heat at initial fillings is 82.9 kDj/mol. The differential heat of adsorption decreases in the form of a wavy step. Based on the values of the adsorption isotherms, the specific surface area was determined using the BET and Langmuir equations. The average integral entropy value is -36.5 Dj/mol*K. The adsorption equilibrium time initially starts at 5 hours and decreases to a few minutes depending on the gradual saturation of the bentonite layers.

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