Benzene Adsorption Energy in Activated Azkamar Bentonite Samples

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Annotation. Clay minerals are based on aluminum, silicon oxide and other alkaline and alkaline earth metals. Clay minerals have different shapes and structures depending on the environment. Researchers are interested in studying the specific surface area of clay mineral adsorbents by adsorption of polar and non-polar molecules on the basis of the laws of surface chemistry. Based on the adsorption properties in the sorption of adsorbate molecules, it is possible to determine the structure of the sorption layers that form bentonite, the migration of cations.Due to the low charge value and weak electrostatic interaction between the three-layer surface and the multilayer cations, the minerals of the montmorillonite group are capable of multi-layer sorption of various substances, cations, water molecules, and many organic compounds. In other words, in this group of minerals, the processes of metabolism, absorption and desorption can take place not only on the outer surface, but also on the inner surface of the crystallite. The obtained data contribute to the development of the theory of adsorption forces and intermolecular interactions. Determination of benzene adsorption isotherm, differential temperatures and thermokinetics in Azkamar bentonite was carried out using the method of adsorption calorimetry in a high vacuum adsorption device. They are based on differential molar entropy and free adsorption energy. Adsorption isotherms were described using BET and Langmuir equations. The mechanism of benzene adsorption in this bentonite is fully explained.

Keywords: Isotherm, differential heats, differential entropies, thermokinetics, Azkamar bentonite, ammonia, adsorption calorimetry.

Kirish.Adsorption from solutions or liquid mixtures is a common subject of both scientific research and industrial applications. Adsorption from solution has been applied in diverse fields such as chromatography, lubrication, adhesives, enhanced oil recovery, bleaching, catalysts, paint, food, cosmetics and waste water treatment [1–4]. In spite of the great importance of adsorption from solution onto solids for natural systems and industrial processes, development in this field has been slow. Various studies of adsorption from aqueous and non-aqueous solutions onto solids were conducted [5–8]. A few articles published recently could be found on this subject [9–13]. Theories of adsorption from solutions have been developed with reference to widely used active carbon [14–17]. The growing importance of other porous solids such as alumina, silica gel, clay minerals and their derivatives, as well as various catalysts, suggested the application of current theories of adsorption to such adsorbents [18–20]. Orientation of molecules on the solid surface, preferential adsorption, and thickness of the adsorbed layer which are dependent to the physicochemical properties both solid surface and adsorbents have not been explained completely.

The lower sorption of benzene molecules in the inner layer of bentonite was characterized by a lower number of sorption cells than in other layers. The initial adsorption heat is 82.9 kJ/mol. The differential heat of adsorption decreases in a wavy step.

The low sorption of benzene molecules in the inner layer of bentonite showed that the number of sorption cells was lower than in other layers. The initial adsorption heat is 82.9 kJ/mol. The differential heat of adsorption decreases in a wavy step [21].

Adsorption processes can be studied in different ways. Calorimetric studies in a highvacuum adsorption device are rare in calculating the amount of adsorbed molecules. Research on synthetic zeolites, clay minerals and other types of sorption substances has been carried out in this way. [22-27].

MATERIALS AND METHODS. The differential heat of adsorption was measured on the Tian-Kalve model DAK 1-1 calorimeter. Adsorption isotherm was used in the determination of the volumetric method. The adsorption isotherm has an error of 0.1% and a heat of up to 1% [28].

Benzene obtained as an adsorbate was purified and dried under vacuum conditions before use in sorption. The dissolved gases were removed until its vapor pressure was the same as the vapor pressure data given in the tables for pure benzene. It was then determined that it was consistent with the information provided in the literature.

Benzene adsorption was performed at 303 K in the activated byentonite samples studied.

RESULTS AND DISCUSSION.Enrichment method is used to clean the composition of Azkamar bentonites from sands. First, samples of bentonite are placed in an agate mortar and finely ground in a laboratory, and large pieces of sand and rock and unbroken residue are sieved to separate the sample. It is then placed in 1-liter containers. Distilled water is added and left for 4 hours, during which the bentonite swells under the influence of water and sinks under the influence of gravity. The container is then cleaned of various water-insoluble additives that fall to the bottom. This process is repeated three times. Centrifuged bentonite is separated to completely separate the bentonite from the water. It is then dried first at room temperature and then in a drying oven at 105 $^{\circ}$ C for 2 hours.

The next step was acid activation of the enriched bentonite. The main mechanism of acid activation consists of the following stages:

- 1. 1. Exchange of ion(Sa²⁺, Mg²⁺, Na⁺, K⁺) exchange complexes for hydrogen ions;
- 2. Dissolution of oxides (R_2O_3) ;
- 3. Disruption of the crystal lattice as a result of dissolution of Al^{2+} , Fe^{3+} , Mg^{2+} ions and exchange with Si4 + in the octahedron.

Acid activation does not reduce the size of the existing pores of bentonite (1.5 mm) but does lead to the formation of transition pores and increase the porosity of the system. Therefore, the high whitening property of activated montmorillonite can be explained by its sour properties.

There is a lot of information in the literature about acid activation. However, for bentonites from different deposits, the acid content and conditions of its activation are different. In particular, the selection of organic acids is important to determine the optimal norms that preserve the structural properties of the clay mineral. It should be noted that the determination of the optimal concentration of organic acid also depends on the initial parameters of bentonite. With this in mind, acid activation was performed in the laboratory. Azkamar bentonite was used as the object. The traditional method of activation was used. That is, the acid concentration was 10–20%, the solid medium in a ratio of 1: 3 and 1: 5 to the liquid medium, for 2–4 h [10,11]. The results obtained are presented in Table 1.

Activati	Acid concentration, N ₂ SO ₄						Acid concentration, NSI					
on time,	10		15		20		10		15		20	
nours	The amount of oxides, %						The amount of oxides, %					
	Si	Al ₂	SiO ₂	Al ₂	SiO ₂	Al ₂	SiO ₂	Al ₂	SiO ₂	Al ₂	SiO ₂	Al ₂
	O ₂	O ₃		O ₃		O ₃		O ₃		O ₃		O ₃
2	62,	18,7	63,1	18,4	63,5	17,8	61,9	17,9	62,4	17,1	63,5	16,8
	3											
4	67,	17,4	68,8	15,5	68,6	14,5	66,6	16,4	67,2	16,1	66,5	15,6
	5											
6	71,	14,9	73,8	13,4	75,7	12,6	70,2	15,9	72,4	14,4	73,8	13,7
	8											
8	80,	12,2	81,7	11,5	82,4	10,4	75,4	14,3	76,5	13,8	77,2	13,1
	3											

 Table 1

 Changes in the basic oxides in bentonite under the influence of acid activation

As can be seen from Table 1, there were significant changes in the chemical composition of the bentonite after acid activation. In particular, an increase in SiO_2 and a decrease in Al_2O_3 can be observed in the crystal lattice. This can be explained by the isomorphic exchange of Si^{4+} to Al^{3+} ; Al^{3+} to Mg^{2+} ; Fe^{3+} to Al^{3+} ; $2Al^{3+}$ to $3Mg^{2+}$; $3Fe^{2+}$ to $2Al^{3+}$ [12,13].

Based on the results obtained, it can be concluded that the exchange of exchangeable cations for complete hydrogen ions under certain conditions resulted in the disruption of the crystal lattice of the clay mineral, as well as maximum sorption and catolytic activity. Therefore, it was found that acidic activation should be carried out at an acid concentration of 15%, solid-to-liquid ratio 1: 4, activation duration 4 hours. Continuing the process with the help of acid leads to the destruction of the crystal lattice and the washing away of aluminum and some valuable components.

For acidic activation of azkamar bentonite, N_2SO_4 acid was found to be more suitable than NSI acid. This is due to the low CaO content of bentonite, which has shown better performance than NSI acid.

Thus, the acidic activation of clay minerals is a complex process that depends on the structure, nature, type of acid, and processing conditions of the aluminosilicate. In this case, the processed material is radically different from the original.

In the study, Azkamar bentonite was activated by adsorbents activated in two acids, namely hydrochloric and sulfuric acid. Therefore, in the following lines, azkamar bentonite-1 (HCl) and azkamar bentonite-2 (N_2SO_4) are indicated. Figure 1 shows the isotherm of benzene adsorption of Azkamar bentonite-1 (HCl) and Azkamar bentonite-2 (N_2SO_4) in semi-logarithmic coordinates.



Figure 1. Benzene vapor adsorption isotherms in samples 1-Azkamar bentonite-1 and 2-Azkamar bentonite-2 at 303 K.

The initial logarithmic value of azkamar bentonite-1 (HCl) benzene adsorption isotherm is -10.08, the initial isotherm value of Azkamar bentonite-2 in the second sample is -10.30. In bentonite of two different samples, the isothermal lines of benzene adsorption gradually rise and move towards the adsorption axis.

In the samples of activated Azkamar bentonite, the logarithmic value of the sorbed benzene molecules 200 μ mol/g isotherm is -5.75, in which the adsorbates are partially localized, that is, the inner adsorption layer of 200 μ mol/g clay minerals is filled with benzene. When the adsorption reaches 800 μ mol, the isotherm value is -1.55 (HCl), -1.32 (H₂SO₄). In the subsequent absorption of benzene molecules tends towards the adsorption axis, and azkamar bentonite-1 1355 mkm/mol, azkamar bentonite-2 benzene saturation reaches 1644 mkm/mol.



Figure 2. Differential heat of benzene adsorption in samples 1-Azkamar bentonite-1 and 2-Azkamar bentonite-2 at 303 K. Benzene adsorption at 303 K Horizontal dashed lines - heat condensation.

The adsorption isotherm is linear in the coordinates of the BET equation in the range of relative pressures $0.017 < P/P^{o} < 0.39$. The capacity of the monomolecular layer was (a_{m}) 617 µmol / g in the first sample and the energy constant value of 637 µmol/g in the second sample was 1.01. The specific surface area for benzene is 178 m² / g in Azkamar bentonite-1 and 184 m² / g in the second Azkamar bentonite-2, where the benzene molecule occupies a dense monomolecular layer (ω_{m}) of 52 Å². These values are expressed in the Langmuir equation.(Q_{d})

In Azkamar bentonite, which is activated in the field of surface monomolecular filling of benzene molecules, the differential heat (Q_d) of the samples decreases in the form of waves (Fig. 2). In the adsorption of benzene in activated bentonite-1, the initial differential temperature in the initial areas decreases from 85.1 kJ/mol to 66.50 kJ/mol, with an adsorption of 18 µmol/g.The adsorption is 74.10 kJ/mol at 39.1 µmol/g, with a slight increase in the adsorption heat. At benzene adsorption up to 250 µmol/g, the cations of alkali and alkaline earth metals (Na⁺, Ca²⁺) in bentonite are characterized by the formation of p-complexes. Bentonites are usually divided into three layers. The differential heat of adsorption shows that when the amount of benzene molecules absorbed reaches 250 µmol/g, sorption of the clay mineral occurs on the inner interlayer surface. In the next step, the benzene molecules travel to the edge layer, where their adsorption ranges from 250 kJ/mol to 701 kJ/mol. At the same time, the adsorption heat decreases from 60.14 kJ/mol to 48.9 kJ/mol. In this layer of clay minerals, the adsorption process is complex, 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, the adsorption heat decreases in the form of waves. In the next stages, the adsorption of benzene is observed in the outer, ie in the basal layer. At this stage, the rate of thermal condensation is gradually reduced from 48.9 kJ/mol.

The differential heat of adsorption of activated bentonite-2 benzene initially starts at 98.58 kJ/mol, and the adsorption rate starts at 4 μ mol/g. For the initial 14 μ mol/g benzene

adsorption, the differential heat decreases from 95.58 kJ/mol to 72.92 kJ/mol. Subsequent adsorption processes of benzene molecules consume 107 μ mol/g of benzene molecules to decrease from 72.92 kJ/mol to 62.11 kJ/mol. Adsorption forms two identical steps in the range of 121 μ mol/g to 741 μ mol/g, and the adsorption decreases from 62.3 kJ/mol to 53.4 kJ/mol. These steps can be explained by the formation of π -complexes with a gradual decrease in adsorption temperatures. Adsorption is 38.90 kJ/mol when it reaches 1050 μ mol/g. The adsorption heat lines are then corrugated to the condensation heat lines. The total adsorption rate is 1644 μ mol/g.



Figure 3. Entropy of 1-Askamar bentonite-1 and 2-Askamar bentonite-2 benzene adsorption at 303 K. Horizontal bar lines are the

mean integral entropy.

Figure 3 shows the differential entropy of benzene adsorption of Azkamar bentonite-1 and azkamar bentonite-2. 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.

$$\Delta S_{\rm d} = \frac{\Delta H - \Delta G}{T} = \frac{-(Q_{\rm d} - \lambda) + A}{T}$$

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

The entropy curve has a wavy shape, corresponding to the wavelength curve of adsorption heat. In the monomolecular area of the surface, 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 the 2nd layer is filled, the entropy is lower than the entropy of liquid benzene. 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, which 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.

Benzene adsorption in Azkamar bentonite samples can be seen from the entropy lines, where benzene initially starts at -55 J/mol*K and -75 kJ/mol. Entropy lines of up to 1000 μ mol show that the second sample is lower than the first sample. This indicates an increase in the number of surface surfaces of bentonite samples activated with sulfuric acid, i.e., the removal of

salts from the adsorption layers on the surfaces, which have a negative effect on various sorption processes. This in turn activates the sorption centers. The average molar integral entropy is - 34.51J/mol*K in low-bentonite-1 and -42.35 J/mol*K in the second sample.



Figure 4. Equilibrium time of 1-Azkamar bentonite-1 and 2-Azkamar bentonite-2 benzene adsorption at 303 K

The adsorption equilibrium time indicates that the equilibrium time is as high as the differential heat of adsorption in the interlayer until it reaches 600 μ mol/g (Figure 4). At this stage, the benzene molecules travel for 3-5 hours. After 600 μ mol/g, the equilibrium lines are slightly different from each other. In the next stage layer, the balance is decided in 1 hour. In the last outer basal layer, equilibrium is reached in 20 minutes during the final stages of adsorption.

CONCLUSION.Compared to azkamar bentonite, the adsorption capacity of activated azkamar bentonite samples increased by 1.4 and 1.6 times, respectively. It is known from the low sorption of benzene molecules in the inner layer of bentonite that the number of sorption cells is lower than in other layers. The initial filling has a high adsorption heat. The differential heat of adsorption decreases in the form of waves. Based on the values of the adsorption isotherms, the specific surface area was determined using the BET and Langmuir equations. The average integral entropy is -34.5 J / mol * K and -42.35 J / 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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