Volumetric Analysis Of Benzene Vapor Adsorption On Lilsx Zeolite İn A High Vacuum Adsorption Device

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Abstract

The study of molecules adsorption of different geometric and electronic structure by zeolites of different composition and structure is of great interest to study the effect on the adsorption of chemical nature of adsorbents surface. Zeolites are porous crystals, so the micropore structure of zeolites is determined with high accuracy, their adsorption properties are physical-chemical constants, which can be calculated theoretically based on the calculation of the potential interaction energy adsorbate-adsorbate and adsorbate-adsorbent in zeolites. These data are of great interest for the development of the theory of adsorption forces and intermolecular interactions. However, the calculation of the potential energy of adsorption is difficult due to the complexity of the crystal structure and the potential field in the zeolite channels. The high benzene content degrades the environmental and technological properties of fuels. To select a highly efficient sorbent for dearomatization of fuel, studies of regularities of benzene adsorption in various zeolites are necessary. The isotherm, differential heats, and thermokinetics of benzene adsorption in LiLSX zeolite at 303K were measured using the adsorption calorimetry method. The differential molar entropy and free adsorption energy are calculated. The adsorption isotherm is completely described by the three-term equation of VMOT. The average molar integral entropy of benzene adsorption in zeolite LiLSX is - 89,22 J/mol*K, which indicates the localization of benzene molecules in LiLSX zeolite.

Key words: Isotherm, differential heats, differential entropies, thermokinetics, LiLSX zeolite, benzene, adsorption calorimetry

1. Introduction

Zeolites are carcass-shaped aluminosilicate crystals composed of alkaline and alkaline earth metals, heated to constant temperature, aluminum and silicon oxides are not exposed to water and slowly evaporate, during which time carcasses are formed for the entry of small molecules consisting of regular channels and cavities [1]. Because synthetic zeolites have the same composition and structure, they are used for more industrial purposes than natural zeolite analogues [1].

In order to achieve an optimum performance for the adsorption column, it is of immense importance to understand the adsorbent–adsorbate interactions occurring, in terms of both the thermodynamics and kinetics of the processes. The dynamics of an adsorption column are influenced by several factors, including its geometry, operating scheme and conditions, the characteristics of mass transfer, the effects of adsorption heat and the type of adsorption equilibrium isotherm involved. In the present study, adsorption equilibrium isotherms for the pure gases and for a gaseous mixture were obtained for a lithium-exchanged low-silica (Si/Al = 1.0), X zeolite (LiLSX) and a carbon molecular sieve (CMS). Such

isotherms were then employed to study the effect of competitive adsorption amongst the constituent gases and thereby establish their suitability for He purification. LiLSX is a synthetic crystalline aluminosilicate with a regular micropore structure. The zeolite possessed a faujasite-type structure (FAU) with a pore size of 9 Å [2, 3].

LSX zeolite is obtained by the cation exchange method to type X zeolites, and the cation exchange in these zeolites reaches a maximum. Further increase in the number of cations does not significantly affect the adsorption amounts. The results obtained are similar to the adsorption of type X zeolites [4, 5].

In our previous research, benzene adsorption on X and Y type zeolites consisting of Na^+ and Li^+ cations was studied [6-9].

2. Research methods and areas

For calorimetric study, LiLSX-type powdered synthetic zeolite ((Linda) Si / Al = 1) obtained using the ion exchange method was used. The composition of the elemental cells of zeolite obtained for the study is LiLSX - $Li_{96}Si_{96}Al_{96}O_{384}$. Absolute benzene was selected for adsorption. In the determination of LiLSX zeolite benzene adsorption was carried out in a high-vacuum adsorption microcalorimetric device [10,11].

The adsorbates were first frozen and then cleaned in a vacuum pump. Palte effect The use of heat flux compensation method increases the accuracy of adsorption heat measurement. A differential calorimeter allows you to measure the amount of heat released over a long period of time. In the determination of adsorption measurements were carried out in a high-volume volumetric adsorption device, low absorption of adsorbates increases the accuracy of adsorption measurements.

3. Results and discussions

Benzene adsorption isotherms to LiLSX zeolite were determined by volumetric method at a temperature of 303 K. Figure 1 shows the benzene adsorption isotherm to LiLSX zeolite. The isotherm (abscissa) axis consists of a logarithmic (*ln*), adsorption (*N*) (*N*-super-cavity and 1/8 C_6H_6 molecule number of elementary cell) (ordinal) axis, which allows us to imagine the adsorption process over the entire pressure equilibrium range. Figure 1 shows the results of the experiment with the number 1 and the number 2 with the symbols processed using the equation of the volume saturation theory of micropores. At the initial saturation it is possible to observe a slight deflection of the isothermal marks, where the isotherm is ln $(p/p°) = -12$, and the adsorption is up to $N = 1$ C_6H_6/1/8 u.c.. The isotherm index then appears as a vertical line until ln $(p/p°) = -8.35$, after adsorption 4.76 C_6H_6/1/8 u.c. the isotherm bends and intersects towards the adsorption axis.
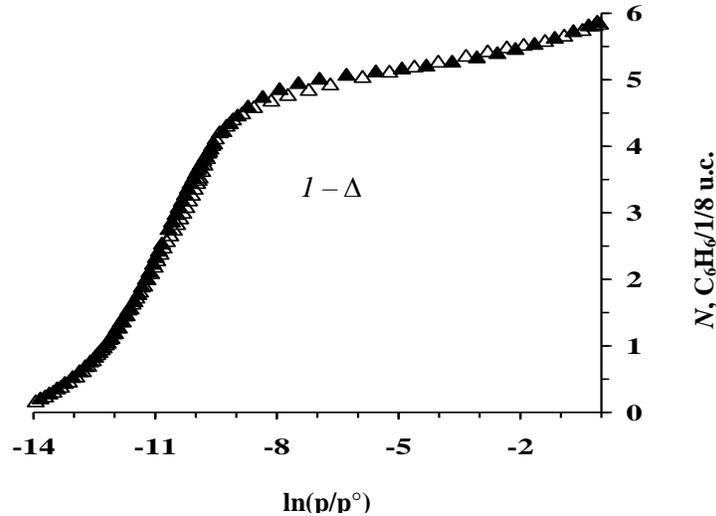
**Figure 1. Benzene adsorption isotherm in the zeolite
LiLSX at 303К**

1 - experimental data. 2-estimating data by VMOT.

Adsorption isotherms were described using the three-term equation of the theory of volumetric saturation of micropores (MHTN) [12, 13]:

$$N = 1{,}669\exp[-(A/32{,}27)^{10}]+3{,}257\exp[-(A/27{,}07)^{10}]+0{,}982\exp[-(A/9{,}06)^{1}],$$

N – adsorption in micropores $C_6H_6/1/8$ e, $A = RT \ln(P^o/P)$ - adsorption energy, kJ / mol.
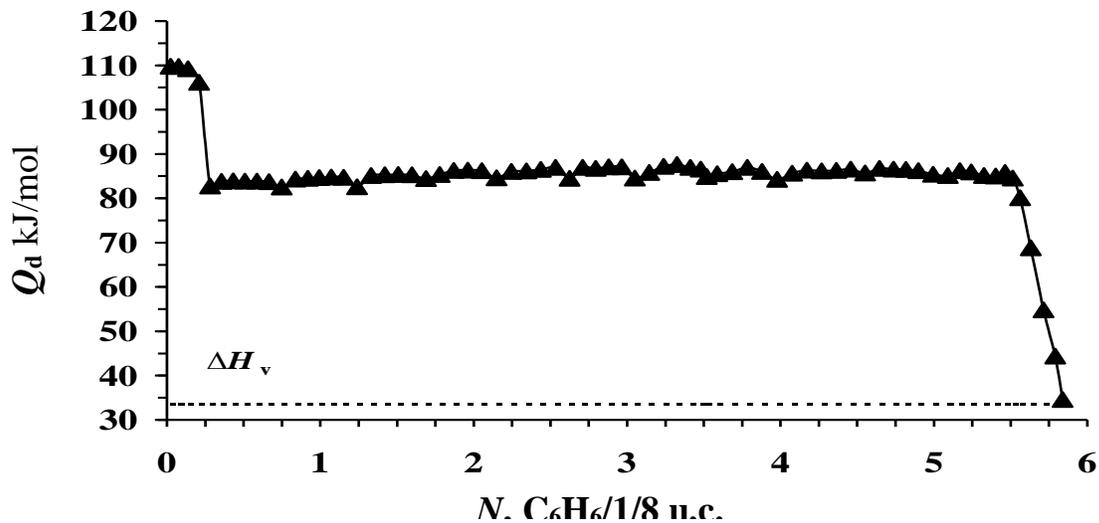

Figure 2 The differential heat of benzene adsorption in the zeolite LiLSX at 303K. The

horizontal dashed line is heat benzene condensation at 303K.

Figure 2 shows a graph of the differential heat (Q_d) change in the amount of benzene adsorption (N) on LiLSX zeolite. Benzene adsorption is indicated by thermal condensation (Q_d) dashed lines. The stable differential heat of benzene adsorption is ~ 2.61 times higher than the thermal condensation. The change in the differential heat of adsorption has its own characteristics. The differential heat starts at 109.79 kJ / mol and decreases slowly to 106.17 kJ / mol, where the adsorption is in the range of 0.02-0.2 C6H6 / 1/8 e. The adsorption heat decreases from 106.17 kJ / mol to 82.76 kJ / mol and the adsorption reaches 0.28 C_6H_6/1/8 u.c.. The differential heat of 82.76 kJ / mol is three times the maximum, and the adsorption intervals are 0.28-0.74 C_6H_6/1/8 u.c., 0.74-1.23 C_6H_6/1/8 u.c. and 1.23-1.68 C_6H_6/1/8 u.c.. represented by. In addition, the adsorption heat goes to Q_d = 84.57 kJ / mol N = 1.68 C_6H_6/1/8 u.c.., And then to Q_d = 85.11 kJ / mol to the maximum value N = 5.09 C_6H_6/1/8 u.c.. The interaction of adsorbate-adsorbates leads to an increase in the adsorption heat due to the contribution of the third and fourth benzene molecules to the total energy at the entrance to the space. The location of the four C_6H_6/Li^+ complexes is in the form of a tetrahedron, with such clusters filling almost all the voids of the super voids. At the entrance of the fifth molecule, the heat is in the form of a slight wave, and the adsorption is N = 5.46 C_6H_6/1/8 u.c.. The temperature drops sharply after In the final stage, the temperature rises slightly and falls sharply at 303 K depending on the temperature of the benzene condensation. Modeling of the benzene / zeolite system shows that the fifth benzene molecule is located in a 12-ring oxygen window that separates the superpowers from each other (position W). For zeolites with Na^+ cations in X and Y zeolites, this position has been discussed several times [14,15].

The adsorption heat can be divided into the following parts according to the Q_d wave curve: 0.28-0.74, 0.74-1.23, 1.23-1.68, 1.68-2.14, 2.14-2.62, 2.62-3.05, 3.05-3.52, 3.52-3.97, 3.97-4.55, 4.55- 5.09 C_6H_6/1/8 u.c.. The curve ends with segments in the range of 5.09-5.84 C_6H_6/1/8 u.c.. LiLSX adsorbs a total of 5.84 molecules of benzene in 1/8 e of zeolite or in one super void.

LiLSX zeolite contains Si / Al = 1: 1 ratio. The zeolites used in our previous studies have Si / Al> 1.09. According to the literature [16], the distribution of cations in the zeolite is as follows: 4 cations in the 1/8 elemental cell (1/8 u.c.) of the S_{II} position (in hexagonal rings connected by a cubic octahedron and a hexagonal prism), the $S_{III'}$ position in the 1/8 u.c. 4 cations (in the hexagonal rings connecting the cubic octahedrons and large cavities) and the remaining 4 cations are located in 1/8 u.c. of the $S_{III'}$ position (in the four-membered rings of the large cavity). There are 12 cations in 1/8 of the superclusters, or a total of 96 cations in the elementary cell, according to calculations. As can be seen from the content, zeolites have a very high density. Due to the size of the benzene molecule, it is not adsorbed on six-membered oxygen glass, i.e., sodalite cavities, which is approximately ~ 0.25 nm. Adsorption occurs mainly in superpowers. Initially, the high adsorption temperatures are related to the benzene adsorption (N = 0.28 C_6H_6/1/8 u.c.) on the Li^+ cations in the $S_{III'}$ position located in the superpowers. Because it is located near the entrance window to the supercosm, the adsorbate molecules are initially adsorbed into this cavity and therefore travel with high energy (Q_d = 109.79 kJ / mol).

In addition to the molecules adsorbed in the superpowels, the adsorption of small-molecule adsorbates on polar water and quadrapul CO_2 molecules to the Li^+ cations in the sodalite cells is observed. The second section has a temperature of ~ 82.68 kJ / mol between 0.28–0.74 and 0.74–1.23 C_6H_6/1/8 u.c., which is explained by the adsorption on lithium cations located in the four-membered oxygen rings (S_{III}). The formation of cations in position S_{III} is associated with the migration of cations in position S_I. The migration of lithium cations is an active process in which the adsorption heat generated by the sorption of benzene would proceed at a much lower energy if the cations were located directly in the superheals. Lithium cations in position S_{III} have a preferred adsorption center than cations in position S_{II} because the 4-membered oxygen ring is located in the part slightly bent into the supercollective. Because the size of the Li^+ cations is small, the S_{II} is more submerged in the 6-membered oxygen ring of the position. Also, the benzene molecules adsorbed on the lithium cations in the S_{II} position do not more favorably move towards the cations forming the 6-membered oxygen ring and the negatively charged oxygen atoms. After

benzene is adsorbed on Li^+ cations in position S_{III}, it begins to be adsorbed on Li^+ in position S_{III}. In the next places, two sections of the lithium cations in positions S_{III} and S_{II} have ~ 0.475 $C_6H_6/1/8$ u.c.. from (~ 0.475x2 = 0.95) benzene molecules are adsorbed on the mixture (0.28-0.74, 0.74-1.23 $C_6H_6/1/8$ u.c.). Six sections: 1.23-1.68, 1.68-2.14, 2.14-2.62, 2.62-3.05, 3.05-3.52 and 3.52-3.97 $C_6H_6/1/8$ u.c..s apply only to adsorption of lithium cations in the SII position from 0.457 $C_6H_6/1/8$ u.c. The remaining sections each reflect adsorption in SIII and SII from 0.58 $C_6H_6/1/8$ u.c.. If we assume that each of these sections adsorbs at SII 0.457 $C_6H_6/1/8$. given the stain, the residual corresponding to position S_{III} is 0.1616. 0.808 $C_6H_6/1/8$ in five sections. the molecule is adsorbed (5 x 0.1616 = 0.808). In general, taking into account the second and third parts, in the S_{III} position 0.808 + 0.56 = 1.368 $C_6H_6/1/8$ u.c.. adsorbed. As for the adsorption at the S_{II} position, according to the six sections, there are 2,742 $C_6H_6/1/8$ u.c. according to these centers. (6x0.457 = 2.742) and plus 1.12 $C_6H_6/1/8$ u.c. (2 to 0.56 $C_6H_6/1/8$ u.c.) Adsorbed. Total SII in 3,862 $C_6H_6/1/8$ u.c. The molecule is adsorbed on benzene.
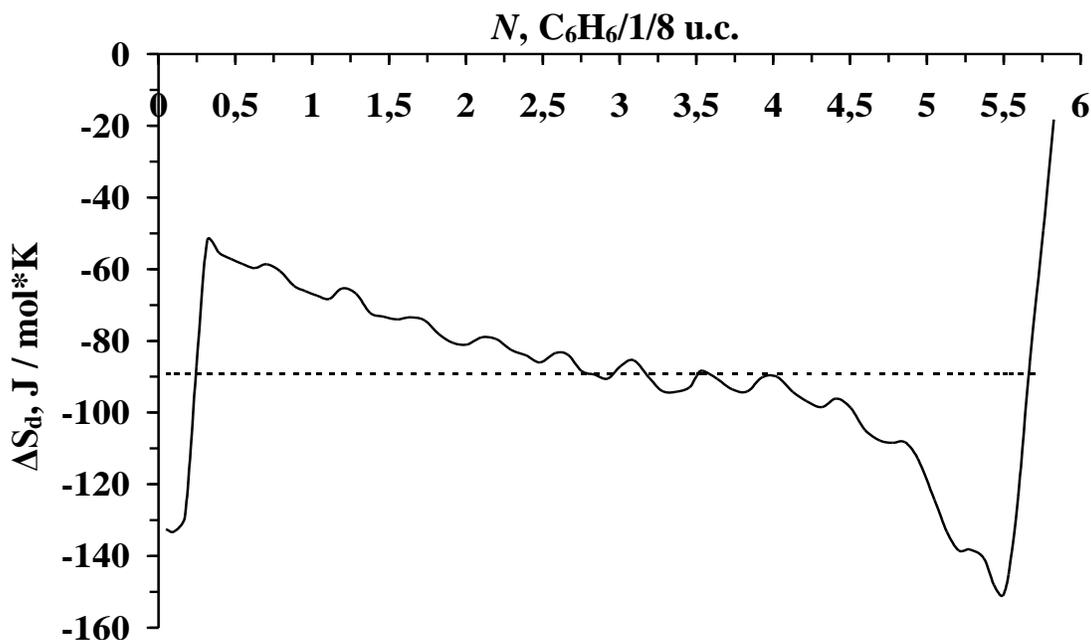

Figure 3. The differential entropy of the benzene adsorption in the zeolite LiLSX at 303K.

Entropy of liquid benzene is taken as zero. The horizontal dashed line – mean molar integral

Figure 3 shows the differential entropy of benzene adsorption on LiLSX zeolite. The formula of the Gibbs-Helmholtz equation was used to calculate the differential entropy using the differential heat and isotherm values of benzene adsorption on LiLSX zeolite [17].

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

λ -heat condensation, ΔH and ΔG-enthalpy and free energy change, T-temperature, $Q_d^{'}$ -average differential heat.

Based on the results of the study, the location of adsorbent voids, surface surfaces, and cations in the study of adsorption entropy was studied. It is known from the beginning of the process that the high adsorption temperature indicates that the benzene molecules at the initial saturation are not strongly

excited to the zeolite micropores.

The differential entropy of adsorption initially starts at -132.54 J / mol * K, with adsorption N = 0.04 C_6H_6/1/8 u.c. Then the entropy goes almost unchanged and rises slowly to -128.91 J / mol * K, followed by a sharp rise to -51.94 J / mol * K. Because of the large number of voids in this part of the zeolite, the adsorption entropy values are high and the adsorbate molecules are inactive because the cations are not fully saturated with benzene vapors. In processes up to this value, water vapor is adsorbed on cations close to the inlet glass in the cavity S_{III}. After adsorption N = 0.31 C_6H_6/1/8 u.c., the adsorption differential entropy gradually decreases in the form of a wavy line, falling below the average integral entropy line to $N \sim 3.63$ C_6H_6/1/8 u.c. The adsorption of benzene molecules in the S_{II} supercosm ranges from N = 0.31 C_6H_6/1/8 u.c. to N = 5.49 C_6H_6/1/8 u.c. Even in the process up to $N \sim 3.63$ C_6H_6/1/8 u.c., benzene is very strongly sorbed in the zeolite matrix and the solid state at 250S is close to the entropy value. Then the adsorption $N \sim 5,6$ C_6H_6/1/8 u.c. is shown from the mean integral lines and approaches 0. This results in the formation of complex compounds with Li^+ cations that migrate from the S_{III} cavity inside the S_{II} cavity of the zeolite matrix while forming small wavy line views. Due to the large number of cations in these cavities, the energy distribution in the migration and adsorption of cations is orderly and strongly adsorbed. The average integral entropy is -89.22 J / mol * K.

Figure 4 shows the benzene adsorption equilibrium time for LiLSX zeolite. In this zeolite, the equilibrium time lines are in the form of weak waves. The equilibrium time of benzene adsorption on LiLSX zeolite is initially 12.53 hours.
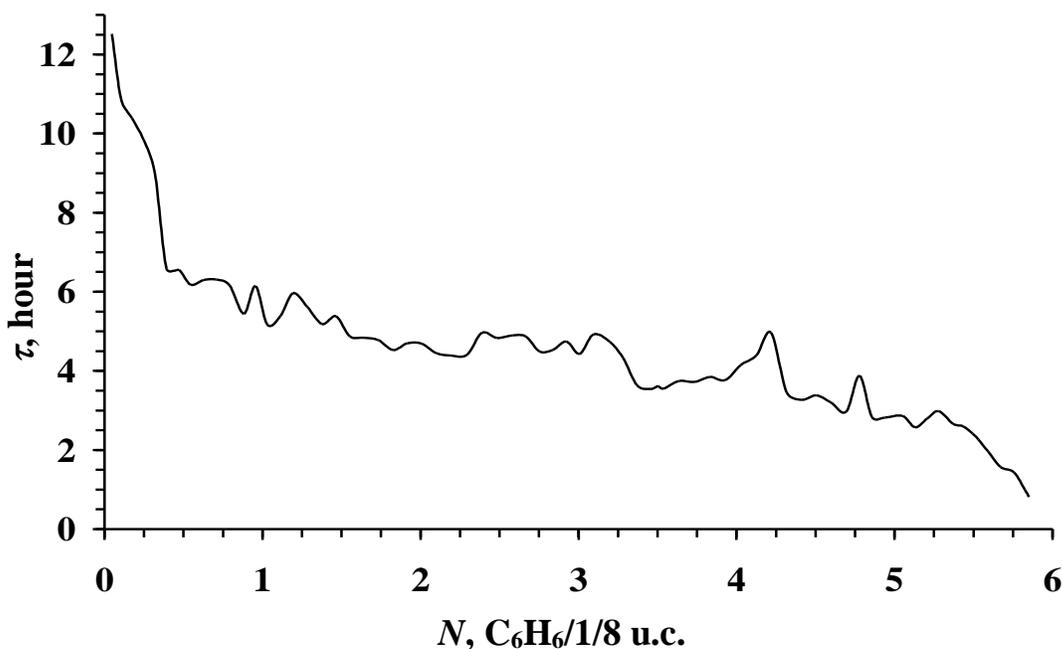

Figure 4.– The set-time of the adsorption equilibrium, depending on the size of the adsorption

of benzene in the zeolite LiLSX at 303K.

Due to the large number of voids and cations in the micropores of zeolite at initial saturation, it takes longer for the water adsorption to settle to equilibrium. The equilibrium time is then reduced to 6 h when the adsorption amount reaches 0.488 C_6H_6/1/8 u.c.. It takes longer for zeolite to break down into pores and due to the large number of cations located in the pores and the small amount of benzene molecules delivered. After 0.488 C_6H_6/1/8 u.c. of adsorption amount, the equilibrium time gradually decreases to 3-5

hours. At the end of the process, the equilibrium time is reduced to 20-30 minutes.

4. Conclusion

Thus, to saturate the voids of LiLSX zeolite with benzene, 0.788 $C_6H_6/1/8$ u.c. to cations in position $S_{III'}$, 3,862 to cations in position S_{II}, and 1,368 $C_6H_6/1/8$ to cations in position S_{III}. adsorbed. Of the 12 lithium cations in 1/8 of the zeolite matrix, 5,838 are involved in the adsorption process. In the last section, after adsorption of 5.46 $C_6H_6/1/8$ u.c. near the end of the adsorption process, the heat begins to decrease from 85.84 to 80.15 kJ / mol as usual. At the end of the process, the adsorbed molecules are adsorbed more densely and the 0.2 $C_6H_6/1/8$ or benzene molecules are redistributed. Their adsorption heat rises sharply to the level of 8,621 kJ / mol. The redistribution of benzene molecules begins mainly after adsorption of 5.56 $C_6H_6/1/8$ u.c.. The average integral differential entropy is -89.22 J / mol * K, and the benzene molecules are adsorbed in the zeolite matrix without solid agitation. It takes a long time for the adsorption equilibrium to be established at the initial saturation. As the saturation gradually increases, the adsorption thermokinetics decreases for a few minutes.

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