# Determination of Ammonia's Adsorption Properties in NaLSX Zeolite by Calorimetric Method

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**Abstract**  The research of the molecules' adsorption of different geometric shapes and electronic structures together with zeolites of different composition and structure arouses simultaneous interest in the research of the influence of the chemical nature of the surface of adsorbents on adsorption. Zeolites are porous crystals, their adsorption properties are physicochemical constants, therefore, it is theoretically possible to determine the micropore structure of zeolites and to calculate their interaction with the potential interacting 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. Nevertheless, 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 voids. In order to determine the acidity and basicity properties of the composition, it is necessary to study the laws of adsorption of ammonia molecules. In the determination of ammonia adsorption isotherm, differential temperatures and thermokinetics in NaLSX zeolite 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. The adsorption isotherm is fully described by the three-dimensional equation of the theory of volumetric micropore occupancy (VMOT). The average molar integral entropy of ammonia molecule adsorption on NaLSX zeolite is 59.64 Dj/mol*K, indicating a strong localization of ammonia molecules in NaLSX zeolite.

**Keywords**  Isotherm, Differential heats, Differential entropies, Thermokinetics, NaLSX zeolite, Ammonia, Adsorption calorimetry

## 1. Introduction

The technologies for ammonia removal from wastewater are based on physicochemical and biochemical treatment methods [1]. One of these treatment methods is adsorption, which is a low-cost process. Different adsorbents, such as wheat straw biochars, pine sawdust or zeolites, can be effective in adsorbing ammonium in wastewater [2–12].

Several studies have reported on the adsorption of ammonium ions by natural or synthetic zeolitic material adsorbents as well [9–12]. Zeolite - aluminosilicate hydrate minerals with a porous, three-dimensional crystal structure are considered an excellent ion-exchange material because of their high selectivity for $NH_4^+$ due to their microstructure [2]. An adsorbent of natural zeolites possesses a polar surface and is therefore able to attract ammonium ions quickly and effectively [1]. The removal of ammonia from water was carried out by using natural and synthetic zeolites. In this research three types of natural zeolites (clinoptilolite, mordenite and ferrierite), and synthetic zeolite A were used. The different forms of zeolites such as sodium, potassium and calcium forms were investigated [9]. It was concluded that natural zeolites show high selectivity for ammonium ions with respect to other monovalent ions despite the much higher theoretical exchange capacity of zeolite A. In the study 11, the clinoptilolite was fused with sodium hydroxide prior to a hydrothermal reaction, and it was transformed to a modified zeolite Na–Y. The results were acceptable, showing that modified zeolite Na–Y exhibited a much higher uptake capacity compared with that of clinoptilolite. At an initial concentration of 250 mg/L $NH_4^+$, the ammonium ion uptake value of sample 2 was 19.29 mg/g $NH_4^+$ adsorbed, while that for sample 1 was only 10.49 mg/g1 $NH_4^+$ adsorbed.

The emergence of high-energy complexes in the adsorption of NaX zeolite ammonia is dependent on the interaction of ammonia molecules in the $S_{III'}$ and $S_{II}$ voids in

two adjacent states, two abutting sodium cations. $S_{III'}$ generates heat of adsorption on cations in the void, when the extrapolation of ammonia is $H^+$ equal to 110 kDj/mol, ~ 90 kDj / mol, relative to the $Q_d$ curve to zero saturation [13-14].

In our research, the adsorption of ammonia molecules in various synthetic zeolites was carried out by the adsorption microcalorimetric method in a high-vacuum adsorption device, and the full thermodynamic properties of the adsorption processes were described [13-38].

## 2. Materials and Methods

The composition of the zeolite obtained for the study is $Na_{96}(AlO_2)_{96}(SiO_2)_{96}$. The adsorption-calorimetric tip used in this study allows to reveal the detailed mechanism of adsorption processes occurring in adsorbents and catalysts, as well as obtaining adsorbents and catalysts, moreover, obtaining high-precision molar thermodynamic characteristics.

Adsorption measurements and doses of adsorbate were performed using a universal adsorption device, in the working part of which only mercury valves were used and the valves were replaced with vacuum grease [39]. The device allows to dose the adsorbate by both gas-volume and liquid-volume methods. As a calorimeter, a modified DAK 1-1 calorimeter with high accuracy and reliability was used.

## 3. Result and Discussion

Ammonia adsorption isotherms to NaLSX zeolite were carried out in a volumetric manner at a temperature of 303 K,

Figure 1 provides the results of the experiment (1) and the re-described characteristics (2) using the equation of the volumetric saturation theory of micropores. The isotherm does not change in the same plane as the pressure increases, but rather each of them reflects the transition of one type of centers to another. The isotherm (abscissa) axis consists of a logarithmic (ln), adsorption (N) (N-supervoid and 1/8 $NH_3$ molecule number of elementary cell) (ordinal) axis, which allows us to imagine the adsorption process over the entire pressure equilibrium range. In the adsorption of the three ammonia molecules, the isotherm line goes vertically at the initial filling of the zeolite micropores, where the isotherm ranges from $\ln(p/p°)=-18$ to $\ln(p/p°)=-16,8$, and the adsorption is $N=3$ $C_6H_6$/1/8 u.c. Na + cations in the $S_{III'}$ void rise sharply when adsorbed, then turns to the adsorption axis and grows to 6 $NH_3$/1/8 u.c ($S_{I'}$). In the adsorption after 6 $NH_3$/1/8 u.c, the isotherm 18 $NH_3$/1/8 u.c. increases with a slope to the adsorption axis and is partially saturated ($S_{II}$).

Adsorption isotherm of ammonia in the NaLSX zeolites is satisfactorily described by three-term equation of the theory of volumetric micropore occupancy (VMOT) [40,41]:

$$N = 3,33\exp[-(A/43,09)^{22}] + 12,32\exp[-(A/22,71)^3] + 3,26\exp[-(A/10,2)^3],$$

$N$ - adsorption in micropores $NH_3$/1/8 u.c., $A = RT \ln(P°/P)$ - adsorption energy, kDj / mol. The parameters of the equation for the first level of the NaLSX zeolite ammonia system are: $N_{01} = 3.33$ $NH_3$/1/8 u.c., $E_{01} = 43.09$ kDj / mol and $n_1=22$; for the second degree $N_{02} = 12,32$ $NH_3$/1/8 u.c., $E_{02} = 22,71$ kDj / mol and $n_2 = 3$; and for the third degree $N_{03} = 3.26$ $NH_3$/1/8 u.c., $E_{03} = 10.2$ kDj/mol and $n_3 = 3$.
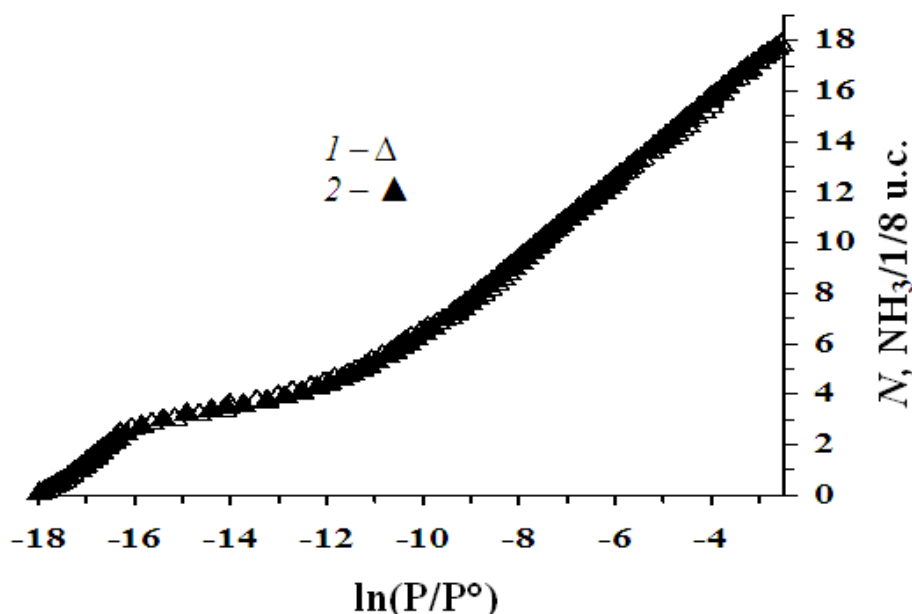


**Figure 1.** Isotherm of ammonia adsorption in zeolite NaLSX at 303 K. 1- experimental data 2 – calculated data using the theory of volumetric micropore occupancy (VMOT)
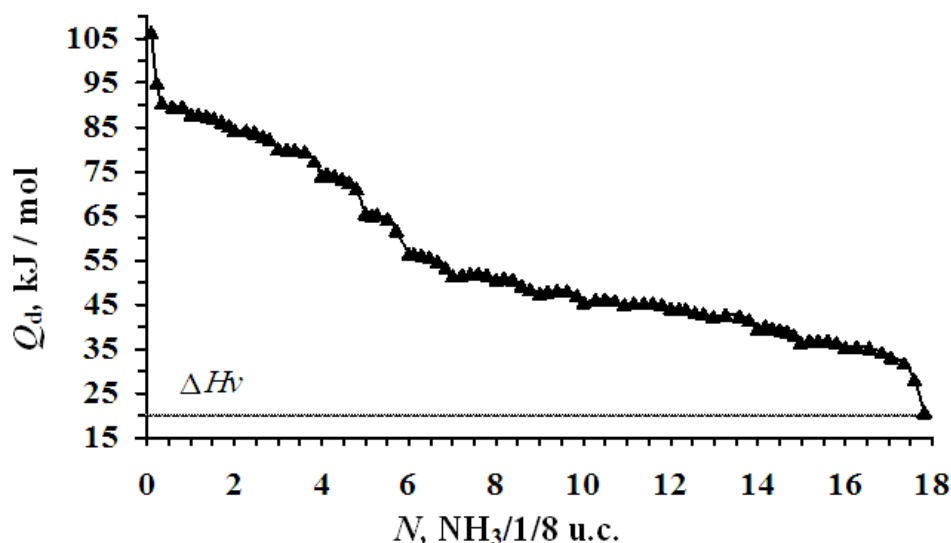
**Figure 2.**   Differential heats of adsorption of ammonia in zeolite NaLSX at 303 K. Horizontal dotted line - heat of condensation of ammonia at 303 K

There is a correlation between the isotherm and the adsorption heat. Figure 2 shows a graph of the differential heat ($Q_d$) change in the amount of ammonia adsorption ($N$) in NaLSX zeolite. Thermal condensation ($\Delta H_v$) of ammonia adsorption is indicated by dashed lines. The differential heat ($Q_d$) curve has a complex wavy shape. Each fragment on the curve represents the stoichiometric ratio between the same number of adsorption centers and the number of molecules adsorbed. NaLSX zeolite contains Si/Al=1:1 ratio. According to the literature [16], the distribution of cations in the zeolite is as follows: 4 cations (in hexagonal rings connected by a cuboctahedron and a hexagonal prism) are in the 1/8 elemental cell (1/8 u.c.) of the $S_{I'}$ position, 4 cations (in hexagonal rings connecting cupoctahedrons and large voids) are in the 1/8 elemental cell (1/8u.c.) of the $S_{II}$ position, and the remaining 4 cations are located in 1/8 u.c. of the $S_{III'}$ void (in four-membered rings of large void). There are 12 cations in 1/8 u.c. of the supervoids, or a total of 96 cations in the unit cell, according to calculations. As can be seen from the content, zeolites have a very high density.

The adsorption heat decreases to a stepped shape of the curve and is divided into 4 main fragments: 0-3 (fragment I), 3-7 (II), 7-15 (III) and 15-18 NH₃/(1/8) u.c.(IV). The first high-energy fragment (0-4 NH₃/(1/8)u.c.) is associated with the adsorption of ammonia to the cations in the $S_{III'}$ void on the $Q_d$ curve with heat varying from 106.4 kDj/mol to 80.20 kDj/mol. These are the most suitable cations in the void because they are bound to 2-4 oxygen atoms of the forming void and therefore the adsorption goes with high heat and lasts to 2 NH₃/1/8 u.c. It can therefore be assumed that the adsorption of ammonia at acidic centers $H^+$ is in a 1: 2 ratio, then half of the number of protons and equal to 1. The total number of cations in the $S_{III'}$ void is 1+3=4, which corresponds to the crystallographically determined value of the number of cations in this position. During the first molecule ammonia adsorption, 106.4 kDj/mol of heat is released. The reason for the high temperature can be

explained by the fact that the cation in position $S_{III'}$ is close to the entrance window, ie near the supervoid, and cations in other positions attract a small number of ammonia molecules, which takes a long time to balance the released energy. The heat of adsorption of the next molecule of ammonia decreases sharply to 90.50 kDj/mol, and we can see the stepwise decrease of 7 NH₃/(1/8) u.c., from the $Q_d$ curve.

In the second fragment, 4 NH₃/1/8 u.c. ammonia is sorbed, which corresponds to the number of cations in the $S_{II}$ or $S_{I'}$ position. Given that ammonia molecules do not enter sodalite voids [42], this section indicates that ammonia is adsorbed in a large void. Given the relatively high adsorption energy, it can be assumed that these centers are sodium cations that migrate from the sodalite voids to the supervoids and are localized in the open $S_{III}$ void. At this stage the adsorption is 3 NH₃/1/8 u.c. and 7 NH₃/1/8 u.c., the adsorption differential heat decreases from 80.20 kDj/mol to 51.60 kDj/mol.

In the third fragment, the heat decreases monotonically from 51.6 to 36.6 kDj/mol with filling. Here adsorption of 8 NH₃/1/8 u.c. ammonia occurs in cations at the $S_{II}$ position. Given that there are four Na + cations for 1/8 u.c., there are two molecules for each center.

In the fourth fragment, the adsorption heat decreases from 36.6 kDj/mol to the condensation heat, i.e., 20 kDj/mol, and 3 molecules of ammonia are adsorbed. Adsorption in this fragment goes between 15 NH₃/1/8 u.c. and 18 NH₃/1/8 u.c. in the range. At this stage, it is known from the differential heat of adsorption in the increasing process that 2 molecules of ammonia are sorbed at the $S_{II}$ position of the supervoid and 1 molecule of ammonia at the $S_{III}$ position.

By extrapolating the $Q_d$ curve at the initial fillings, we obtain the adsorption of ammonia is equal to 90 kDj/mol on the $Na^+$ cation in the $S^{III}$ state. The average adsorption heat of ammonia is equal to 75.5 kDj/mol on Na + cations in the $S^{III}$ state, while that in the $S^{II}$ is ~ 50 kDj/mol.
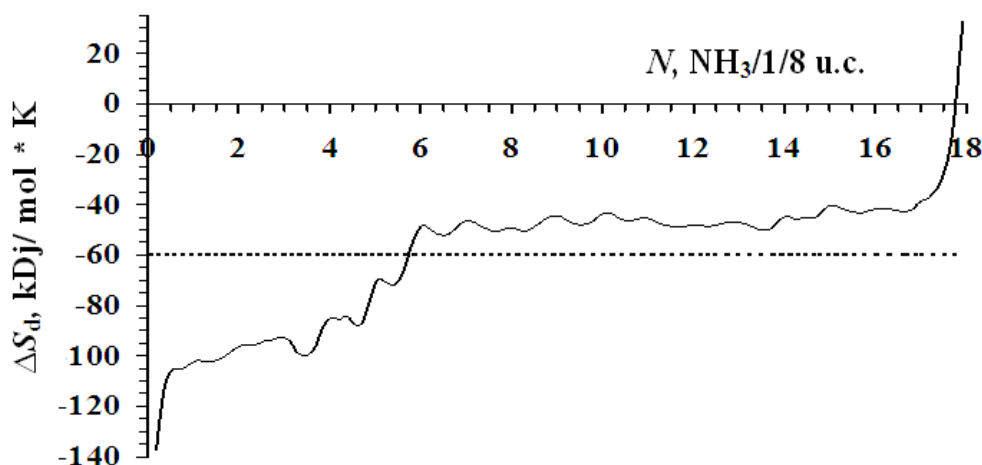
**Figure 3.**   Differential entropies of adsorption of ammonia in zeolite NaLSX at 303 K. Entropy of liquid ammonia is taken as zero. The horizontal dashed line is the mean integral entropy
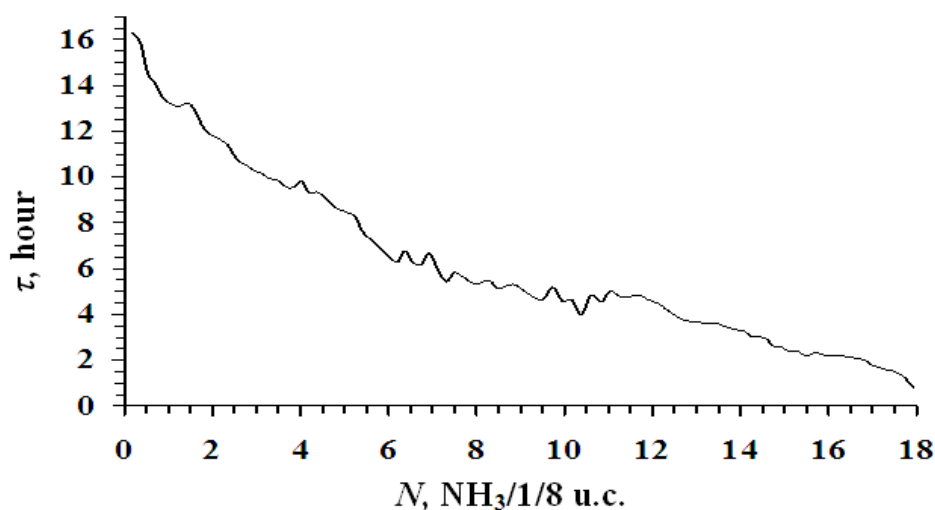


**Figure 4.**    Time to establish adsorption equilibrium depending on the adsorption of ammonia gases in NaLSX zeolite at 303 K

The adsorption entropy calculated by the Gibbs-Helmholtz equation shows the state of ammonia molecules in zeolite. Molar differential entropy of ammonia (Fig. 3). It is much lower than the liquid ammonia entropy at NaLSX. This indicates that the mobility of ammonia in zeolite voids is severely limited.

Ammonia is adsorbed on NaLSX zeolites in the same amount but with different strength. β-voids are not available for ammonia molecules under standard conditions. $Na^+$ cations in position $S^{III}$ form four-dimensional $(NH_3)_4/Na^+$ complexes in supervoids. The mobility of ammonia in the voids is lower than that of the liquid.

Figure 4 shows the equilibrium time of benzene adsorption on NaLSX zeolite. At initial fillings, the time to establish adsorption equilibrium in the $NH_3$-NaLSX system is greatly slowed down. This is due to the fact that the zeolite takes longer to be distributed due to the voids in the pores and the zeolite pores and the large number of cations in the pores and the small amount of ammonia molecules present. It takes longer for the ammonia adsorption to reach equilibrium. Equilibrium is set at 10-16.5 hours. This process is then accelerated, slowly accelerates the rest down for N= 8 $NH_3$/1/8.

The thermokinetics of ammonia adsorption in NaLSX zeolite show that the initial ammonia molecules are slowly adsorbed, and then the adsorption equilibrium is reduced by 40 min.

# 4. Conclusions

At differential temperatures of ammonia adsorption, there are 4 fragments corresponding to the formation of monomeric complexes of ammonia with $Na^+$ cations in position $S_{III}$, then $S^{III}$, the adsorption process ends with the formation of four-dimensional complexes with cations in position $S^{II}$. The temperatures of ammonia adsorption with $Na^+$ cations at positions $S_{III'}$, $S_{I'}$ and $S_{II}$ are 90, 75.5 and 50 kDj/mol, respectively. The adsorption isotherm is fully described by the three-term equation of VMOT). $Na^+$ cations in the $S^{II}$ position form four-dimensional $(NH_3)_4/Na^+$ complexes in the supervoid. The average integral differential

entropy is -59.64 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.

## ACKNOWLEDGEMENTS

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