

THERMODYNAMICS OF (NH₄⁺) CATION ADSORPTION
UNDER STATIC CONDITIONSVira Sabadash^{1, *}, Jaroslaw Gumnitsky¹, Oksana Lyuta¹, Iryna Pochapska¹<https://doi.org/10.23939/chcht12.02.143>

Abstract. The adsorption of ammonium ions by natural zeolite and Al₂O₃ under static conditions has been investigated. The reason for changing the investigated solution pH during adsorption of ammonium ions on Al₂O₃ has been grounded. A phase diagram of the two-component system has been constructed and the composition of the adsorption system in the state of equilibrium has been determined. The thermodynamic calculations of the adsorption system Al₂O₃–NH₄Cl–H₂O have been carried out. It was established that the adsorption of ammonium with aluminum oxide occurs *via* the mechanism of physical adsorption.

Keywords: adsorption, thermodynamics, ammonium ions, zeolite, Al₂O₃.

1. Introduction

Aluminum oxides and silicon are the basis of zeolites, used as natural adsorbents. The percentage ratio of silicon to aluminum strongly influences the adsorption of cations. Aluminum content in zeolite provides the presence of exchange cations, and thus, the ion exchange properties of the sorbent. Apart from the ion exchange between zeolite and solution cations a physical adsorption occurs in points of the crystal lattice fracture. In environmental technologies zeolites are often used to adsorb ammonium ions. To determine the nature of the adsorption forces that hold ammonia in the zeolite framework it is necessary to investigate the sorption capacity of Al₂O₃ under static conditions taking into account that the zeolite sorption capacity depends on the content of aluminum. Data on calcium ammonium ions adsorption by clinoptilolite of Sokirnitsky deposit were published [1]. The maximum sorption capacity of the adsorption process was found to be at the concentration of 4.5 g/dm³. In this case, the sorption capacity of zeolite was 0.1 g/g of the adsorbent. It was found that during the

ammonium ions adsorption by clinoptilolite, sodium and calcium ions are released into the solution, indicating ion exchange processes in the adsorption system. Their equivalent quantity is smaller than that in zeolite, which is explained by the sorbent ability not only to exchange ions on the adsorbent-adsorbate phase interface, but also to physically adsorb the ions. Demir *et al.* [2] and Gomelya *et al.* [3] investigated the cations sorption over zeolites and reported about the ion-exchange mechanism of adsorption. Kawasaki *et al.* [4] present data on the dependence of aluminum oxide adsorption properties relative to anions and cations on its crystalline structure. As regards the sorption of ammonium ions on aluminum oxide, Zhang and He [5] investigated catalytic oxidation of ammonium in the presence of catalysts based on aluminum oxide. With regard to adsorption of other cations, there are only data concerning Fe(III) adsorption from the aqueous solution by alumina nanopowder in a column type apparatus [6, 7]. The experimental results and thermodynamic calculations of these authors show that the adsorption process is exothermic and occurs *via* the mechanism of physical adsorption; it is described by the Langmuir isotherm and the kinetics model of the pseudo second order. The value of enthalpy (ΔH^0), mean free energy (E) and activation energy (E_a) indicate that the adsorption process is a physical sorption.

The aim of this work is to calculate thermodynamic parameters of Al₂O₃–NH₄Cl system to determine the mechanism of ammonium ions adsorption by aluminum oxide.

2. Experimental

To study the adsorption of ammonium ions over zeolite it is necessary to know the mechanisms of adsorbate binding, in fact, by the alumina itself (an active element of zeolites), and silicon oxide. For the researches ammonium chloride was chosen.

To determine the sorption capacity of zeolite regarding the ammonium ions the samples of ammonium chloride solution (200 cm³) were placed in glass flasks. The samples were prepared in distilled water at different

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initial concentrations ($C = 2 \cdot 10^{-3} - 0.1 \text{ g/dm}^3$), with the addition of 1 g of Al_2O_3 . The samples were kept in a thermostat at $293 \pm 0.1 \text{ K}$ for 48 h under periodic stirring. The concentration of ammonium ions was determined by the atomic absorption method in accordance with [7].

To determine the solutions pH a potentiometric method was used.

3. Results and Discussion

The experimental results about the adsorption of ammonium ions by aluminum oxide are represented in Fig. 1.

When comparing the results from Fig. 1 and previous experimental results obtained using clinoptilolite of Sokirnitsky deposit [2], we can assert that the sorption capacity of clinoptilolite is about twice less than that of aluminum oxide. This fact is explained by more developed surface of Al_2O_3 . The specific surface of zeolite is $59 \text{ m}^2/\text{g}$ versus $340 \text{ m}^2/\text{g}$ of aluminum oxide. In addition, the absorption capacity is influenced by a considerable diffusion resistance of the sorbent ($\sim 1 \cdot 10^{-11} \text{ m}^2/\text{s}$) [11]. Obviously, the limiting stage of adsorption is the diffusion of the solution components toward the active centers of zeolite, whereas the sorption surface of aluminum oxide is in direct contact with a solution of ammonium chloride due to insignificant size of the crystals. In this case, the following tendency of pH change (before the sorbent addition) is observed (Fig. 2), depending on the concentration of ammonium chloride initial solution.

Despite the fact that the solution of ammonium chloride creates an acidic medium (weak base and strong acid) as a result of hydrolysis, the pH value > 7 is set in the adsorption system $\text{NH}_4\text{Cl}-\text{Al}_2\text{O}_3$ in 48 h. This indicates that not only ammonium ions are removed from

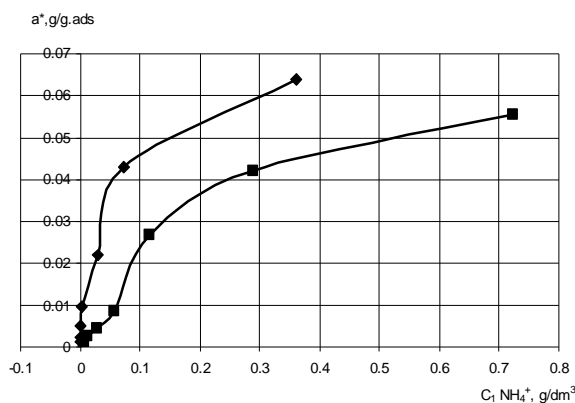


Fig. 1. Isotherms of ammonium ions adsorption over Al_2O_3 (\blacklozenge), and zeolite (\blacksquare)

the solution, but other related processes occur, in particular adsorption of H^+ . Kawasaki *et al.* [4] observed the formation of hydroxyl groups on Al_2O_3 surface due to the contact with water; these groups can enter the reaction of ion exchange. To determine the mechanism of ammonium adsorption by the sorbent and the cause of pH change, a phase diagram (Fig. 3) was constructed for the reaction of ammonium chloride with Al_2O_3 in the coordinates $\lg(C) = f(\text{pH})$ using the programs MEDUSA (Make Equilibrium Diagram Using Sophisticated Algorithms) and HYDRA (Hydrochemical Equilibrium Constant Database). Taking into account that there is an excess of ammonium chloride in the solution, and Al_2O_3 is a slightly soluble compound, the most probable is the production of the solution of the following phase composition (Fig. 3).

To determine the regularities of the interaction of aqueous ammonium chloride solution with the surface of aluminum oxide, we calculate the change of the standard Gibbs energy ($\text{kJ}/(\text{mol} \cdot \text{K})$) [10].

$$\Delta G_0^{298} = \Delta H_0^{298} - T \Delta S_0^{298} \quad (1)$$

The equilibrium state of the thermodynamic system is provided by the ratio of entropy and enthalpy factors. At the temperature of $T_{eq} = dH/dS$ the system will be in the equilibrium state.

Since entropy ($\text{kJ}/(\text{mol} \cdot \text{K})$) is a function of the state, its change as a result of the chemical reaction is equal to the difference in entropy of the reaction products formation and entropy of the initial substances:

$$\Delta S_0^{298} = \sum \Delta S_0^{298}{}_{prod} - \sum \Delta S_0^{298}{}_{in} \quad (2)$$

According to Hess's law we calculate the heat effect ($\text{kJ}/\text{mol} \cdot \text{K}^{-1}$):

$$\Delta H_0^{298} = \sum \Delta H_0^{298}{}_{prod} - \sum \Delta H_0^{298}{}_{in}$$

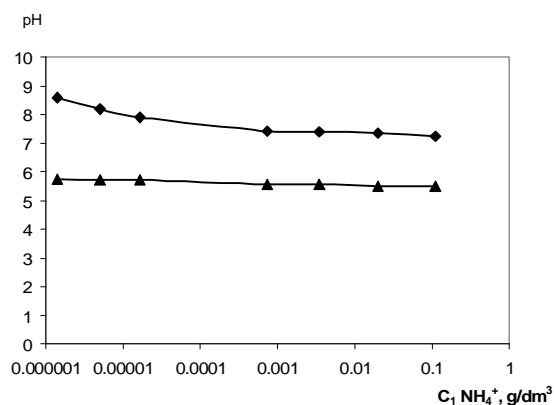


Fig. 2. Change of solution pH during ammonium ions adsorption over Al_2O_3 : pH of the initial solutions NH_4Cl (\blacktriangle) and pH of NH_4Cl solutions after adsorption over Al_2O_3 (\blacklozenge)

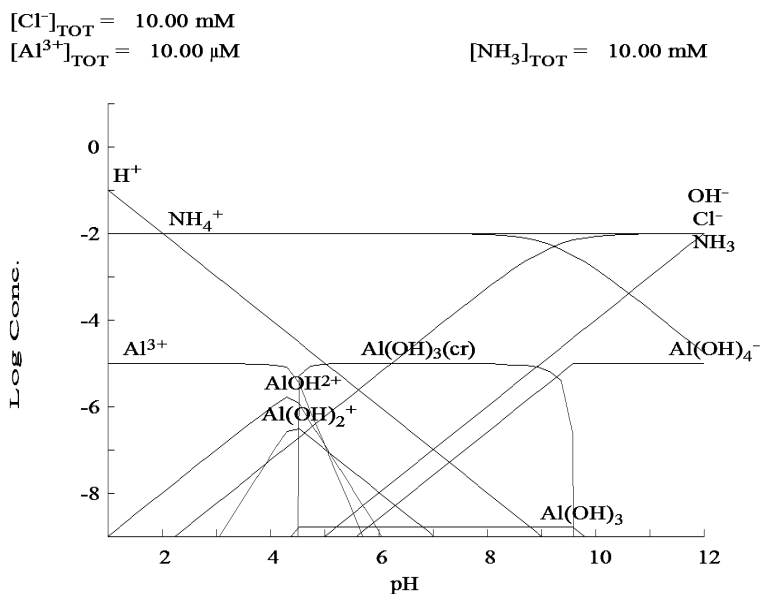


Fig. 3. The diagram of two-component system in the logarithmic coordinate system

Table 1

Calculations of thermodynamic parameters of Eq. (4)

Compound type	Compound	ΔG , kJ/(mol·K)	ΔH , kJ/(mol·K)	ΔS , kJ/(mol·K)
reagent	NH ₄ Cl	-1218.96	-299.45	0.096
reagent	Al ₂ O ₃	-1582.27	-1676	50.919
reaction product	H ₂ O	-711.74	-285.8	69.96
reaction product	NH ₃	-100.24	10.042	0.193
reaction product	AlCl ₃	-1767.2	-1031.02	0.314
Thermodynamic parameters of the reaction	–	-47.11·10³	613.49	160.17

Table 2

Calculations of thermodynamic parameters of Eq. (5)

Compound type	Compound	ΔG , kJ/(mol·K)	ΔH , kJ/(mol·K)	ΔS , kJ/(mol·K)
reaction product	Al(OH) ₃	-2314.00	-1275.7	70.1
reagent	Al ₂ O ₃	-1582.27	-1275.7	50.919
reagent	H ₂ O	-711.74	-285.8	69.96
Thermodynamic parameters of the reaction	–	35520.202	-418.3	-120.599

Table 3

Calculations of thermodynamic parameters of Eq. (6)

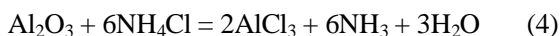
Compound type	Compound	ΔG , kJ/(mol·K)	ΔH , kJ/(mol·K)	ΔS , kJ/(mol·K)
reaction product	HAlO ₂	-2496.34	-934.87	-0.046
reagent	Al ₂ O ₃	-1582.27	-1676	50.92
reagent	H ₂ O	-711.74	-285.8	69.96
Thermodynamic parameters of the reaction	–	77487.94	-271.216	-260.94

Under standard conditions ($T = 298 \text{ K}$), the change in Gibbs energy depends on the ratio of enthalpy and entropy factors.

Tables 1-3 show the results of calculations of the standard Gibbs energy for different variants of sorbent interaction with the investigated solution.

In Fig. 3 the following insoluble and soluble complexes are given: NH_4OH , AlCl_3 , $\text{Al}(\text{OH})_3$, NH_4AlO_2 , $\text{Al}(\text{OH})\text{Cl}_2$ (the complex $\text{NH}_4\text{Al}(\text{OH})_4$ is only in water).

On the basis of reference data on enthalpy and entropy of the corresponding substances formation, we calculate the change of entropy and the heat of Eq. (4):



The calculation of the thermodynamic parameters of this equation is given in Table 1. The change of the standard Gibbs energy $\Delta G < 0$. This means that the reaction (4) can take place at room temperature. The increase in the reaction mixture temperature will increase the rate of chemical reaction.

According to Fig. 3 there is a large quantity of $\text{Al}(\text{OH})_3$ in the solution. We can assume the possible interaction of microquantity of Al_2O_3 and water (taking into account the insolubility of Al_2O_3) according to Eq. (5):

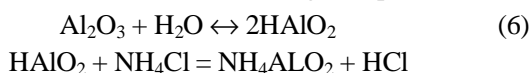


Thermodynamic calculations of this system are given in Table 2, which shows that the reaction of Al_2O_3 with water does not occur, *i.e.* a reverse reaction takes place.

So, the formation of aluminum hydroxide occurs only due to the hydrolysis of reaction products (Eq. (4)).

Thus, analyzing the data of Fig. 3 and Tables 1-3, insoluble complexes of aluminum and ammonium are not formed and ammonium absorption by Al_2O_3 has a purely physical nature.

We can assume the possible formation of water-soluble aluminates NH_4AlO_2 according to Eq. (6):



Similarly to the reaction (5), the reaction (6) proceeds in the reverse direction and only at $T < T_{eq}$ ($T_{eq} = \Delta H / \Delta S = 3.5 \text{ K}$), which is impossible for physical and technical reasons.

Thus, presented in Fig. 3 water-soluble and insoluble complexes are formed as a result of the hydrolysis of reaction products (see Eq. (4)).

4. Conclusions

The comparison of the adsorption capacity of natural zeolite and Al_2O_3 relative to ammonium ions under static conditions was carried out. It was found that aluminum oxide can absorb twice as much ammonium as natural zeolite, but taking into account that the specific

surface of the studied zeolite is almost 6 times smaller, we assert that zeolite is a better sorbent. During adsorption there is a chemical reaction of aluminum oxide with ammonium chloride and the hydrolysis of the reaction products resulting in the formation of soluble ammonium compounds. Taking into account the results of thermodynamic calculations and sorption capacity of aluminum oxide relative to ammonium ions, it was confirmed that the absorption of ammonium by aluminum oxide occurs *via* the mechanism of physical adsorption.

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ТЕРМОДИНАМІКА АДСОРБЦІЇ КАТІОНІВ (NH_4^+) НА Al_2O_3 ЗА СТАТИЧНИХ УМОВ

Анотація. Експериментально досліджено адсорбцію іонів амонію природним цеолітом та Al_2O_3 за статичних умов. Обґрунтовано причину зміни рН досліджуваного розчину під час адсорбції іонів амонію на Al_2O_3 . Побудовано діаграму складу двокомпонентної системи і встановлено склад адсорбційної системи в стані рівноваги. Здійснено термодинамічні розрахунки адсорбційної системи $\text{Al}_2\text{O}_3\text{-NH}_4\text{Cl-H}_2\text{O}$. Встановлено, що поглинання амонію оксидом алюмінію відбувається за механізмом фізичної адсорбції.

Ключові слова: адсорбція, термодинаміка, йони амонію, цеоліт, Al_2O_3 .