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Study of isotherm, thermodynamic characteristics and sorption mechanism of toluene adsorption on zeolite CsZSM-5 by adsorption-calorimetric method

Khayot Bakhronov[1*], Oybek Ergashev[2], G'olibjon Ochilov[3], Nazirahon Esonkulova[3], Abror Ganiev[1], Nodira Akhmedova[1], Ozoda Ochilova[1]
[1]Tashkent University of Information Technologies named after Muhammad al-Khwarizmi, Tashkent, Uzbekistan; baxronov@mail.ru (K.B.).
[2]Namangan Institute of Engineering and Technology, Namangan, Uzbekistan.
[3]Kokand state pedagogical institute named after Mukumi, Namangan, Uzbekistan.

Abstract: This paper presents experimental results of isotherm and basic (ΔH, ΔF and ΔS) thermodynamic characteristics of toluene adsorption in CsZSM-5 zeolite. A system consisting of a universal high-vacuum adsorption unit and a Tiana-Calvet type differential microcalorimeter DAC-1-1A coupled to it was used to measure the adsorption isotherm and differential heats of adsorption, giving directly quantitative and qualitative characteristics of the nature and forces of adsorption interaction between adsorbent and adsorbate. A correlation between adsorption-energy characteristics was found and the molecular mechanism of toluene adsorption in CsZSM-5 zeolite throughout the filling region was revealed. Toluene adsorbed in CsZSM-5 zeolite is located in the first coordination sphere with Cs+ cation, forming two-dimensional complexes. It was found that the charge density of cesium cation significantly affects the molecular mechanism, adsorption energetics and the number of adsorbed toluene molecules. It was determined that the average molar entropy of toluene adsorption in CsZSM-5 zeolite is equal to -73 J/mol·K indicating that the mobility of toluene molecules in CsZSM-5 zeolite is lower than the liquid phase and close to the mobility of the solid phase, indicating a strong inhibition of the mobility of toluene molecules both on cesium cations and without cationic parts of the zeolite, i.e. where there are no cesium cations. This work shows how calorimetric data can be used to complement crystal structure results and to detect subtle adsorbent/adsorbate interactions at the molecular level.

Keywords: *Adsorption enthalpy, Adsorption isotherm, Adsorption, Entropy, Free energy, Kinetics, Microcalorimeter, Toluene, Zeolite.*

1. Introduction

In the world, adsorbents obtained from natural raw materials or synthetically produced adsorbents are widely studied and used in industry, construction, agriculture and other fields [1-5].

However, before using these adsorbents in production, it is necessary to study their adsorption, energetic and catalytic characteristics under laboratory conditions.

The phenomenon of adsorption of vapours and gases underlies many chemical and biological processes and the interest of researchers has long been determined by the need to solve purely practical problems. The study of adsorption energy of gases and vapours is of paramount importance not only for understanding interesting phenomena and valuable in practical terms processes occurring on various synthetic zeolites, but also for accumulation, systematisation and standardisation of the most important thermodynamic characteristics of heterogeneous systems, one of the components of which is zeolite.

Natural and synthetic zeolites have found wide applications as adsorbents. Synthetic zeolites are aluminosilicate, microporous adsorbents possessing not only high selective adsorption, but also the ability to separate substances with different sizes and shapes of adsorbate molecules. They are

* Correspondence: baxronov@mail.ru

characterised by a strictly crystalline structure and a large specific surface area. At present industrial enterprises produce zeolites of different grades, differing in cations and pore sizes. Zeolites of A, X, and ZSM-5 types have the greatest practical application [2, 6-16].

Zeolites are most widely used in gas and petrochemistry, adsorption and separation of vapours and gases and removal of impurities (in particular, environmentally and biologically hazardous) from gases and solutions. In addition, zeolites are finding increasing applications in ecology, agriculture, animal husbandry, paper industry and construction [17].

Recently, research has been reported on the use of zeolites as low dielectric constant materials for microprocessors [18-20].

One of the highly efficient catalysts for various processes in petrochemical and refining industries are MFI type catalysts. Therefore, all side study of physicochemical and especially energetic characteristics of MFI type zeolites is of great theoretical and practical importance. Energy characteristics, due to the strict certainty of the chemical composition and crystal structure of zeolites, should be well reproducible and can be applied in practical calculations or theoretical discussions. In this connection, the accumulation and systematisation of the most important thermodynamic characteristics of adsorption systems, of which zeolite is one of the components, is of great importance. However, a number of questions of specificity of zeolite structure, especially those related to the problem of active centres dispersion, mechanism of adsorption of polar and nonpolar molecules, nature and participation of defects in adsorption are still unclear. The solution of these questions is crucial for successful application of adsorbents and directed regulation of their properties, as well as provides an opportunity to study and establish general laws of adsorption and catalysis.

Active research of zeolites in the world involves the study of the structure of zeolites with the determination of the location of their cations. However, there are practically no data on thermodynamic characteristics and mechanisms of adsorption processes of aromatic, quadrupole, polar and nonpolar molecules. Among foreign scientists, some of the first to address these issues were M.M.Dubinin, Xomeritakis, G.Tsapatsis, Bas Delphine, Goursot Annick, Weber Jacques, Wesolowski Tomasz, Zhenhao Wena, Daqiang Yanga, Xuan Hea, Yunsheng Lia, Xuedong Zhu, Wacław Makowski and others [21-32].

Oxygen plays an important role in the formation of the crystal structure of zeolites and superconductors. The crystal structure affects the adsorption and catalytic properties of zeolites and the phase transition temperature of superconductors [33-38].

Data on the arrangement of sodium cations in zeolite ZSM-5 are available in [39], in which the properties of zeolites NaZSM-5, HZSM-5 and silicalite were studied. At adsorption of various hydrocarbons on these zeolites, sodium cations in NaZSM-5 create some steric hindrances for penetration deep into the channels of toluene, xylene and 3-methylpentane molecules, which are well adsorbed on the other two samples mentioned above. Hence, the authors made the assumption that the sodium cations in NaZSM-5 are located in the 10-membered channels of this zeolite.

The localisation of cations in Cs-substituted MFI zeolites was reviewed in [40], where it was concluded that the Cs ion of dehydrated CsZSM-5 was localised close to the oxygen atom (018) of the four-membered ring of the MFI lattice with a Cs-O distance of 3.68 Å. It is likely that the Al atom is localised in the four-membered ring.

Among aromatic hydrocarbons, p-xylene, toluene and benzene adsorb most easily on MFI-type zeolites. The authors investigated the enthalpy of adsorption of toluene and benzene vapours without cationic form of this zeolite and have a complex dependence on the degree of filling [6, 12].

Toluene is the only aromatic hydrocarbon whose adsorption does not cause a change in the lattice size of the zeolite. In adsorption of aromatic hydrocarbons, the influence of molecule size is more important than their nature and adsorption of all aromatic hydrocarbons, large toluene, causing a decrease in the lattice constants **a** and **c** and an increase in the constant **b** [6, 12].

There are a large amount of data on the adsorption of organic substances in MFI type zeolites, which have been obtained by various physicochemical methods of investigation. The adsorption-calorimetric method applied in this work reveals the mechanism of adsorption processes occurring on adsorbents and catalysts.

The enthalpy of adsorption together with other differential adsorption-energy characteristics (free energy and entropy) most fully characterise the physical, chemical, crystallochemical and geometrical nature of the adsorbent surface and allows us to study adsorption phenomena at the molecular-structural level.

2. Testing Methods

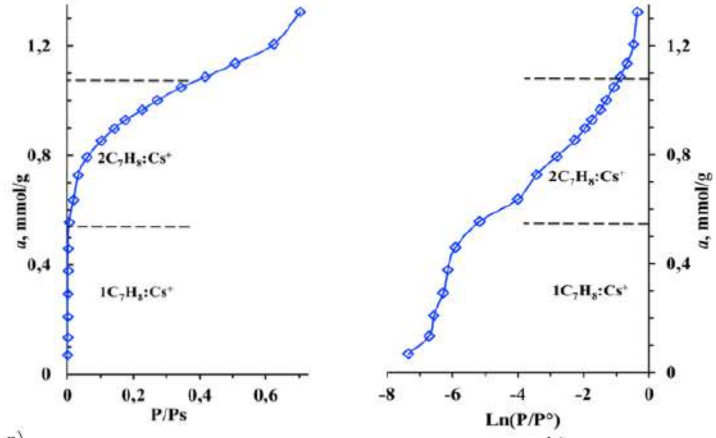
The adsorption-calorimetric method used in this work makes it possible to obtain highly accurate mole thermodynamic characteristics, as well as to reveal detailed mechanisms of adsorption processes occurring on adsorbents and catalysts. Adsorption measurements and adsorbate dosing were performed using a universal high-vacuum adsorption unit. The unit allows dosing of adsorbate by both gas-volume and volume-liquid methods. A modified DAC-1-1A microcalorimeter with high accuracy and stability was used as a calorimeter.

Differential molar adsorption calorimetric studies of toluene adsorption in CsZSM-5 zeolite were carried out using the device described in [2-8, 11-13]. The use of the method of compensation of heat fluxes by the Peltier effect made it possible to increase the accuracy of measuring the heat of adsorption. Adsorption studies were performed on CsZSM-5 zeolite at 303 K. Composition of the unit cell CsZSM-5 - $Cs_{3,17}[(SiO_2)_{95,23}(AlO_2)_{3,17}]$.

3. Results and Discussion

The adsorption calorimetric method used in this work allows for the acquisition of highly accurate molar thermodynamic characteristics, as well as revealing detailed mechanisms of adsorption processes occurring on adsorbents and catalysts. To characterize the adsorption properties of the zeolite, differential heats and adsorption isotherms of toluene in CsZSM-5 zeolite were measured, and the entropy and free energy of toluene adsorption were calculated.

The adsorption isotherm of toluene on CsZSM-5 zeolite, represented in coordinates of relative pressure and logarithmic coordinates, is shown in Figures 1a and 1b.



a)

b)

Figure 1.
Adsorption isotherms of toluene in CsZSM-5 zeolite.

The equilibrium pressures at low loadings reach $P/P_s=6{,}43\cdot10^{-4}$, indicating strong adsorption of toluene in CsZSM-5 zeolite. The adsorption isotherm is extended to 1.32 mmol/g at relative pressures $P/P_s=0{,}7$ (or up to 25.8 torr). Assuming the density of toluene in the zeolite is the same as that of a typical liquid at the experimental temperature, and calculating the volume occupied by a toluene molecule at saturation, it is found that toluene occupies approximately ~0,124 cm^3/g of the adsorption volume of CsZSM-5 zeolite, which constitutes about ~75%.

From Figures 1a and 1b, it is evident that the adsorption isotherm of toluene on CsZSM-5 is S-shaped, with an almost vertical section in the middle. At low values of approximately P/P_s~$6{,}43\cdot 10^{-4}$, the curve rises sharply, indicating strong sorption of toluene. At medium loadings (approximately ~0.55 mmol/g and P/P_s~0,0066), the isotherm forms a step. The content of Cs+ cations, according to the chemical composition of the zeolite, is 0.54 mmol/g, meaning that each cesium cation forms a monomeric ion-molecular complex with toluene molecules, represented as $1C_7H_8{:}Cs^+$.

At P/P_s=0,42, the degree of filling reaches θ~0,83 (1.08 mmol/g), forming a dimeric ion-molecular complex, represented as $2C_7H_8{:}Cs^+$. Thus, the isotherm is almost completely confined within a narrow range of P/P_s from $6{,}43\cdot 10^{-4}$ to 0.42. This form of the isotherm is characteristic of phase transitions of the adsorbed substance and is one of the main phenomenological signs of the homogeneity of the sorption system as a whole.

The stepwise changes in the isotherm graphs expressed in relative pressure and logarithmic coordinates are closely related to the amount of cesium cations (0.54 mmol/g) in the zeolite. As illustrated in Figures 1a and 1b, toluene molecules form monomeric ion-molecular complexes $1C_7H_8{:}Cs^+$ at an adsorption level of 0.54 mmol/g, while at approximately ~1.1 mmol/g adsorption, dimeric complexes $2C_7H_8{:}Cs^+$ are formed. This indicates the significant role of cesium cations in the adsorption processes on the zeolite.

The adsorption isotherm of methanol is fully described by the three-term VMOT equation [41]:

$$a=0.59\exp[-(A/16.66)^{10}]+0.375\exp[-(A/8.16)^{3}]+0.242\exp[-(A/3)^{3}] \quad (1)$$

where a is the adsorption amount in mmol/g, and $A=RT\ln P_s/P$ is the work of adsorption in kJ/mol.

Figures 2a and 2b show the adsorption isotherm plotted in logarithmic and relative coordinates based on the values calculated using the volumetric model of adsorption theory (VMOT). The values obtained from the VMOT equation correspond closely to the experimental data, indicating a good fit between the theoretical predictions and the observed adsorption values.

The first term of the equation (0.59 mmol/g) corresponds to the amount of cesium cations (0.54 mmol/g) in the zeolite composition. This indicates that the VMOT equation confirms the formation of the monomeric ion-molecular complex $1C_7H_8{:}Cs^+$ between toluene molecules and cesium cations in the MFI-type zeolite.

Despite the increasing relative pressure, the adsorption values generated by the second and third terms of the equation become zero at an adsorption amount of 0.59 mmol/g. This indicates that the initial active center of the zeolite is equal to 0.54 mmol/g and that toluene molecules are adsorbing at a single type of active center, specifically the cesium cations.

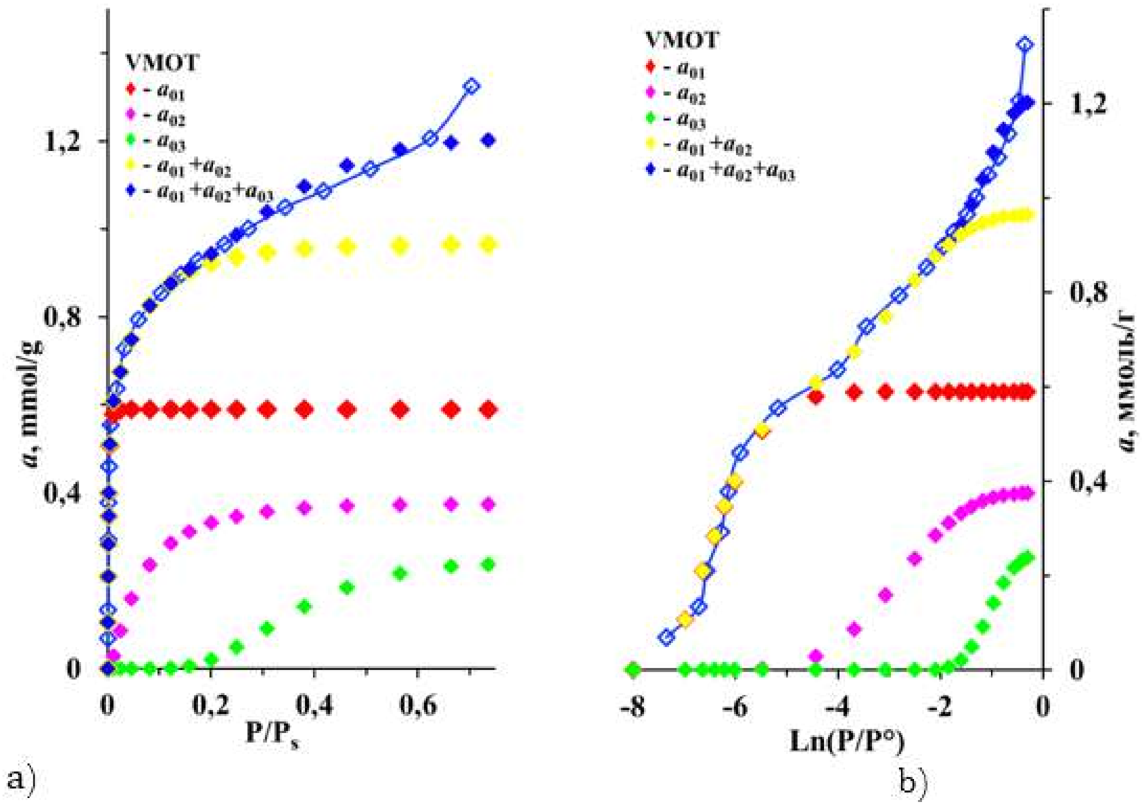


Figure 2.

Adsorption isotherm of toluene in CsZSM-5 Zeolite at 303 K. ◊ -isotherm values obtained experimentally; ◆, ◆, ◆, ◆, ◆ -values calculated using the VMOT equation.

After the formation of the $1C_7H_8:Cs^+$ complex, the value of the first term remains unchanged. This is related to the completion of the initial energetic adsorption process at the zeolite's active center. However, starting from an adsorption amount of approximately ~0.54 mmol/g and a relative pressure of about P/P_s=~0,0066, the second term begins to activate. At a relative pressure of about P/P_s=~0,032 (1.18 torr), the value of the second term reaches 0.087 mmol/g, and at a relative pressure of about P/P_s=~0,06 (2.2 torr), it increases to 0.16 mmol/g. This indicates that the adsorption of toluene molecules continues with the cesium cations.

The value of the third term at a relative pressure of approximately P/P_s=~0,34 (12.6 torr) is equal to 0.05 mmol/g. At this relative pressure, the total adsorption amount is 1.05 mmol/g, meaning that at this pressure, toluene molecules form the dimeric ion-molecular complex $2C_7H_8:Cs^+$, and the second term also remains constant.

The third term of the equation indicates adsorption occurring in the cation-free, silicic part of the zeolite.

The main thermodynamic results of toluene adsorption in CsZSM-5 zeolite contribute to identifying the adsorption mechanism, determining the presence of defects or hierarchical structures in the zeolite structure, and selecting effective adsorbents for the purification of natural gas and petroleum products from impurities, including sulfur and its compounds.

Figure 3 presents the differential enthalpy of toluene adsorption in CsZSM-5 zeolite. The differential enthalpy of adsorption can be divided into four stages based on the saturation degree of the adsorption volume. The first three stages correspond to the initial binding of toluene with the cation, with the first stage exhibiting a high differential enthalpy value of around 75 kJ/mol, the second stage averaging 60 kJ/mol, and the third stage reflecting adsorption on the cation-free portion of the zeolite.

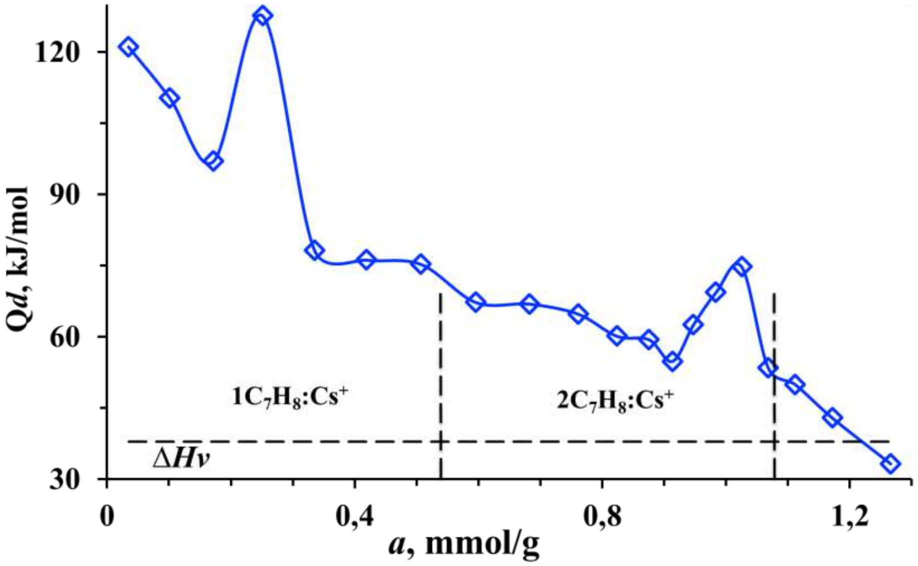


Figure 3.
Differential heat of toluene adsorption in CsZSM-5 Zeolite at 303 K (Q_d). Dashed lines represent the condensation value of toluene at 303 K.

The adsorption quantities at each extremum in the initial region, which consist of three cation-adsorbate bindings, are directly proportional to the total amount of cesium cations in the zeolite (0.54 mmol/g). This suggests the formation of ion-molecular complexes with an N/M (molecule/cation) ratio involving cesium cations in the first coordination sphere. The fourth part of the differential heat graph corresponds to the adsorption process occurring in the cation-free silicalite part of the zeolite.

The differential enthalpy of toluene adsorption in CsZSM-5 decreases from approximately ~121 kJ/mol at an adsorption value of 0.17 mmol/g to about ~97 kJ/mol. As the adsorption volume saturates, the differential enthalpy increases to a maximum of 128 kJ/mol at an adsorption of 0.25 mmol/g, then decreases to 80 kJ/mol at 0.3 mmol/g. Initially, toluene molecules form various complexes with several Cs+ cations. However, after introducing additional toluene molecules, the Cs+ cations redistribute, releasing extra energy and raising the enthalpy to 128 kJ/mol. At 0.54 mmol/g of adsorption, the differential heat decreases to 71 kJ/mol, indicating that this adsorption amount corresponds to the amount of Cs^+ cations in the zeolite.

Thus, in the cesium cation form of the MFI-type zeolite, toluene molecules create the monomeric ion-molecular complex $1C_7H_8{:}Cs^+$ within the first coordination sphere. As the adsorption volume becomes saturated with toluene molecules, the differential enthalpy oscillates, decreasing to about 52 kJ/mol at an adsorption of 1.08 mmol/g, indicating the formation of the dimeric ion-molecular complex $2C_7H_8{:}Cu^{2+}$. This complex can only fit within the intersecting straight and sinusoidal channels of the zeolite. Subsequent increases in enthalpy are linked to the formation of π-complexes and the van der Waals interactions between the initially adsorbed toluene molecules.

The adsorption of toluene in the first coordination sphere concludes, leading to adsorption in the cation-free part of the zeolite, which consists of straight and sinusoidal channels. At an adsorption level of 1.32 mmol/g, the differential enthalpy decreases to the condensation heat of liquid toluene at the experimental temperature.

The initial high-energy level of toluene molecules forming π-complexes with Cs^+ cations is observed in the intersections of the straight and sinusoidal channels. The subsequent adsorption of toluene molecules occurs in the sinusoidal (second stage) and straight (third stage) channels, as the enthalpy of adsorption corresponds to that of benzene in these channels.

The average entropy change, calculated using the Gibbs-Helmholtz equation, is approximately -73 J/mol·K. This indicates that the mobility of toluene molecules within the zeolite matrix is close to that of a solid state.

4. Conclusion

Calorimetric studies of toluene adsorption in Cs^+ZSM-5 zeolite were conducted, resulting in isotherms and complete thermodynamic characteristics (ΔH, ΔF, and ΔS) of toluene adsorption. A correlation was found between the adsorption-energy characteristics, revealing the molecular mechanism of toluene adsorption throughout the entire filling range. Adsorbed toluene in CsZSM-5 is situated in the first coordination sphere with the Cs^+ cation, forming dimeric complexes. The heat of adsorption and isotherm correlate with the number of cesium cations in the zeolite structures.

It was determined that the average molar entropy of toluene adsorption in CsZSM-5 is -73 J/mol·K, indicating that the mobility of toluene molecules in the zeolite is lower than in the liquid phase and closer to that of the solid phase. This suggests a strong inhibition of the mobility of toluene molecules, both in the presence of cesium cations and in the cation-free portions of the zeolite.

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