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DIFFERENTIAL HEAT AND ENTROPY OF ADSORPTION OF METHANETHIOL IN SODALITE

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Abstract: This article presents experimentally obtained values of the differential enthalpy of methane thiol (methanethiol) adsorption in sodalite at a temperature of 303 K. The enthalpy values were measured using a Tian-Calvet type DAC-1-1A microcalorimeter connected to a universal high-vacuum system. Based on equilibrium pressure values, the differential values of free energy (Gibbs energy) were calculated. Using the experimentally measured differential heat and Gibbs energy values, the change in adsorption entropy and its average value were theoretically estimated using the Gibbs–Helmholtz equation. A regular correlation between the amount of methanethiol adsorbed on sodalite and the changes in differential enthalpy and entropy was demonstrated. Furthermore, the mechanism of adsorption was determined—from the initial adsorption region to the region corresponding to the condensation heat of methanethiol—as well as the law governing the filling of the zeolite pore volume by methanethiol molecules. The regular variation of differential enthalpy values with the amount of Na^+ cations in the zeolite structure indicated that methanethiol molecules form sequential mono- and dimeric ion-molecular complexes of the type $2CH_3SH:Na^+$ with sodium cations. The average entropy change was found to be -37 J/mol·K, indicating that the mobility of methanethiol molecules was significantly restricted.

Keywords: adsorption, enthalpy, free energy, isotherm, pressure, relative pressure, microcalorimeter, methanethiol.

Introduction. Sodalites represent a group of crystalline materials characterized by a porous framework structure. Due to their close structural relationship with many types of zeolites [1–6], they can be used as model systems for studying various structural aspects of zeolites. Examples include the stability of their frameworks, the technical application of zeolites in intra- and inter-framework reactions, and cation exchange processes. Naturally occurring Al–Si sodalites and their synthetic analogues are well known [7–9]. Additionally, sodalite-type structures have been identified in Al–Ge systems [9–13] as well as in frameworks containing mixed cations [14–16]. In terms of the technical applications of sodalites and zeolites, thermal stability is one of their most important properties. Most sodalites do not exhibit a specific decomposition temperature. Instead, there exists a temperature range in which sodalite coexists with its amorphous and/or crystalline decomposition products. As a result, it is difficult to directly compare the thermal stabilities of sodalites with related structures and/or cavity fillings. This behavior can be clearly illustrated by the broad decomposition signals observed in thermogravimetric/differential thermal analysis (TG/DTA), such as the gradual dehydration of sodalites in the temperature range of 100–200°C. Moreover, X-ray diffraction studies across such a structural transition range in sodalites to describe detailed structural parameters are labor-intensive. Unfortunately, X-ray crystallographic analysis often does not yield complete results, and the quality of the obtained data may be compromised due to the small crystal sizes and the high degree of structural degradation.

Hydrosodalites of sodium zinc phosphate (ZnPO–SOD) crystallize in the space group P-43n, which is the most commonly observed for sodalites [17]. The crystal structure consists of corner-sharing alternating ZnO_4 and PO_4 tetrahedra forming the so-called sodalite cavity (also referred to as the β- or toc-cage). These cavities are filled with sodium cations and water molecules, located at the cubic corners and centered beneath the six-membered ring windows of the framework. This type of sodalite can be synthesized at room temperature [18]; however, the resulting material is not stable during synthesis, product washing, or thermal treatment. Stirring the sample during synthesis leads to the formation of a hexagonal $NaZnPO_4$ phase [18], and intensive washing with water can result in complete framework collapse [19].

The low stability and high sensitivity of synthesis conditions make it relatively easy to obtain sodium zinc phosphate sodalite via sol-gel synthesis under ambient conditions, or even under dry conditions using simple mortar grinding techniques [20]. This approach yields a highly crystalline product suitable for further structural analysis. Compared to other sodalites incorporating group 13 and 14 elements in the framework, ZnPO–SOD can be stabilized only through the clathration of water molecules. The removal of water—which plays a crucial role in filling the sodalite cages—leads to framework distortion and the formation of a water-free $NaZnPO_4$ phase [20]. This phase features corner-sharing alternating ZnO_4 and PO_4 tetrahedra forming a three-dimensional six-membered-ring channel system containing sodium cations.

Sodalites are microporous solids that can host various guest molecules in their cavities. In addition to the extensive body of theoretical and experimental studies on host–guest interactions in zeolite chemistry, recent research has focused on the practical applications of sodalites in industrial processes. These include wide-ranging investigations into their use in pigments, the synthesis of nanocomposites, and specialized host matrices for quantum dot materials.

The use of sodalites as storage materials, due to their wide chemical diversity, has recently emerged as a promising area of research. The thermal behavior of these intriguing compounds suggests the potential for encapsulating gases such as CO_2, NO, and SO_2 within sodalite cavities through high-temperature intracrystalline reactions. As a result of these heterogeneous processes, exhaust gases can be captured in the sodalite matrix in the form of carbonates, nitrates, and sulfites. Based on this, sodalite can be considered a model system for flue gas immobilization at elevated temperatures [21].

In recent years, the study of salt clathration and its impact on the chemical and thermal properties of sodalites has gained interest, particularly in the development of new ion-exchange materials, adsorbents, or materials with special physical properties such as photochromism. Due to the structural similarity between sodalites and zeolites A, X, and Y, research on sodalites is also important for gaining deeper insights into zeolite-based sorbents. Although various literature sources address the synthesis and thermal analysis of salt-containing sodalites, only a few focus specifically on their sorption properties.

However, studies on the synthesis of solid solutions of basic sodium nitrite and their intracrystalline reactions with carbon dioxide at elevated temperatures indicate that this new material could serve as a suitable sorbent for CO_2. These properties result from a specific combination of two types of guest molecules—$NaOH{\cdot}H_2O$ (reactive component) and $NaNO_2$ (stabilizing component)—which together stabilize the host sodalite structure. Sodium hydroxide hydrate was chosen for its reactivity, while sodium nitrite was selected for its stabilizing effect, as the thermal behaviors of both pure basic sodalite and nitrite sodalite are already well established. Thus, intracrystalline reactions in sodalite offer an interesting model system for modifying zeolites to enhance their capacity to reduce CO_2 content in exhaust gases [22].

Molecular sieves with sodalite-type structures belong to the class of nanoporous adsorbents characterized by well-defined crystalline frameworks. They serve as effective catalysts for numerous chemical reactions. The growing interest in zeolites is largely due to their broad use in industrial technologies as catalysts, which has motivated researchers to develop new types of zeolitic materials [23–24]. The sodalite framework consists of nearly spherical cavities with a unit cell size of approximately 8.8 Å, comprising 12 tetrahedra arranged in 3 layers formed by six-membered rings. The unit cell dimension along the c-axis is about 7.5 Å.

The active sites within these structures include acidic centers, associated with the presence of extra-framework metal cations—such as alkali, alkaline-earth, and transition metal ions. The activity of these sites often depends on the zeolite structure and is typically investigated using spectroscopic techniques with molecular probe attachments. In particular, acid properties are analyzed at the molecular level using weakly interacting molecular probes and infrared (IR) spectroscopy. However, there is a limited number of studies employing calorimetric methods to investigate the acidity of zeolites, despite their potential to provide accurate and quantitative information. In this work, we focus primarily on sodalite, a zeolite with wide-ranging applications. Zeolites are porous crystalline materials that act as adsorbents due to the localization of surface charges on small cations and the distribution of negative charges across multiple oxygen atoms within the Al–O and Si–O tetrahedra. Of particular interest is the adsorption of substances on this surface that contain atoms capable of specific interactions with these cations.

Research methods and materials.

For measurements of isotherms and differential adsorption heats, a system consisting of a universal high-vacuum adsorption unit and a Tian-Calvet-type, DAK-1-1A thermally conductive differential microcalorimeter connected to it was used, which has high accuracy and stability. The instrument's calorimeter sensitivity is extremely high, and its reliability is high. It can be used confidently to measure the heat of processes of almost unlimited duration. The calorimeter makes it possible to obtain the thermokinetics of the process of adsorption systems under study, which is very important for elucidating the adsorption mechanism. Most of the heat (about 99%) released into the calorimeter chamber is dissipated into the calorimeter block immediately after release. Only about 1% of the heat released remains in the calorimeter chamber, raising its temperature slightly. The measurement is mainly concerned with the heat flux that passes through the surface of the calorimeter chamber and the calorimeter block. The adsorption-calorimetric method used in this work provides highly accurate molar thermodynamic characteristics and reveals detailed mechanisms of adsorption processes occurring on adsorbents and catalysts. Adsorption measurements and adsorbate dosing were carried out using a universal high-vacuum adsorption unit. The unit allows adsorbate dosing by both gas-volume and volume-liquid methods. We used a BARATRON B 627 membrane pressure gauge to measure the equilibrium pressures [24-27].

In the adsorption study, the adsorption of methanethiol on β-zeolite at a temperature of 303 K was investigated, and the adsorption mechanism was thoroughly analyzed. The unit cell composition of this zeolite is represented as $Na_6[AlSiO_4]_6(H_2O)_{12}$. Based on its chemical composition, the total amount of calcium and sodium cations in 1 gram of the zeolite is approximately 0.6 mmol/g.

Results. In addition to hydrogen sulfide, natural gas, gas condensate, and petroleum products may contain organosulfur compounds, such as methyl mercaptan. For the removal of such sulfur-containing compounds, zeolites represent a promising class of adsorbents. The objective of this study was to investigate the sorption properties of sodalite with respect to methyl mercaptan. The main goal of this research cycle was to measure the differential enthalpy (Q_d) and entropy change (ΔS_d) of adsorption in order to identify an effective adsorbent for purifying natural gas and petroleum products from sulfur-containing impurities.

We conducted studies on the differential heat of adsorption of methyl mercaptan on synthetic sodalite-type zeolite.

It is important to note that due to the high saturated vapor pressure of methanethiol (P_s=1515 torr) at the experimental temperature of 303 K, it was not possible to obtain a complete adsorption isotherm of methanethiol in sodalite.

The differential enthalpy of methanethiol adsorption on sodalite zeolite at 303 K was experimentally measured, covering the range from low coverage to the region corresponding to the condensation heat of methanethiol. The mechanism of the sorption process was investigated in detail. It was found that in the initial adsorption region, the enthalpy values for methanethiol are approximately 30–40 kJ/mol lower than those for the adsorption of various polar molecules, such as ammonia, and nonpolar molecules on this zeolite. During the adsorption process, methanethiol molecules were shown to interact with Na^+ cations in the zeolite structure, forming dimeric ion–molecular complexes.

It is well known that in zeolites such as MFI, MOR, FAU, and LTA, the differential adsorption enthalpies of molecules of different physicochemical nature and size often exhibit a stepwise behavior.Figure 1 presents the graph of the differential enthalpy of CH_3SH adsorption on sodalite zeolite.

In general, the differential heat shows a wave-like and stepwise profile, which can be divided into two distinct regions. In both regions, the total amount of adsorbed methanethiol corresponds to approximately ~0.6 mmol/g. In the initial region, at an adsorption amount of 0.02 mmol/g, the differential heat of adsorption is approximately ~47 kJ/mol. As the adsorption amount increases, the differential enthalpy decreases to 39 kJ/mol at 0.17 mmol/g, forming the first local minimum. With further filling of the sorption volume, the enthalpy rises again to 41 kJ/mol at about ~0.28 mmol/g. This increase is attributed to the complete localization of the initially adsorbed methanethiol molecules and to Van der Waals interactions (induction effects) between the first-layer and subsequently adsorbed molecules, which result in additional energy release.

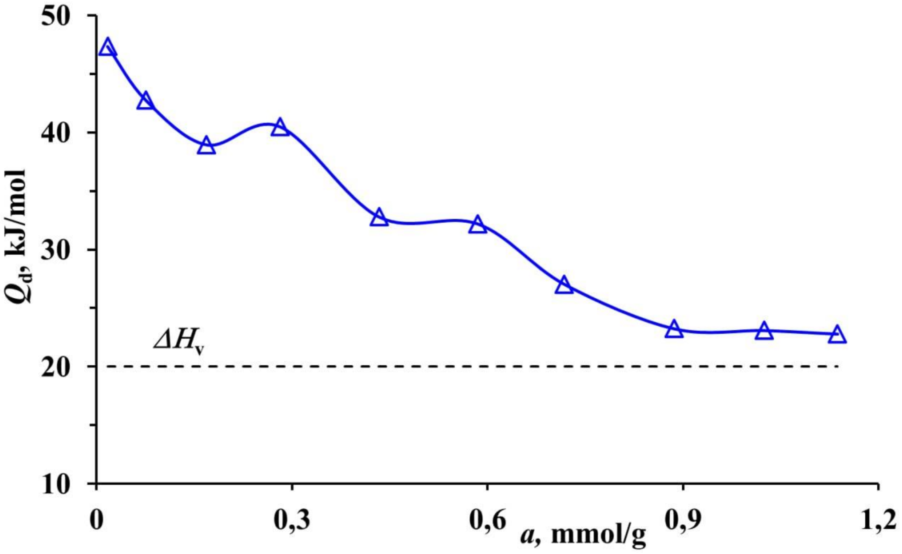

Figure 1. Differential heat of methanethiol adsorption (Q_d) on CaA (M-34) zeolite at 303 K. The dashed line represents the heat of condensation of methanethiol at 303 K

As more methanethiol molecules are adsorbed, the differential enthalpy drops to about 33 kJ/mol and remains constant up to an adsorption amount of 0.6 mmol/g. This value corresponds to the amount of Na^+ cations in the zeolite (0.6 mmol/g). Therefore, it can be concluded that the initial CH_3SH molecules are adsorbed directly onto Na^+ cations in the zeolite framework. The step observed in the adsorption range between 0.43–0.6 mmol/g indicates the formation of monomeric ion–molecular complexes in a 1:1 ratio, i.e., $1CH_3SH{:}Na^+$. As the saturation level increases further, the differential enthalpy decreases to 23 kJ/mol at an adsorption amount of 0.9 mmol/g, and remains constant up to 1.14 mmol/g. This amount is twice the quantity of Na^+ cations in the zeolite, indicating that CH_3SH molecules form dimeric ion–molecular complexes with Na^+ cations, with a $2CH_3SH{:}Na^+$ stoichiometry.

As the sorption volume of the zeolite approaches saturation, the differential enthalpy decreases to 59 kJ/mol at an adsorption amount of 1.24 mmol/g, and then increases again to approximately ~63 kJ/mol at around ~1.6 mmol/g. This adsorption amount, as previously noted, corresponds to twice the quantity of Na^+ cations in the zeolite. Therefore, it can be concluded that at the second maximum, CH_3SH molecules form dimeric ion–molecular complexes $2CH_3SH{:}Na^+$ with Na^+ cations, marking the completion of sorption within the first coordination sphere of the Na^+ cations.

Figure 2 shows the variation in the molar differential adsorption entropy (ΔS_a) of CH_3SH molecules on sodalite zeolite as a function of adsorption saturation (the entropy of liquid methanethiol was taken as zero). The adsorption entropy was calculated using the Gibbs–Helmholtz equation as follows:

$$\Delta S_a = \frac{\Delta H - \Delta G}{T} = \frac{-(Q_a - \lambda) + RT \ln P_S / P}{T} \quad (1)$$

Here, λ represents the heat of condensation, while ΔH and ΔG correspond to the changes in enthalpy and Gibbs free energy during the transition from the standard state to the adsorbed state.

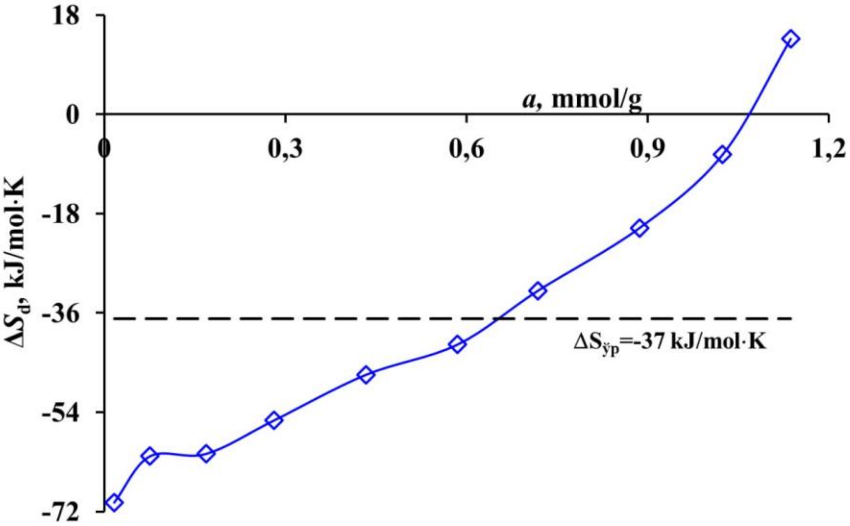

Figure 2. Molar differential entropy change (ΔS_a) of CH_3SH adsorption on sodalite at 303 K. The dashed line represents the average entropy change

In general, the adsorption entropy exhibits a wave-like variation that corresponds to each ion–molecular mechanism of interaction. The entropy values lie well below that of liquid CH_3SH, indicating a strongly restricted mobility of CH_3SH molecules within the zeolite. Each stage in the entropy change correlates with the formation of specific ion–molecular complexes, as confirmed by the differential heat data. In the initial region, at an adsorption amount of 0.02 mmol/g, the entropy is approximately –70 J/mol·K, suggesting that the mobility of methanethiol molecules within the sodalite matrix is highly restricted. As adsorption proceeds and the sorption volume fills, the entropy increases nearly linearly to –42 J/mol·K at 0.6 mmol/g. This adsorption quantity corresponds to the amount of Na^+ cations in the zeolite, confirming that CH_3SH molecules are adsorbed directly onto Na^+ sites. As previously noted in the enthalpy analysis, CH_3SH molecules at this stage form monomeric ion–molecular complexes in a 1:1 ratio, i.e., $1CH_3SH:Na^+$.

With further adsorption, the entropy increases to about 14 J/mol·K at an adsorption level of ~1.2 mmol/g, corresponding to the formation of dimeric $2CH_3SH:Na^+$ ion–molecular complexes in a 2:1 adsorbate-to-adsorbent ratio. The observed entropy trend—from a partial bend after 0.6 mmol/g to a near-linear increase up to 1.2 mmol/g—matches the step in enthalpy associated with the formation of dimeric ion–molecular complexes. This signifies the completion of the methanethiol sorption process in sodalite through the formation of these dimers.

Conclusion. The differential enthalpy of methanethiol adsorption on the nanostructured sodalite zeolite was studied using the adsorption-calorimetric method. The mechanism of the sorption process and the pattern of methanethiol molecules filling the sodalite pore volume were determined in the range from low degrees of saturation up to the experimental pressure of 617 torr. Based on the values of differential enthalpy and the Gibbs free energy calculated from equilibrium pressures under thermodynamic conditions, the entropy change (ΔS) and its average value for CH_3SH molecules were determined. The differential enthalpy and molar differential entropy change exhibited a stepwise trend, correlating with the amount of Na^+ cations in the sodalite structure. It was established that methanethiol molecules form dimeric ion–molecular complexes ($2CH_3SH:Na^+$) within the first coordination sphere of Na^+ cations in sodalite. The values of entropy change for methanethiol adsorption were found to be significantly lower than the entropy of liquid methanethiol at the experimental temperature, with an average value of –37 J/mol·K. This indicates that the mobility of methanethiol molecules in the sodalite matrix is highly restricted compared to the liquid phase. The adsorption–calorimetric data obtained in this study provide a valuable basis for developing theoretical concepts of chemical and physical adsorption in zeolites like sodalite, and are essential for calculating sorption processes and designing adsorption-based technologies and apparatuses in practical applications.

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